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On the Development of Nonequilibrium Thermodynamics*

S. R. DE GROOT
Lorentz Institute of Theoretical Physics, University of Leiden, Leiden, Netherlands
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A general view of the history of nonequilibrium thermodynamics shows how two main lines of development have recently fused into a single branch of science. The field theoretical formulation of thermodynamics (leading to a balance equation for the entropy) constitutes the framework of a theory in which the Onsager reciprocal relations form the *pièce de résistance*, the fundamental importance of which is outlined in this paper.

I. INTRODUCTION

THIRTY one years ago, two articles appeared in the Physical Review, in which Lars Onsager, then of Brown University, derived the celebrated reciprocal relations between irreversible processes, which bear his name.[1] This work formed the culmination of a theoretical development started seventy seven years before, when thermodynamic considerations were first applied to the treatment of irreversible phenomena. That was done by William Thomson who gave an analysis. published in the Proceedings of the Royal Society of Edinburgh,[2] of the various thermoelectric effects. He established two relations between them, of which the first followed simply from the conservation of energy. The second Thomson relation, which connects the thermoelectric potential of a thermocouple to its Peltier heat, was obtained from the two laws of thermodynamics and an additional assumption concerning the so-called reversible contributions to the process. Later, Boltzmann[3] attempted to justify the Thomson hypothesis, but he was unable to find a basis for it. We now know that this hypothesis cannot be justified. Thomson's second relation was finally proved correctly by Onsager who showed that it was an example of his reciprocal relations, which are themselves a consequence of microscopic reversibility, i.e., ultimate invariance of the microscopic equations of motion under time reversal.

II. THE ONSAGER RELATIONS

Since 1931, the Onsager relations have played an essential role in all thermodynamic treatments of coupled irreversible phenomena. Let us write, to fix the ideas, the following linear laws for two irreversible phenomena and their interference effects:

$$J_1 = L_{11}X_1 + L_{12}X_2, \tag{1}$$

$$J_2 = L_{21}X_1 + L_{22}X_2, \tag{2}$$

where J_1 and J_2 are called fluxes, such as, for example, the heat flow and the electric current (in Thomson's thermoelectric case), and X_1 and X_2 are called thermodynamic forces, such as the temperature gradient and the electric field. The diagonal

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[1] L. Onsager, Phys. Rev. **37**, 405 (1931); *Ibid.* **38**, 2265 (1931).

[2] W. Thomson (Lord Kelvin), Proc. Roy. Soc. Edinburgh **3**, 225 (1854); Trans. Roy. Soc. Edinburgh part I **21**, 123; (1857); Math. Phys. Papers **1**, 232 (1882).

[3] L. Boltzmann, Sitzber. Math. Naturwiss. Akad. Wiss. Wien II **96**, 1258 (1887); Abh. **3**, 321 (1909).

coefficients L_{11} and L_{22} are then related to the heat and electric conductivities, and the off-diagonal coefficients L_{12} and L_{21} to the Peltier heat and the thermoelectric power. Onsager proved quite generally for an arbitrary set of two or more coupled irreversible phenomena, that (with an appropriate choice of fluxes and thermodynamic forces) the scheme of coefficients L is symmetric, i.e., for the example considered,

$$L_{12} = L_{21}, \tag{3}$$

which is Thomson's second relation. These reciprocal relations reflect, on the *macroscopic* level, the time-reversal invariance of the microscopic equations of motion. Onsager's proof was based on two starting points, (in addition to a few well-known concepts of statistical mechanics), viz., (a), microscopic reversibility, and (b), linear laws of the type (1) and (2). I would like to discuss both of these points in a little more detail.

A. Microscopic Reversibility

The microscopic state of a system of N particles without internal structure is described in the classical theory by a point $\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \cdots, \mathbf{p}_N$ in phase space, where the $\mathbf{r}_i$ are the position vectors of the particles and $\mathbf{p}_i$ their momenta. (For particles with an internal structure more parameters are needed, but the following reasoning is not essentially changed.) The dynamics of an adiabatically insulated system of this kind is given by a Hamiltonian $H(r, p)$ which depends on the coordinates and momenta (written here symbolically as r, p), but not explicitly on the time. The Hamiltonian of such a system of molecules is invariant under time reversal, i.e., in the classical case, for the transformation $p \rightarrow -p$,

$$H(r, p) = H(r, -p). \tag{4}$$

This property expresses the *time-reversal invariance* of the mechanical equations of motion of the N-particle system.

We assume that the behavior of the system can be studied by means of classical statistical mechanics. In particular, the time-dependent average value $\bar{\alpha}(t)$ of any dynamical quantity $\alpha(rp)$ is obtained by multiplying $\alpha(rp)$ with a probability density $\rho(rpt)$ of a representative ensemble of systems, and integrating over phase space. The time behavior of $\rho(rpt)$ follows from the knowledge of H by means of the Liouville equation.

For the macroscopic description of the system, one is not interested in the complete set of mechanical variables describing its microscopic state, but only in a much more restricted number of variables. One may choose for these variables, the extensive properties (such as the energies, masses, electric charges) of macroscopically infinitesimal subsystems. These subsystems should still contain enough particles so that the concepts of statistical mechanics may be applied to them. Let us denote this restricted set of variables by $\alpha_1, \alpha_2, \cdots, \alpha_n$ (or α, to abbreviate the notation), where n is much smaller than N. We normalize these variables in such a way that their mean values in equilibrium [which is described by $\rho = \rho_m(rp)$, the microcanonical ensemble] is zero. We can introduce a probability density $f(a, t)$ which gives the probability of finding the system at time t in a state for which $\alpha = a$. This quantity $f(a)$ will be independent of time in a stationary ensemble $\rho_m(rp)$. We can also introduce a joint probability density $f(a, t; a', t + \tau)$ for finding the system in a state $\alpha = a$ at time t, and in a state $\alpha = a'$ at time $t + \tau$. In a stationary ensemble this quantity will be independent of t, and will be denoted by $f(a, a', \tau)$. Finally, one can define a conditional probability density

$$P(a, t; a', t + \tau) = f(a, t; a', t + \tau)/f(a, t), \tag{5}$$

which in the stationary ensemble, can be written as

$$P(a, a', \tau) = f(a, a', \tau)/f(a). \tag{6}$$

Let us suppose for the moment that the α variables are *even* functions of the particle velocities. We can then formulate the property of *microscopic reversibility* which follows from time-reversal invariance (4) by means of statistical mechanics as the equality

$$f(a, a', \tau) = f(a, a', -\tau), \tag{7}$$

or alternatively, making use of the stationarity of the system, as

$$f(a, a', \tau) = f(a', a, \tau), \tag{8}$$

which expresses the property of *detailed balance* in the α space of the macroscopic variables. It is usually written, using (6), as

$$f(a)P(a, a', \tau) = f(a')P(a', a, \tau). \tag{9}$$

In this form the property of detailed balance is written for the stationary ensemble (equilibrium) quantities. If, however, a system not in equilibrium has been found by measurement to be in a specified state a at a given initial time t_0, then it can be shown that its conditional probability density is equal to the equilibrium quantity, i.e.,

$$P(a, t_0; a', t_0 + \tau) = P(a, a', \tau). \qquad (10)$$

This relation between a nonequilibrium and an equilibrium quantity is only true for $t = t_0$, and not for all times.

A direct corollary of (8) or (9) can be obtained by introducing the time-correlation matrix R_{ik} which is defined as the expectation value of $\alpha_i(t)\alpha_k(t + \tau)$ in the stationary ensemble. It can also be written as

$$R_{ik} = \iint a_i a'_k f(a, a', \tau)\, da\, da' \quad (i, k = 1, 2, \cdots, n), \qquad (11)$$

where we have used the joint probability density $f(a, a', \tau)$. Then it follows from detailed balancing (8) that

$$R_{ik} = R_{ki} \qquad (i, k = 1, 2, \cdots, n). \qquad (12)$$

Onsager used this equality as a starting point, and called it the principle of microscopic reversibility.

The proof of the property of detailed balancing (9) from time reversal invariance (4) was first given by Wigner,[4] who used classical statistical mechanics. It can also be obtained if the motion of the particles is governed by quantum-mechanical laws.[5,6]

Let us now make a few additional remarks on the preceding.

1. The property of time-reversal invariance of the microscopic motion, i.e., the invariance of H under the operation $t \rightarrow -t$, was the fundamental symmetry which lead to detailed balancing. One might alternatively call this property "invariance under reversal of the motion," because it means, classically, that if one were to reverse all velocities, all particles would retrace their former paths; (a similar statement could be made in quantum mechanics). In this way, the wording is such that one could, at least in principle, perform the reversal operation, which is not the case for $t \rightarrow -t$.

2. In the usual irreversible phenomena the systems consist of particles which have "molecular" interaction, i.e., one must deal ultimately with a system consisting of an electromagnetic field in interaction with electrons and nuclei. The time-reversal invariance of the equations of motion for such systems is well established. In recent years much attention has been paid to time reversal, and the other noncontinuous symmetry operations in nuclear phenomena, especially in view of the nonconservation of parity in weak interaction. It seems today that in both strong and weak interactions, time-reversal invariance is valid. If nuclear forces really influence irreversible phenomena, then it might be reassuring to know that at least the foundation of the Onsager relations, namely time-reversal invariance, is still valid in such cases.

3. If an external magnetic field B acts on the system, the Hamiltonian will only be invariant for time reversal if one includes reversal of the magnetic field B in this operation. (Similarly one must reverse the angular velocity vector if the system is subjected to Coriolis forces.) One derives then, along the same lines as before,

$$f(a)P(a, a', \tau, B) = f(a')P(a', a, \tau, -B), \qquad (13)$$

instead of (9).

4. Casimir[7] remarked in 1945 that it may occur that one needs for the macroscopic description of the system not only variables α, which are even functions of the particle velocities, but also variables β, which are odd functions of the particle velocities (e.g., momentum densities). Then time-reversal invariance leads to a form

$$f(a, b)P(a, b, a', b', \tau) = f(a', b')P(a', -b', a, -b, \tau) \qquad (14)$$

for detailed balancing, where b and b' indicate values of β, just as a and a' indicated values of α.

B. Linear Laws

In order to find the effect of microscopic reversibility on the macroscopic properties of irreversible phenomena, one must make a statement about the time behavior of the "coarse-grained" variables a and b introduced above. In particular, it is now postulated that the conditional averages $\bar{a}(t)$ obey linear first-order differential equations of the form

$$\dot{\bar{a}}_i(t) = -\sum_k M_{ik}\bar{a}_k(t) \qquad (i = 1, 2, \cdots, n), \qquad (15)$$

where the conditional averages are defined by

$$\bar{a}_i(t) = \int a_i P(a_0, a, t)\, da \quad (i = 1, 2, \cdots, n), \qquad (16)$$

and M_{ik} is a matrix of phenomenological coefficients (which are independent of time). The conditional probability $P(a_0, a, t)$ refers to a nonstationary ensemble, which corresponds to a system which at time $t = 0$, is in a specified state a_0, as indicated by measurement. This nonstationary probability den-

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sity is, according to (10), identical with the stationary probability density.

Before investigating the influence of microscopic reversibility on the properties of the linear laws (15), we must specify how these laws are related to the phenomenological laws mentioned in the beginning, and which were written as

$$J_i = \sum_k L_{ik} X_k \qquad (i = 1, 2, \cdots, n). \tag{17}$$

This can be achieved in the following way: The deviation of the value of the entropy $S(a) = k \ln f(a) + \text{const.}$ from its maximum value will be a quadratic expression in the $\bar{a}_i$, which can be written as

$$\Delta S = -\tfrac{1}{2} \sum_{ik} g_{ik} a_k a_i, \tag{18}$$

where the g_{ik} are certain equilibrium properties (second derivatives of S with respect to the a_i). If we now define the fluxes J_i as the time derivatives of $\bar{a}_i$, and the forces X_i as linear combinations of the a_i in the following fashion:

$$J_i = \dot{\bar{a}}_i, \qquad X_i = -\sum_k g_{ik} \bar{a}_k, \tag{19}$$

then the regression laws [Eq. (15)] take the form of Eq. (17) with

$$L_{ik} = \sum_j M_{ij} g^{-1}_{jk}. \tag{20}$$

In this way the connection of the linear laws with thermodynamics is established, and a prescription is given for finding the proper thermodynamic forces X_i conjugate to the α_i variables. One of the problems of nonequilibrium thermodynamics is precisely to arrive at a proper form of the linear laws (17) for which the Onsager relations will be valid.

Now from (10), and (15)-(20), and statistical mechanics, it can be shown that the phenomenological coefficients L_{ik} are directly related to the correlation matrix R_{ik} (11) in the following way:

$$L_{ik} = -k^{-1} \lim_{t \to 0} \frac{\partial R_{ki}}{\partial t}, \tag{21}$$

where k is Boltzmann's constant. From detailed balancing in the form $R_{ik} = R_{ki}$ (12) the Onsager relations

$$L_{ik} = L_{ki} \qquad (i, k = 1, 2, \cdots, n) \tag{22}$$

now follow immediately. A number of remarks on this derivation can be made.

1. It is known empirically that linear laws of the form (15) are valid for a large class of irreversible phenomena, if the initial values a_0 lie in the macroscopic region, i.e., far outside the region of average equilibrium fluctuations. In the course of the derivation however the regression law (15) is assumed to hold also for small values of a_0, i.e., for values lying in the region of equilibrium fluctuations, since the main contributions to R_{ik} are due to small values of a_0. This assumption is in agreement, for instance, with Svedberg's and Westgren's experiments on colloid statistics. Their results show that the *average* behavior of density fluctuations is in perfect agreement with the macroscopic law of diffusion.

2. The derivation of the Onsager relations is based solely on microscopic reversibility and in the assumption of the validity of linear regression laws. The problem of establishing these linear laws from first principles is not approached here, and the existence of irreversible behavior is taken for granted.

3. If an external magnetic field acts on the system, we have the expression (13) for the property of detailed balancing. This leads to Onsager relations of the form

$$L_{ik}(B) = L_{ki}(-B) \tag{23}$$

instead of (22).

4. If odd variables β must be taken into account, we have formula (14) for detailed balancing. We then obtain reciprocal relations in Casimir's form, which show a minus sign on one side of the equality, if an α-variable i is coupled with a β-variable k. For the coupling of two α variables or of two β variables, (22) or (23) remains valid.

5. Macroscopic equations describing irreversible phenomena are often partial differential equations containing derivatives of state variables with respect to space coordinates. This is, in particular, the case for vectorial phenomena such as heat conduction, diffusion and electric conduction, and also for tensorial phenomena such as viscous flow. The point is namely that for such phenomena, the fluxes are not direct time derivatives of state variables, as is required in the proof of the Onsager relations. Casimir[7] was the first to show how one can cast the macroscopic equations for these phenomena into the form (15) or (17), in order to find the proper Onsager relations. Subsequently one can then find the effect of these Onsager relations on the properties of the measurable phenomenological coefficients which occur in the differential equations. It may be stressed that this program has been worked out for all irreversible processes. In particular formulas of the type (15), (18), and (19) have been given either explicitly (for instance for heat conduction,

diffusion and electric conduction) or in such a form that it is immediately clear how these expressions are to be obtained.[8]

6. If independent state variables other than the set a_i, occurring in (18) are chosen, one can of course derive Onsager relations in exactly the same way. One method of obtaining a new set of independent-state variables is to take linear combinations of the original variables.

7. The phenomenological equations may be of a more general type than (15) in still another way than that discussed above in the fifth point. This is the case in systems in which some properties (described by the variables α_i) respond to external driving forces F_i. We can now study the influence of microscopic reversibility without making assumptions on the mean regression of fluctuations. Let us assume that the Hamiltonian is of the form

$$H(rpt) = H_0(rp) - \sum_i \alpha_i(rp)F_i(t), \tag{24}$$

where H_0 is the Hamiltonian of the system in the absence of driving forces. If one supposes that at $t = -\infty$ the system was in equilibrium before the forces F_i were switched on, then one can derive from (24) and statistical mechanics for the linear response of α_i to the forces

$$\bar{\alpha}_i(t) = \int_{-\infty}^{\infty} \sum_i \kappa_{ik}(\tau)F_k(t-\tau)\,d\tau, \tag{25}$$

where, for macroscopic systems,

$$\left.\begin{aligned} \kappa_{ik}(\tau) &= 0 && (\tau < 0), \\ \kappa_{ik}(\tau) &= -(kT)^{-1}\,\partial R_{ki}/\partial\tau && (\tau \geq 0), \end{aligned}\right. \tag{26}$$

a matrix which fulfills a causality condition.

The microscopic reversibility property, [Eq. (12)] leads here to the following symmetry property for the Fourier transform $\hat{\kappa}_{ik}(\omega)$ of $\kappa_{ik}(\tau)$, namely

$$\hat{\kappa}_{ik}(\omega) = \hat{\kappa}_{ki}(\omega), \tag{27}$$

which constitutes a generalization[9] of the Onsager relations for the laws (25). These laws are themselves more general than the laws (15). (If magnetic fields and odd variables play a role, then modifications similar to those discussed before are necessary.)

One can also derive for this system a connection between the equilibrium correlation matrix $R_{ik}(\tau)$ and the imaginary part $\hat{\kappa}''_{ik}(\omega)$ of $\hat{\kappa}_{ik}$:

$$R_{ik}(\tau) = \frac{kT}{\pi}\,\mathcal{P}\int_{-\infty}^{\infty} \cos\omega\tau\,\frac{\hat{\kappa}''_{ik}(\omega)}{\omega}\,d\omega. \tag{28}$$

This formula represents the *fluctuation dissipation theorem*, due to Callen and Greene, and discussed also by Kubo.[9] It connects the correlation function matrix R_{ik}, which characterizes the time behavior of fluctuations in an equilibrium system, to the imaginary part $\hat{\kappa}''_{ik}(\omega)$ of the "susceptibility" matrix, which is a measure for the dissipation of energy in the system.

8. Finally we remark that linear laws of the type (15) or (17) can only hold on a "macroscopic" time scale, i.e., for times larger than some characteristic microscopic time τ_0 (but still small compared to the relaxation time M^{-1}). Indeed, the limit in formula (21), which for a single α variable is equal to the microcanonical average of $\alpha\dot{\alpha}$, would vanish due to the stationarity of the microcanonical ensemble. However for sufficiently long times, where the limit discussed is to be considered as difference quotient instead of a differential quotient, one obtains a finite result for (21). Regression laws of the type (15) or (17) can then hold.

III. THE CONSERVATION AND BALANCE EQUATIONS

A second main line in the development of nonequilibrium thermodynamics is the "field theoretical" formulation of the laws of thermodynamics. Indeed in nonequilibrium situations, the state variables are field quantities in the sense that they are continuous functions of space coordinates and of time. One must formulate the basic equations of the theory in such a way that they contain quantities referring to a single point in space at one time, i.e., in the form of local equations. This should be done in the first place for the various conservation laws of mass, momentum, angular momentum, and energy. Then if one uses these results along with the thermodynamic Gibbs relation—which connects the rate of change of entropy in each mass element to the rate of change of energy, the rate of change of composition etc.—one can establish a balance equation for the entropy. This balance equation expresses the fact that the entropy of a volume element changes with time for two reasons. First it changes because entropy flows into the volume element, second because there is an entropy source due to irreversible phenomena inside the volume element. This is the local formulation of the second law of thermodynamics. It is found that the entropy source is a sum of products of fluxes and thermodynamic

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forces, the latter being related to the nonuniformity of the system or to the deviations of some internal state variable from its equilibrium value. The entropy source strength can thus serve as a basis for the systematic description of irreversible processes occurring in a system.

While several authors, beginning with Clausius, had attempted to obtain entropy balance equations, a systematic treatment along the lines just mentioned was completed in the early forties by Meixner[10] and by Prigogine,[11] whose work will be discussed in the next section.

Just as was done for the Onsager relations in the preceding section, one can discuss the microscopic basis for the second law of thermodynamics outside equilibrium. This discussion has mainly been performed for two models, in both of which the irreversibility itself is already contained in the fundamental equations, viz., the Gaussian Markoff process and the kinetic theory of gases. Onsager and Machlup[12] contributed to the study of the first model, while Prigogine[13] started to derive the thermodynamic laws from the kinetic theory of gases. It is possible to justify the use of the second law outside equilibrium in both cases. In particular, it can be proven that for macroscopic initial states, both the Boltzmann and the Gibbs definitions of entropy lead to the macroscopic entropy law

$$\Delta S = -\tfrac{1}{2} \sum_{ik} g_{ik}\bar{\alpha}_i\bar{\alpha}_k \tag{29}$$

for the Gaussian Markoff process. Such a law, and incidentally, also the Onsager relations, may be derived from the kinetic theory of gases.

IV. THERMODYNAMICS OF IRREVERSIBLE PROCESSES

A consistent phenomenological theory of irreversible processes incorporating both Onsager's reciprocity theorem and the explicit calculation of the entropy source strength was set up first by Meixner[10] and by Prigogine.[11] Thus, by the systematic amalgamation of the two lines of development treated in Secs. I and II, a new field of "thermodynamics of irreversible processes" was created. The set of conservation laws, together with the entropy balance equation and the equations of state, must be supplemented by the linear laws which relate the fluxes and thermodynamic forces appearing in the entropy source strength. One then has at one's disposal, a complete set of partial differential equations for the state parameters of a system, which may be solved with the proper initial and boundary conditions.

It is one of the main aims of nonequilibrium thermodynamics to study the physical consequences of the Onsager reciprocal relations in applications of the theory to various physical situations. In addition to the reciprocity theorem, possible spatial symmetries of the system may further simplify the scheme of phenomenological coefficients. This reduction of the number of independent coefficients, which results from invariance under special orthogonal transformations, goes under the name of the Curie principle, but should more appropriately be called Curie's theorem. Pierre Curie[14] devotes only a few lines to his statement, which make apparent however, that he clearly understood the basis of his theorem. An explicit proof can be given by performing the relevant orthogonal transformations, as mentioned above. It is then possible to find out, for systems with arbitrary symmetry elements, which fluxes are coupled to which thermodynamic forces.

There are a few additional theorems of nonequilibrium thermodynamics which determine the transformations of fluxes and thermodynamic forces under which the Onsager relations remain valid, and other theorems which determine the special properties of the entropy source strength at mechanical equilibrium and in nonequilibrium stationary states.

The theory has found a great variety of applications in physics and chemistry, which can be classified according to their tensorial character. First, one has scalar phenomena. These include chemical reactions and structural relaxation phenomena. Onsager relations are of help in this case, in solving the set of ordinary differential equations which describe the simultaneous relaxation of a great number of variables. A second group of phenomena is formed by vectorial processes, such as heat conduction, diffusion and their cross effects (e.g., thermal diffusion). (Recently, Onsager relations were found experimentally for ternary diffusion in a very nonideal system.) Viscous phenomena (shear, bulk and rotational viscosity) and the theory of sound absorption and dispersion have been consistently developed within the framework of nonequilibrium

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[13] I. Prigogine, Physica **15**, 272 (1949).

[14] P. Curie, Oeuvres (Gauthier-Villars, Paris, 1908) p. 129.

thermodynamics.[15] Completely new aspects arise when an electromagnetic field acts on a material system. Then the continuity laws for electromagnetic energy and momentum must also be taken into account. Applications include electric conduction, thermomagnetic and galvanomagnetic effects, electro-kinetic processes, effects in polarized media (e.g., the problem of ponderomotive forces). A great number of membrane and similar effects have also been studied.

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Thermodynamics of Electrical Networks and the Onsager–Casimir Reciprocal Relations

J. MEIXNER
Institute of Theoretical Physics, Technische Hochschule, Aachen, Germany

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Electrical networks furnish an excellent example for the application of thermodynamics of irreversible processes. In particular, they provide one of the simplest cases where, besides Onsager coefficients, one has Casimir coefficients in the phenomenological equations. Two thermodynamic formulations of the network equations are given, which closely resemble the Lagrangian and the Hamiltonian formalism, respectively, of classical mechanics. In the first formulation, only Onsager coefficients occur, but the thermodynamic forces are of a peculiar type in that they are Lagrangian derivatives. Incidentally, it is shown that Casimir reciprocal relations can generally be replaced by Onsager reciprocal relations if the independent variables in the linear phenomenological relations are chosen in a proper way. As a generalization of the network equations, Maxwell's equations in continuous matter with dielectric, magnetic, and Joulean heat losses are considered. Matter is assumed to be isothermal, but not necessarily uniform nor isotropic. Under the influence of impressed electric fields, current distributions are produced. The connection of these fields is expressed by a generalized admittance function. A well-known reciprocity theorem for electromagnetic fields is seen to hold even if all types of losses, as mentioned before, are present. This is due to the Onsager–Casimir reciprocal relations for the dielectric tensor, the permeability tensor, and the resistivity tensor. From the reciprocity theorem, a symmetry relation can be derived for the generalized admittance function. A generalized version is given in the presence of a static magnetic field.

1. INTRODUCTION

OUR first objective is to give a simple example in which Onsager and Casimir reciprocal relations (OCRR) occur in a natural way. This is achieved by considering electrical networks as isothermal thermodynamic systems. The OCRR are here a simple consequence of well-known results in network theory and there is no need to take recourse to fluctuation theory for their derivation.

Electrical networks are then considered as special cases of arbitrary electromagnetic fields with continuously distributed impressed electrical fields. Besides the Joulean heat, we also admit dielectric and magnetic losses.

It can be shown that the symmetry of the impedance function is a consequence of a reciprocity theorem of Maxwell's theory which in turn, in the general case considered here, is a consequence of the OCRR. This gives a particular justification for the word "reciprocal" in the OCRR.

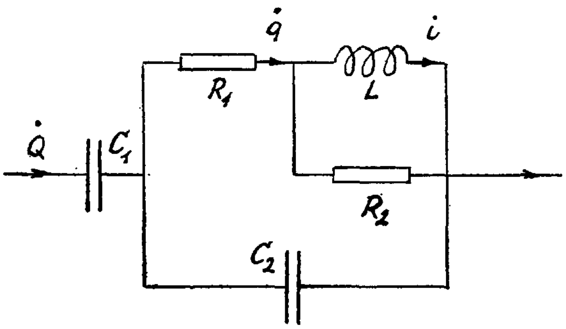

FIG. 1. The electrical network.

2. A SIMPLE NETWORK

We consider, at first, a special electrical network as depicted in Fig. 1. The various quantities are readily read off from the figure. The system is assumed to be isothermal at constant temperature T. Then the free energy is

$$f = \tfrac{1}{2}Q^2/C_1 + \tfrac{1}{2}(Q - q)^2/C_2 + \tfrac{1}{2}Li^2. \qquad (2.1)$$

The quantities Q and q are the integrals of the respective currents $\dot{Q}$ and $\dot{q}$. They may be normalized to zero for $t \to -\infty$. We think of the network as enclosed in a "black box." Then Q is an external variable, q is an even and i an odd internal variable. The differential of the free energy is

$$df = u\,dQ - A\,dq - B\,di, \qquad (2.2)$$

where

$$u = Q/C_1 + (Q - q)/C_2,$$
$$A = (Q - q)/C_2, \qquad B = -Li. \qquad (2.3)$$

Obviously, the coefficients u, A, B are to be interpreted as the voltage applied to the network, as the voltage across the capacitance C_2, and as the magnetic flux in the inductance L.

The energy dissipation $2\mathfrak{D}$ (T times the rate of entropy production) can be written in two ways. From the energy law we obtain

$$2\mathfrak{D} = \dot{Q}u - df/dt = A\dot{q} + B\dot{i}, \qquad (2.4)$$

and by inspection of the figure results,

$$2\mathfrak{D} = R_1\dot{q}^2 + R_2(\dot{q} - i)^2. \tag{2.5}$$

The quantity $\mathfrak{D}$ itself is called the dissipation function.

In equilibrium, A and B are zero as well as q and i. The energy dissipation (2.4) has, therefore, the properties required in thermodynamics of irreversible processes and we can set up linear phenomenological equations in the usual way. Since q is even, i odd, the Casimir relations apply and we obtain

$$A = C_{11}\dot{q} + C_{12}\dot{i}, \qquad B = C_{21}\dot{q} + C_{22}\dot{i}, \tag{2.6}$$

with

$$C_{21} = -C_{12}. \tag{2.7}$$

Of course, these coefficients can be expressed in terms of the elements of the network. One finds

$$C_{11} = R_1,\ C_{12} = L,\ C_{21} = -L,\ C_{22} = L^2/R_2. \tag{2.8}$$

Thus, the Casimir relation is directly verified in this case. We remark that the dissipation function can also be written in terms of rates of the internal variables q and i; one obtains

$$2\mathfrak{D} = R_1\dot{q}^2 + (L^2/R_2)\dot{i}^2. \tag{2.9}$$

3. GENERAL THERMODYNAMICS OF ELECTRICAL NETWORKS

We restrict ourselves again to the isothermal case with the Joulean heat being removed immediately as it is generated. The general network equations for an electrical network with n independent meshes will be formulated without proof. The total impressed voltages in the meshes are denoted by $u_1, u_2, \cdots u_n$, the respective currents by $i_1, i_2, \cdots i_n$, their time integrals by $q_1, q_2, \cdots q_n$, normalized to zero for $t \to -\infty$. The voltages are not applied before some instant $t_0 > -\infty$. Then we have (see, for instance, Guillemin[1])

$$u_i(t) = \sum_{k=1}^{n} [\Gamma_{ik}q_k(t) + R_{ik}\dot{q}_k(t) + L_{ik}\ddot{q}_k(t)]. \tag{3.1}$$

Γ_{ik} is the reciprocal of the element C_{ik} of the capacitance matrix, R_{ik} is the resistance matrix, and L_{ik} the inductance matrix. The following symmetry relations are inferred from network analysis

$$\Gamma_{ik} = \Gamma_{ki}, \qquad R_{ik} = R_{ki}, \qquad L_{ik} = L_{ki}. \tag{3.2}$$

These matrices have non-negative quadratic forms. We shall assume here, in particular, that $\det \Gamma_{ik} \neq 0$. Then there exists an equilibrium with $\dot{q}_k = 0$ if arbitrary constant voltages are applied.

First Thermodynamic Formulation

We introduce a Lagrangian function

$$\mathfrak{L}(q_i, \dot{q}_i, u_i) = -\frac{1}{2}\sum_{i=1}^{n}\sum_{k=1}^{n}\Gamma_{ik}q_iq_k + \frac{1}{2}\sum_{i=1}^{n}\sum_{k=1}^{n}L_{ik}\dot{q}_i\dot{q}_k + \sum_{i=1}^{n}u_iq_i\ , \tag{3.3}$$

and a dissipation function

$$\mathfrak{D}(\dot{q}_i) = \frac{1}{2}\sum_{i=1}^{n}\sum_{k=1}^{n}R_{ik}\dot{q}_i\dot{q}_k. \tag{3.4}$$

Then Eqs. (3.1) can be rewritten as

$$\frac{\partial\mathfrak{L}}{\partial q_i} - \frac{d}{dt}\frac{\partial\mathfrak{L}}{\partial\dot{q}_i} = \frac{\partial\mathfrak{D}}{\partial\dot{q}_i} \qquad (i = 1, 2, \cdots, n). \tag{3.5}$$

Following Machlup and Onsager,[2] we define thermodynamic forces or affinities by

$$A_i = \frac{\partial\mathfrak{L}}{\partial q_i} - \frac{d}{dt}\frac{\partial\mathfrak{L}}{\partial\dot{q}_i}. \tag{3.6}$$

Then the energy dissipation can be expressed by virtue of (3.4), (3.5), and (3.6) as

$$2\mathfrak{D} = \sum_{i=1}^{n}\dot{q}_i\frac{\partial\mathfrak{D}}{\partial\dot{q}_i} = \sum_{i=1}^{n}\dot{q}_iA_i. \tag{3.7}$$

It again has the form of a sum of products of thermodynamic forces and rates of change of charges. Both vanish in equilibrium and one expects phenomenological relations which express the A_i as linear functions of the $\dot{q}_i$. In fact, one obtains from (3.4), (3.5), and (3.6),

$$A_i = 2\partial\mathfrak{D}/\partial\dot{q}_i = \sum_{k=1}^{n}R_{ik}\dot{q}_k. \tag{3.8}$$

In this thermodynamic description, only Onsager relations $R_{ik} = R_{ki}$ prevail, no Casimir coefficients being present. But it is to be said that the thermodynamic forces (3.6) are of an unusual type. They contain in general the second derivatives of the variables q_i.

Second Thermodynamic Formulation

One knows from Hamiltonian mechanics how one can transform from variables q_i and their derivatives $\dot{q}_i$ into two sets of independent variables which are, in mechanics, the coordinates and the canonically conjugate momenta. The same type of Legendre transformation can be applied here. We introduce the quantities

$$\Phi_i = \partial\mathfrak{L}/\partial\dot{q}_i = \sum_{k=1}^{n}L_{ik}\dot{q}_k, \tag{3.9}$$

which are the magnetic fluxes through the independent meshes and we assume that these equations

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[1] E. A. Guillemin, *Introductory Circuit Theory* (John Wiley & Sons, Inc., New York, 1953), pp. 368–371.

[2] S. Machlup and L. Onsager, Phys. Rev. 91, 1512 (1953).

can be solved for the $\dot{q}_i$;

$$\dot{q}_i = \sum_{k=1}^{n} L^{ik}\phi_k. \tag{3.10}$$

Then a Hamiltonian will be defined by

$$\begin{aligned}\mathcal{H}(q_i, \phi_i, u_i) &= -\mathcal{L} + \sum_{i=1}^{n} \dot{q}_i\phi_i \\ &= \frac{1}{2}\sum_{i=1}^{n}\sum_{k=1}^{n} \Gamma_{ik}q_iq_k \\ &\quad + \frac{1}{2}\sum_{i=1}^{n}\sum_{k=1}^{n} L^{ik}\phi_i\phi_k - \sum_{i=1}^{n} u_iq_i,\end{aligned} \tag{3.11}$$

with

$$\begin{aligned}d\mathcal{H} &= \sum_{i=1}^{n}\left(\sum_{k=1}^{n} \Gamma_{ik}q_k - u_i\right) dq_i \\ &\quad + \sum_{i=1}^{n}\left(\sum_{k=1}^{n} L^{ik}\phi_k\right) d\phi_i - \sum_{i=1}^{n} q_i\, du_i.\end{aligned} \tag{3.12}$$

We denote the coefficients by

$$-A_i = \sum_{k=1}^{n} \Gamma_{ik}q_k - u_i, \quad -B_i = \sum_{k=1}^{n} L^{ik}\phi_k. \tag{3.13}$$

They are the thermodynamic forces conjugate to the even variables q_i and the odd variables Φ_i, respectively. The rate of energy dissipation is again expressible in two ways:

$$\begin{aligned}2\mathfrak{D} &= \sum_{i=1}^{n} u_i\dot{q}_i - (d/dt)\left(\mathcal{H} + \sum_{i=1}^{n} u_iq_i\right) \\ &= \sum_{i=1}^{n} (A_i\dot{q}_i + B_i\dot{\Phi}_i),\end{aligned} \tag{3.14}$$

$$2\mathfrak{D} = \sum_{i=1}^{n}\sum_{k=1}^{n} R_{ik}\dot{q}_i\dot{q}_k. \tag{3.15}$$

Linear phenomenological relations can now be written down. The coefficients connecting the A_i with the q_i and the B_i with the ϕ_i are Onsager coefficients; the coefficients connecting the A_i with the ϕ_i and the B_i with the q_i are Casimir coefficients. In fact, one obtains explicitly, from (3.5), (3.4), (3.10), and (3.11),

$$A_i = -\partial\mathcal{H}/\partial q_i = \sum_{k=1}^{n} R_{ik}\dot{q}_k + \dot{\Phi}_i, \tag{3.16}$$

$$B_i = -\partial\mathcal{H}/\partial\phi_i = -\dot{q}_i. \tag{3.17}$$

The original network equations (3.1) are regained if one eliminates the affinities A_i and B_i from Eqs. (3.13), (3.14), and (3.17) and makes use of (3.9). It is remarkable that the energy dissipation comes only from the rates of the even variables, no Φ_i terms being contained in (3.17).

We can summarize as follows: In the theory of electrical networks with lumped elements, the Onsager–Casimir reciprocal relations are an immediate consequence of the symmetry of the resistance matrix R_{ik} which can be verified, either directly or via the reciprocity theorem of Maxwell's theory.

One can also take the opposite point of view, disregard the dissipation function (3.4) and derive the symmetry of R_{ik} from the Onsager–Casimir reciprocal relations. This is done by applying the method of thermodynamics of irreversible processes.

The thermodynamic properties of the network are contained in the Lagrangian $\mathcal{L}$ or the Hamiltonian $\mathcal{H}$ and in Eqs. (3.6) or (3.13), respectively, which are derived therefrom. We assume det $\Gamma_{ik} = 0$. Then there exists an equilibrium state for constant values of the voltages. In this equilibrium state the affinities are zero. In the vicinity of the equilibrium we are permitted to set up linear phenomenological laws which connect the rates of change of the extensive variables q_i, or q_i and Φ_i linearly with the affinities A_i, or A_i and B_i, respectively. We elaborate only on the case of the Hamilton formalism. Then the phenomenological laws can be written as

$$\dot{q}_i = \sum_{k=1}^{n} (t_{ik}A_k + S_{ik}B_k), \tag{3.18}$$

$$\dot{\Phi}_i = \sum_{k=1}^{n} (-S_{ki}A_k + r_{ik}B_k). \tag{3.19}$$

Use is made here already of the Casimir reciprocal relations by having written $-S_{ki}$ for the coefficient of A_k in the second equation. The Onsager reciprocal relations require

$$t_{ik} = t_{ki}, \qquad r_{ik} = r_{ki}. \tag{3.20}$$

Now we take account of the special relations which prevail in the network under consideration. They are contained in (3.10) and in the second equation of (3.13), or

$$\dot{q}_i = -B_i. \tag{3.21}$$

By combining this with (3.18), we obtain the identity

$$\sum_{k=1}^{n} [t_{ik}A_k + (S_{ik} + \delta_{ik})B_n] = 0 \tag{3.22}$$

for arbitrary values of the A_k and B_k. From this we derive

$$\begin{aligned}&t_{ik} = 0, \\ &S_{ik} = -\delta_{ik}\ (= 0 \text{ for } i \neq k, = -1 \text{ for } i = k).\end{aligned} \tag{3.23}$$

When we now eliminate the affinities A_k and B_k from (3.18), (3.19), and (3.13), we arrive at Eqs. (3.1) with $R_{ik} = r_{ik}$. Thus the symmetry of R_{ik} is a consequence of (3.20).

4. THE IMPEDANCE MATRIX

We turn back to the general network equations (3.1) and assume that $u_{m+1} = u_{m+2} = \cdots = u_n = 0$.

Then one can solve these equations for $u_1, u_2, \cdots u_m$ in terms of $q_1, q_2, \cdots, q_m$ and their derivatives only. The result can be formally written as

$$u_i(t) = \sum_{k=1}^{m} pZ_{ik}(p)q_k(t) \qquad (i = 1, 2, \cdots, n), \tag{4.1}$$

where p denotes the operator

$$p = d/dt. \tag{4.2}$$

If, in particular,

$$u_i(t) = u_i^0 \exp{(pt)}, \tag{4.3}$$

with $p = p_1 + ip_2$, $p_1 > 0$, p_2 real, then one has solutions

$$q_i(t) = q_i^0 \exp{(pt)}, \tag{4.4}$$

and p has the character of an ordinary quantity. The matrix $Z_{ik}(p)$ is then called the impedance matrix of the $2m$-terminal network. It has some general properties which have been known in network theory for a long time.

First of all, it is symmetric. This can be directly proved by network analysis and is traced back to the symmetry of the resistance matrix R_{ik}; hence, the symmetry of the impedance matrix $Z_{ik}(p)$ is also a direct consequence of the Onsager reciprocal relations. Secondly, let ξ_i be any real numbers. Then the function

$$\zeta(p) = \sum_{i=1}^{n} \sum_{k=1}^{n} Z_{ik}(p)\xi_i\xi_k \tag{4.5}$$

has the following properties:

1. $\zeta(p)$ is a holomorphic function for Re $p > 0$;
2. $\zeta(p)$ is real for real positive p;
3. $\zeta(p)$ has positive real part for Re $p > 0$.

The proof uses only the inequality

$$\int_{-\infty}^{\tau} \sum_{i=1}^{n} u_i(t)\dot{q}_i(t)\, dt \geqq 0 \quad \text{(all values of } \tau\text{)}, \tag{4.6}$$

which holds for any network which was originally empty. If one inserts the u_i from the general equations (3.1) with $u_{m+1} = \cdots, = u_n = 0$, one recognizes that the condition (4.6) rests on two principles, the thermodynamic stability of the electrical network (i.e., Γ_{ik} and L_{ik} are matrices with a non-negative quadratic form) and on the positive value of the energy dissipation (i.e., the matrix R_{ik} has a non-negative quadratic form).

These results are not restricted to electrical networks. If we consider linear thermodynamic systems with external variables X_i and Y_i which remain close to their reference values X_i^+ and Y_i^+ corresponding to a state of complete thermodynamic equilibrium and with even or odd variables or both, we can define an impedance matrix $Z_{ik}(p)$ such that

$$Y_i(t) - Y_i^+ = p \sum_{k=1}^{n} Z_{ik}(p)[X_k(t) - X_k^+], \tag{4.7}$$

with the general properties as expressed before, provided the variables Y_i are of intensive character while the thermodynamically conjugate variables X_i are of extensive character.[3]

Relaxation phenomena with small departures from thermodynamic equilibrium can be thermodynamically described in this way. Impedance matrices with the above-named properties exist for the external thermodynamically conjugated variables. From this one concludes that the relaxation behavior can, to a large extent, be described by network models. In the special case of one extensive and one intensive external variable and of a finite number of internal variables, there is possible, according to the theorem of Bott and Duffin,[4] a general mapping onto 2-terminal networks. This is, in fact, the case of greatest interest.

We want to add a remark on the expression of Casimir reciprocal relations by Onsager reciprocal relations. It is true that, for the derivation of the reciprocal relations, one has to consider the fluctuations of extensive variables. Hence, the Casimir relations are by no means trivial and dispensable. But after they have been derived, one can express them formally by Onsager reciprocal relations. This is done in the following way. Denote by $\boldsymbol{\alpha}$ the set of α variables, by $\boldsymbol{\beta}$ the set of β variables, the first ones being even, the others odd with respect to time reversal. Let the thermodynamically conjugate affinities be designated by A and B, respectively. Then the rate equations are

$$d\boldsymbol{\alpha}/dt = \mathbf{p}_{11}\mathbf{A} + \mathbf{p}_{12}\mathbf{B}, \tag{4.8}$$

$$d\boldsymbol{\beta}/dt = \mathbf{p}_{21}\mathbf{A} + \mathbf{p}_{22}\mathbf{B}, \tag{4.9}$$

with matrix coefficients $\mathbf{p}_{ik}$ $(i, k = 1, 2)$.

The Onsager reciprocal relations are

$$\mathbf{p}_{11} = \tilde{\mathbf{p}}_{11}, \qquad \mathbf{p}_{22} = \tilde{\mathbf{p}}_{22}, \tag{4.10}$$

while the Casimir reciprocal relations require

$$\mathbf{p}_{12} = -\tilde{\mathbf{p}}_{21}. \tag{4.11}$$

The energy dissipation (apart from a factor T, it is equal to the rate of entropy production) is

$$\begin{aligned} 2\mathfrak{D} &\equiv \tilde{\mathbf{A}}\cdot d\boldsymbol{\alpha}/dt + \tilde{\mathbf{B}}\cdot d\boldsymbol{\beta}/dt \\ &= \tilde{\mathbf{A}}\cdot d\boldsymbol{\alpha}/dt + d\tilde{\boldsymbol{\beta}}/dt\cdot\mathbf{B}. \end{aligned} \tag{4.12}$$

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[3] J. Meixner and H. Reik, in *Encyclopedia of Physics* (Julius Springer-Verlag, Berlin, 1959), Vol. III, Part 2, pp. 482–487.

[4] R. Bott and R. J. Duffin, J. Appl. Phys. **20**, 816 (1949).

Ordinarily, one writes the linear phenomenological equations by setting the rate factors equal to linear functions of the affinities. We observe that the affinities **A** are even and the affinities **B** odd with respect to time reversal. If now we write the rate equations in the form that the factors of the individual terms which are odd with respect to time-reversal are expressed as linear functions of those factors which are even with respect to time reversal, we obtain

$$d\boldsymbol{\alpha}/dt = \mathbf{q}_{11}\mathbf{A} + \mathbf{q}_{12}\, d\boldsymbol{\beta}/dt, \tag{4.13}$$

$$\mathbf{B} = \mathbf{q}_{21}\mathbf{A} + \mathbf{q}_{22}\, d\boldsymbol{\beta}/dt. \tag{4.14}$$

It is clearly permissible to write the phenomenological equations in this way, provided the inverse of the matrix $\mathbf{p}_{22}$ in (4.9) exists. In fact, one derives from (4.8) and (4.9), Eqs. (4.13) and (4.14) with the following values of the coefficients

$$\begin{aligned} \mathbf{q}_{11} &= \mathbf{p}_{11} - \mathbf{p}_{12}\mathbf{p}_{22}^{-1}\mathbf{p}_{21}, & \mathbf{q}_{22} &= \mathbf{p}_{22}^{-1}, \\ \mathbf{q}_{12} &= \mathbf{p}_{12}\mathbf{p}_{22}^{-1}, & \mathbf{q}_{21} &= -\mathbf{p}_{22}^{-1}\mathbf{p}_{21}. \end{aligned} \tag{4.15}$$

From (4.10) and (4.11) one now concludes immediately that

$$\mathbf{q}_{11} = \tilde{\mathbf{q}}_{11}, \qquad \mathbf{q}_{12} = \tilde{\mathbf{q}}_{21}, \qquad \mathbf{q}_{22} = \tilde{\mathbf{q}}_{22}. \tag{4.16}$$

That is, all of the coefficients in (4.13) and (4.14) are Onsager coefficients.

Theorem 1. If the entropy production is known as a bilinear form in the thermodynamic forces and fluxes (or rates), and if one writes the factors which are even with respect to time reversal as linear functions of the factors which are odd with respect to time reversal, the entity of phenomenological coefficients satisfy Onsager reciprocal relations.

5. MAXWELL'S EQUATIONS WITH ARBITRARY EXCITATION

We consider an arbitrary continuous distribution of matter. Any motion of matter is excluded. Furthermore, it is assumed that the system is isothermal and that the Joulean heat is somehow removed as it is generated. Though this might seem to be a serious restriction, it is not when we consider sufficiently weak fields, because the development of Joulean heat is a second-order effect.

Maxwell's equations are in the usual notation

$$\begin{gathered} \nabla \times \mathbf{E} = -\dot{\mathbf{B}}, \qquad \nabla \times \mathbf{H} = \dot{\mathbf{D}} + \mathbf{J}, \\ \nabla \cdot \mathbf{D} = \rho, \qquad \nabla \cdot \mathbf{B} = 0. \end{gathered} \tag{5.1}$$

We assume the existence of linear constitutive equations

$$D_i = \epsilon_{ik}E_k + \lambda_{ik}H_k, \tag{5.2}$$

$$B_i = \nu_{ik}E_k + \mu_{ik}H_k, \tag{5.3}$$

$$E_i + E_i' = \rho_{ik}J_k. \tag{5.4}$$

It is understood that a repeated suffix is a suffix of summation from 1 to 3. $E_i'(x_1, x_2, x_3, t)$ is the impressed electric-field strength. We admit that the coefficients ϵ_{ik}, λ_{ik}, etc. depend on the frequency in the harmonic case or on the operator $p = d/dt$ in the general case which is equivalent to after-effect relations instead of (5.2), (5.3), and (5.4).[5]

Then we shall expect that the impressed field determines the current distribution J. We express this relation formally by

$$J = YE', \tag{5.5}$$

where Y is a linear operator of nonlocal and of after-effect type. This means that $J(x_1\ x_2\ x_3\ t)$ depends on the values of $E(x_1'\ x_2'\ x_3'\ t')$ at all points in space and at all times t' previous to t. Such operators can be written in the form

$$J_i(P;t) = \int_0^\infty ds \int Y_{ik}(P,Q;s)E_k'(Q;t-s)\, d\tau_Q, \tag{5.6}$$

with $P = (x_1\ x_2\ x_3)$, $Q = (x_1'\ x_2'\ x_3')$.

Let us now consider impressed fields of the form

$$E_k'(Q, t) = e_k(Q)e^{pt} \text{ with } p = p_1 + ip_2,\ p_1 > 0. \tag{5.7}$$

Then we obtain

$$J_i(P, t) = j_i(P)e^{pt}, \tag{5.8}$$

with

$$j_i(P) = \int Y_{ik}(P, Q; p)e_k(Q)\, d\tau_Q, \tag{5.9}$$

where

$$Y_{ik}(P, Q; p) = \int_0^\infty Y_{ik}(P, Q; s)e^{-ps}\, ds. \tag{5.10}$$

The matrix $Y_{ik}(P, Q; p)$, which depends on a pair P, Q of points in space, will be called the generalized admittance.

We take now two impressed fields $E_{i\mathrm{I}}'$ and $E_{i\mathrm{II}}'$ of the type (5.7) with the same value of p. Then, from Maxwell's equations, one obtains

$$\begin{aligned} &E_{i\mathrm{I}}'J_{i\mathrm{II}} - E_{i\mathrm{II}}'J_{i\mathrm{I}} = J_{i\mathrm{II}}\rho_{ik}J_{k\mathrm{I}} - J_{i\mathrm{I}}\rho_{ik}J_{k\mathrm{II}} \\ &+ p[E_{i\mathrm{I}}D_{i\mathrm{II}} - E_{i\mathrm{II}}D_{i\mathrm{I}} + H_{i\mathrm{I}}B_{i\mathrm{II}} - H_{i\mathrm{II}}B_{i\mathrm{I}}] \\ &+ \nabla\cdot(\mathbf{E}_{\mathrm{I}} \times \mathbf{H}_{\mathrm{II}} - \mathbf{E}_{\mathrm{II}} \times \mathbf{H}_{\mathrm{I}}). \end{aligned} \tag{5.11}$$

If integrated over the whole space, the last term gives a vanishing contribution, provided the impressed fields are restricted to a finite portion of

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[5] H. König and J. Meixner, Math. Nachr. **19**, 265 (1958).

space. Upon insertion of (5.2) and (5.3), and integration over the whole space, we obtain

$$\begin{aligned}\int [E'_{i\mathrm{I}}J_{i\mathrm{II}} - E'_{i\mathrm{II}}J_{i\mathrm{I}}]\,d\tau &= \int [(\rho_{ik} - \rho_{ki})J_{i\mathrm{II}}J_{k\mathrm{I}} \\ &\quad + p[(\epsilon_{ik} - \epsilon_{ki})E_{i\mathrm{I}}E_{k\mathrm{II}} \\ &\quad + (\lambda_{ik} - \nu_{ki})(E_{i\mathrm{I}}H_{k\mathrm{II}} - E_{i\mathrm{II}}H_{k\mathrm{I}}) \\ &\quad + (\mu_{ik} - \mu_{ki})H_{i\mathrm{I}}H_{k\mathrm{II}}]\,d\tau. \qquad (5.12)\end{aligned}$$

Hence, we have the following theorem.

Theorem 2. If

$$\epsilon_{ik}(p) = \epsilon_{ki}(p), \qquad \lambda_{ik}(p) = \nu_{ki}(p),$$
$$\mu_{ik}(p) = \mu_{ki}(p), \qquad \rho_{ik}(p) = \rho_{ki}(p),$$

then

$$\int [E'_{i\mathrm{I}}J_{i\mathrm{II}} - E'_{i\mathrm{II}}J_{i\mathrm{I}}]\,d\tau = 0. \qquad (5.13)$$

This is one of the reciprocity theorems of Maxwell's theory. Obviously, it is always satisfied if all the materials are isotropic and if the constitutive equations are not of nonlocal character.

By inserting (5.9) we obtain

$$\iint [E'_{i\mathrm{I}}(P)Y_{ik}(P,Q;p)E'_{k\mathrm{II}}(Q) - E'_{i\mathrm{II}}(P)Y_{ik}(P,Q;p)E'_{k\mathrm{I}}(Q)]\,d\tau_P\,d\tau_Q = 0 \qquad (5.14)$$

for arbitrary impressed fields. We rewrite this equation as

$$\iint E'_{i\mathrm{I}}(P)[Y_{ik}(P,Q;p) - Y_{ki}(Q,P;p)] \times E'_{k\mathrm{II}}(Q)\,d\tau_P\,d\tau_Q = 0. \qquad (5.15)$$

Since $E'_{i\mathrm{I}}$ and $E'_{i\mathrm{II}}$ are arbitrary, one has the next theorem.

Theorem 3. If the reciprocity theorem (5.13) holds, the generalized admittance has the symmetry property

$$Y_{ik}(P,Q;p) = Y_{ki}(Q,P;p). \qquad (5.16)$$

Now the symmetry properties expressed in Theorem 2 can be proved from the thermodynamic theory of relaxation phenomena, provided the eventual dependence of the coefficients on a magnetic field can be neglected. They are a direct consequence of the Onsager–Casimir reciprocal relations.[6] Hence, we have theorem 4.

Theorem 4. The symmetry property (5.16) of the generalized admittance $Y_{ik}(P, Q, p)$, and hence the reciprocity theorem (5.13), are consequences of the Onsager–Casimir reciprocal relations, if the dependence of the coefficients ϵ_{ik} etc. on the magnetic field can be neglected.

Incidentally, we remark that the symmetry of the impedance and admittance matrices of a $2n$-terminal network is a special case of the symmetry property of the generalized admittance.

Moreover, we should like to mention that the representations (5.6) and (5.9) can be derived from the inequality

$$\int_{-\infty}^{s} dt \int J_i(P,t)E'_i(P,t)\,d\tau \geqq 0, \qquad \text{(all values of } s) \qquad (5.17)$$

which expresses the fact that, under the given conditions, no energy can be extracted from the system if $E'_i(P, t) = 0$ for $t < t_0$, and $J_i(P, t) = 0$ for $t < t_0$ with some finite value of t_0.[7]

There is also a generalization of the function $\zeta(p)$ defined in (4.5).

Theorem 5. Let $e_i(P)$ be any real vector field such that the following integral exists. Then the function

$$\eta(P) = \iint e_i(P)Y_{ik}(P,Q;p)e_k(Q)\,d\tau_P\,d\tau_Q \qquad (5.18)$$

is a positive real function, i.e., it shares with the function $\zeta(p)$ in (4.5) the properties mentioned there.

The proof goes along the same lines as the proof that is given for the analoguous property of the admittance function $Y(p)$ in network theory.

So far we have assumed that the magnetic field is sufficiently weak in order that the coefficients ϵ_{ik} etc. can be considered as practically independent of the magnetic field. If, in addition to the weak electromagnetic field described by the Maxwell equations (5.1) there is a constant magnetic field H_0, B_0 present, then the generalized admittance depends also on the field of the magnetic induction B_0. Due to the Onsager–Casimir reciprocal relations for the ϵ_{ik} etc. in a magnetic field, one can derive the generalized result

$$Y_{ik}(P,Q;p;B_0) = Y_{ki}(Q,P;p;-B_0). \qquad (5.19)$$

The proof goes along the same lines as before with the modification that the current distribution $J_{i\mathrm{II}}$ now refers to the reversed constant magnetic field $-B_0$.

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[6] See reference 3.

[7] See reference 5 and also J. Batt and H. König, Arch. Math. 10, 273 (1959).

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Theory of the Soret Effect in Electrolytic Solutions

E. HELFAND
Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey
R. J. BEARMAN*† AND V. S. VAIDHYANATHAN‡
Department of Chemistry, University of Kansas, Lawrence, Kansas
(Received 17 September 1962)

The limiting law for the square-root concentration dependence of the heat of transport of a simple electrolyte is calculated by considering the Soret effect. The calculation is accomplished by relating the intermolecular forces arising from the temperature gradient in the nonuniform Soret stationary state to the equilibrium gradients of chemical potential required to maintain the same concentration gradients. The contribution arising from ion–ion interactions is identical with that determined by Helfand and Kirkwood from a consideration of heat flow accompanying diffusion. Hence, the present work provides a verification of the heat–matter reciprocal relation without explicitly invoking time-reversal invariance.

I. INTRODUCTION

Of the numerous contributions of Lars Onsager to theoretical chemistry, his discussions of irreversible processes in dilute electrolytic solutions and of the famous reciprocal relations are among those which have had the greatest impact on the scientific world. We therefore regard it as most appropriate, in this volume of tribute, that we make a contribution relating to both of these fields by explicitly calculating the limiting law for the heat of transport of dilute electrolytic solutions from the Soret effect, and verifying the heat–matter reciprocal relation.

The general equations of transport may be derived readily from statistical mechanics, and transport parameters written in terms of nonequilibrium distribution functions.[1] It is often convenient to split a transport property into the sum of two terms, the first of which is related to equilibrium distribution functions and the second of which contains nonequilibrium contributions. Ordinarily, the second term is rather difficult to evaluate. However, in the stationary state of thermal diffusion of a solution of a binary electrolyte, a symmetry condition causes the nonequilibrium contribution to the heat of transport to vanish. In this case, the calculation of the effect of interionic forces on the heat of transport is a relatively simple matter. It is to this computation that we turn our attention.

II. PHENOMENOLOGICAL THEORY

Suppose that we have a simple electrolyte which dissociates completely into (+) positive ions and (−) negative ions in the solvent, 1. Consider that this electrochemical system is isobaric and is undergoing ordinary and thermal diffusion.

There are a number of forms in which the linear laws relating the thermodynamic forces and fluxes may be written. The one most convenient for our theoretical discussion, as well as for experimental investigations, of heat–matter cross effects is[2,3]:

$$-\nabla^T\tilde{\mu}_\alpha = \sum_\beta R_{\alpha\beta}\mathbf{j}_\beta - Q^*_\alpha(-\nabla \ln T), \qquad (2.1)$$

$$\mathbf{q} = \sum_\alpha Q^*_\alpha\mathbf{j}_\alpha + \lambda T(-\nabla \ln T),$$

$$\alpha, \beta = 1, +, -, \qquad (2.2)$$

where $\mathbf{q}$ is the heat flux and $\mathbf{j}_\alpha$ is the particle diffusion flux. The flux $\mathbf{j}_\alpha$ is expressed in terms of the concentration of α, c_α, in particles per cc, and in terms of the average velocity relative to the center of mass velocity, $\mathbf{u}_\alpha - \mathbf{u}$, by

$$\mathbf{j}_\alpha = c_\alpha(\mathbf{u}_\alpha - \mathbf{u}).$$

The isothermal gradient of total chemical potential $\nabla^T\tilde{\mu}_\alpha$ is defined by the relations

$$\nabla\tilde{\mu}_\alpha = \nabla\mu_\alpha - \mathbf{X}_\alpha, \qquad (2.3)$$

$$\nabla^T = \nabla - \nabla T\left(\frac{\partial}{\partial T}\right)_{P,x_\gamma}, \qquad (2.4)$$

where μ_α is the electrochemical potential per

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[†] John Simon Guggenheim Memorial Foundation Fellow.

[‡] Present address: Veterans Administration, Little Rock Hospital Division, Little Rock, Arkansas.

[1] R. J. Bearman and J. G. Kirkwood, J. Chem. Phys. **28**, 136 (1958).

[2] H. Holtan, Jr., P. Mazur and S. R. DeGroot, Physica **19**, 1109 (1953).

[3] E. Helfand, J. Chem. Phys. **33**, 319 (1960).

particle, $\mathbf{X}_\alpha$ is any nonelectrical external force on α,[4] and the partial temperature differentiation is performed at constant pressure P and mole fractions x_γ. An Onsager reciprocal relation has already been employed, since the same symbol Q_α^*—the heat of transport of species α—is used to relate both temperature gradient to chemical potential gradient and heat flow to matter flow. The antisymmetry, rather than symmetry, between these two phenomenological coefficients is a result of using the $\mathbf{j}_\alpha$'s, which are antisymmetric in time, as independent variables.[5]

Under conditions of vanishing net current density

$$\mathbf{i} = z_+c_+\mathbf{u}_+ + z_-c_-\mathbf{u}_- = 0, \tag{2.5}$$

and electroneutrality

$$z_+c_+ + z_-c_- = 0 \tag{2.6}$$

the positive and negative species have the same velocity;

$$\mathbf{u}_+ = \mathbf{u}_- = \mathbf{u}_s. \tag{2.7}$$

We then need speak only of the properties of the solute, s, notably the concentration

$$c_s = c_+/\nu_+ = c_-/\nu_-, \tag{2.8}$$

where ν_α is the number of moles of ion α per formula weight of solute; the diffusion flux

$$\mathbf{j}_s = c_s(\mathbf{u}_s - \mathbf{u}), \tag{2.9}$$

and the heat of transport

$$Q_s^* = \nu_+Q_+^* + \nu_-Q_-^*. \tag{2.10}$$

The electrochemical potential μ_s of the solute, in the presence only of electrical forces, is equal to the chemical potential, since the neutral salt experiences no net force even with the electric field.

The heat of transport Q_s^* is then measured either as the proportionality constant between heat flux and diffusion flux in an isothermal diffusion experiment,[2,3]

$$\mathbf{q} = Q_s^*\mathbf{j}_s + Q_1^*\mathbf{j}_1, \tag{2.11}$$

$$\left.\begin{aligned} c_sQ_s^* + c_1Q_1^* &= 0,\\ m_1\mathbf{j}_1 + m_s\mathbf{j}_s &= 0,\\ m_s &= \nu_+m_+ + \nu_-m_-, \end{aligned}\right. \tag{2.12}$$

or as the proportionality constant between the temperature gradient and chemical potential gradient when the Soret stationary state of zero diffusion flux is achieved in the absence of nonelectrical external fields,

$$\nabla^T\mu_s = -Q_s^*\nabla \ln T. \tag{2.13}$$

Equations (2.11) and (2.12) were employed by Helfand and Kirkwood[6] to derive the limiting law for the concentration dependence of the heat of transport of an electrolyte. In this paper, we shall calculate the contribution of interionic forces to the limiting law for Q_s^* from arguments based on Eq. (2.13), the other aspect of the reciprocal relation.

III. INTERIONIC FORCES

In the usual models of electrolytic solutions, the solvent is viewed as a dielectric continuum with dielectric constant $\epsilon(T, P)$. The potential between a pair of ions of types α and β is taken to be $z_\alpha z_\beta e^2/\epsilon r$ where z_α and z_β represent signed charge numbers, e is the magnitude of the charge on the electron, and r is the distance separating the ions. In the Soret stationary state, however, the dielectric constant varies by virtue of the temperature gradient. One must therefore return to fundamentals and calculate the electrical potential at $\mathbf{r}_2$ near a point charge $z_\alpha e$ at $\mathbf{r}_1$ in a medium with dielectric constant $\epsilon(\mathbf{r}_2) = \epsilon(\mathbf{r}_1) + \mathbf{r}\cdot\nabla\epsilon$, where $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. The Maxwell equation appropriate to the problem is

$$\nabla_{r_2}\cdot\epsilon(\mathbf{r}_2)\nabla_{r_2}\varphi_\alpha(\mathbf{r}_1, \mathbf{r}_2) = -4\pi z_\alpha e\delta(\mathbf{r}). \tag{3.1}$$

In order to avoid difficulties arising from the dielectric constant becoming infinite at large $\mathbf{r}$, it is best to confine the dielectric to a region surrounding the charge, large compared to the distances $r = |\mathbf{r}|$ of interest, but small compared to distances over which ϵ changes significantly. The potential energy between an ion α at $\mathbf{r}_1$ and β at $\mathbf{r}_2$ is then, from the solution of Eq. (3.1), to lowest order in $\nabla\epsilon$ and the reciprocal of the size of the box,

$$\mathbf{V}_{\alpha\beta} = z_\beta e\varphi_\alpha = (z_\alpha z_\beta e^2/\epsilon(\mathbf{r}_1)r)(1 - \tfrac{1}{2}\mathbf{r}\cdot\nabla \ln \epsilon), \tag{3.2}$$

and the force β exerts on α is

$$\mathbf{F}_{\beta\alpha} = -\nabla_{r_1}V_{\alpha\beta} = -(z_\alpha z_\beta e^2/\epsilon(\mathbf{r}_1)r^2) \times [\mathbf{e}_r - \tfrac{1}{2}r(\mathbf{e}_r\mathbf{e}_r + \mathbf{1})\cdot\nabla \ln \epsilon], \tag{3.3}$$

where $\mathbf{e}_r$ is a unit vector in the $\mathbf{r}$ direction and $\mathbf{1}$ is the unit tensor.

Equation (3.2) may also be arrived at by a sym-

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[4] The electrochemical potential is equal to the sum of the chemical and electrical potentials. For the purposes of this paper we never find it necessary to separate these two parts. Thus, for notational simplicity, we do not introduce additional symbols, such as the prime, to distinguish between the electrochemical potential and the chemical part. The somewhat arbitrary distinction between electrical and other forces is made here, for the sake of convenience later in the paper.

[5] H. B. G. Casimir, Rev. Mod. Phys. 17, 343 (1945).

[6] E. Helfand and J. G. Kirkwood, J. Chem. Phys. 32, 857 (1960); in this reference the more general problem of mixed electrolytes is treated.

metry argument. Since $V_{\alpha\beta}$ must be symmetric with respect to interchange of the ions α and β (a consequence of Newton's third law), it has the form

$$V_{\alpha\beta} = z_\alpha z_\beta e^2/[e(\mathbf{r}_1) + \epsilon(\mathbf{r}_2)]r + \text{a term symmetric in } \mathbf{r}_1 \text{ and } \mathbf{r}_2 \text{ and linear in } \nabla\epsilon + O(\nabla^2\epsilon) + O(\nabla\epsilon)^2. \tag{3.4}$$

The only vector, other than $\nabla\epsilon$, out of which the second term on the right-hand side may be composed is $\mathbf{r}$, so that this term must have the form $\omega(r)\mathbf{r}\cdot\nabla\epsilon$ which is odd in $\mathbf{r}_1$ and $\mathbf{r}_2$ unless $\omega = 0$. Thus to lowest order in $\nabla\epsilon$, Eq. (3.4) is identical with Eq. (3.2).

IV. AVERAGE INTERIONIC FORCES IN THE SORET STATIONARY STATE

The limiting laws for the properties of strong electrolytes are composed of an infinite dilution term, containing the effect of ion-solvent interaction, and a term proportional to the square root of the concentration (or equivalently, proportional to κ, the inverse Debye length). Only the contributions to the latter term arising from interionic forces will be calculated here.

The principle behind the present derivation is that the forces and differential stresses on an ion must be balanced in the stationary state. The calculation begins with the partial hydrodynamic equation of motion for ions of type α. This equation was first derived by Bearman and Kirkwood[1] by multiplication of Liouville's equation by the momentum of one of the particles of α, followed by integration over all momenta and over the positions of all the particles except the one of interest. Their result is

$$\partial(m_\alpha c_\alpha \mathbf{u}_\alpha)/\partial t = -\nabla(c_\alpha kT) + c_\alpha\bar{\mathbf{F}}_\alpha + c_\alpha X_\alpha, \tag{4.1}$$

$$= 0 \text{ in the stationary state.} \tag{4.2}$$

The time is t, the Boltzmann constant is k, the mass of α is m_α, and $\mathbf{X}_\alpha$ is the external force.

The average intermolecular force on a particle of species α, $\bar{\mathbf{F}}_\alpha$, may be written as the sum of forces due to each species present:

$$\bar{\mathbf{F}}_\alpha = \sum_{\gamma=+,-} \bar{\mathbf{F}}_{\gamma\alpha} + \bar{\mathbf{F}}_{1\alpha}, \tag{4.3}$$

$$c_\alpha\bar{\mathbf{F}}_{\gamma\alpha}(\mathbf{r}_1) = \int \mathbf{F}_{\gamma\alpha}(\mathbf{r}_1, \mathbf{r})c_{\alpha\gamma}^{(2)}(\mathbf{r}_1, \mathbf{r})\, d^3\mathbf{r}. \tag{4.4}$$

We write the pair concentration $c_{\alpha\gamma}^{(2)}$ in the symmetrized form[1]:

$$c_{\alpha\gamma}^{(2)}(\mathbf{r}_1, \mathbf{r}) = \tfrac{1}{2}[c_{\alpha\gamma}^{(2)}(\mathbf{r}_1, \mathbf{r}) + c_{\gamma\alpha}^{(2)}(\mathbf{r}_2, -\mathbf{r})], \tag{4.5}$$

$$= \tfrac{1}{2}[c_{\alpha\gamma}^{(2)}(\mathbf{r}_1, \mathbf{r}) + c_{\gamma\alpha}^{(2)}(\mathbf{r}_1, -\mathbf{r})] + \tfrac{1}{2}\mathbf{r}\cdot\nabla_{r_1}^{(r)}c_{\alpha\gamma}(\mathbf{r}_1, -\mathbf{r}), \tag{4.6}$$

where $\nabla_{r_1}^{(r)}$ indicates a gradient taken with respect to $\mathbf{r}_1$ at constant $\mathbf{r}$. Inserting the forces $\mathbf{F}_{\gamma\alpha}$ found in the previous section and changing the variable of integration from $\mathbf{r}$ to $-\mathbf{r}$ when necessary, enables us to write $\bar{\mathbf{F}}_{\gamma\alpha}$, to first order in gradients, as the sum of three terms:

$$c_\alpha\bar{\mathbf{F}}_{\gamma\alpha} = \nabla\cdot(\boldsymbol{\sigma}_{\gamma\alpha})_V + c_\alpha\bar{\mathbf{F}}_{\gamma\alpha}^{*} + c_\alpha\bar{\mathbf{F}}_{\gamma\alpha}^{**}. \tag{4.7}$$

Here,

$$(\boldsymbol{\sigma}_{\gamma\alpha})_V = -\frac{1}{2}\int \mathbf{e}_r\mathbf{e}_r \frac{z_\alpha z_\gamma e^2}{\epsilon(\mathbf{r}_1)r} c_{\gamma\alpha}^{(2)}\, d^3\mathbf{r} \tag{4.8}$$

is a potential energy contribution to the partial stress tensor. Note that in Eq. (4.1) one also has the kinetic contribution to the partial stress tensor; i.e., $-c_\alpha kT\mathbf{1}$. In the absence of even tensorial perturbations, only the equilibrium part of the pair concentration, to be defined below, can contribute to $\boldsymbol{\sigma}_V$. The nonequilibrium pair space distribution makes its contribution in the term

$$c_\alpha\bar{\mathbf{F}}_{\gamma\alpha}^{*} = -\frac{1}{2}\int \mathbf{e}_r \frac{z_\alpha z_\gamma e^2}{\epsilon(\mathbf{r}_1)r^2} \times [c_{\alpha\gamma}^{(2)}(\mathbf{r}_1, \mathbf{r}) - c_{\gamma\alpha}^{(2)}(\mathbf{r}_1, \mathbf{r})]\, d^3\mathbf{r}. \tag{4.9}$$

These first two terms are quite similar to those obtained by Bearman[7] and Bearman and Kirkwood[1] in their study of nonelectrolytes. For electrolytes an additional contribution, arising from the dielectric approximation, discussed in the previous section, is

$$\bar{\mathbf{F}}_{\gamma\alpha}^{**} = \frac{1}{2}\int \frac{z_\alpha z_\gamma e^2}{\epsilon(\mathbf{r}_1)r} c_{\alpha\gamma}^{(2)}(\mathbf{r}_1, \mathbf{r})\, d^3\mathbf{r}\ \nabla \ln \epsilon. \tag{4.10}$$

Again, only the equilibrium distribution contributes, because this term is already linear in the gradients. Together with the $\boldsymbol{\sigma}_V$, $\bar{\mathbf{F}}_{\gamma\alpha}^{**}$ makes what has been termed[8] quasithermodynamic contributions to the heat of transport, since only averages over equilibrium distributions are involved.

To clarify this division into quasi-equilibrium and perturbation terms, it is necessary to analyze the nature of the reference equilibrium state. Out of this discussion will also emerge the connection between the previous hydrodynamical equations and the phenomenological linear laws of Sec. II. Let us take the system from its original state to the reference state by a two step process. First, bring the system to a uniform temperature equal to that at $\mathbf{r}_1$,

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[7] R. J. Bearman, J. Chem. Phys. 30, 835 (1959). The notation of this reference and footnote reference 1 has been slightly changed and simplified in the present paper.

[8] R. J. Bearman, J. G. Kirkwood, and M. Fixman, Advan. Chem. Phys. 1, 1 (1958).

leaving the local thermodynamic properties at $\mathbf{r}_1$ unchanged. This does not completely specify the new local diffusive flow pattern which remains indeterminate until two additional gradients are fixed.[9] It might be supposed that we could simply assert that all gradients except that of temperature are the same as in the original system. That, however, would violate the principle of local equilibrium in neighboring regions. To clarify, consider the variables pertinent to the present problem: temperature, pressure, and the concentrations of solvent and solute. By the assumption of local equilibrium, we may write

$$\beta\nabla T - \beta'\nabla P + \bar{v}_1\nabla c_1 + \bar{v}_s\nabla c_s = 0, \tag{4.11}$$

where β is the coefficient of thermal expansion, β' is the coefficient of isothermal compressibility, and $\bar{v}_\alpha$ is the partial molecular volume of species α. Equation (4.11) holds both in the original state and in the new isothermal state. In the latter case, it takes the form

$$-\beta'\nabla P + \bar{v}_1\nabla c_1 + \bar{v}_s\nabla c_s = 0. \tag{4.12}$$

It follows from Eqs. (4.11) and (4.12) that only two of the three gradients in Eq. (4.12) can be the same as in the original state. In the present instance, we shall find it convenient to specify that the two gradients of concentration are the same and thus that the gradient of pressure differs. This may be indicated by writing $\nabla^{(0)}c_\alpha = \nabla c_\alpha$ and $\nabla^{(0)}P \neq \nabla P$, where the superscript 0 signifies that the system is in the reference state, and the right-hand sides of these equations are gradients in the Soret stationary state.

It remains for us to bring the system to a state of complete equilibrium. This is accomplished in the second stage of the production of the reference state: the invoking of hypothetical forces which act selectively on the constituents.[10] These forces, $\mathbf{X}_\alpha^{(0)}$, are adjusted to balance the gradients of chemical potential, so that the gradients of total potential vanish,

$$-\nabla^{(0)}\tilde{\mu}_\alpha = -\nabla^{(0)}\mu_\alpha + \mathbf{X}_\alpha^{(0)} = 0. \tag{4.13}$$

What is the relation of the gradient $\nabla^T\mu_\alpha$, which enters into the linear laws, [Eq. (2.1)] to the gradient $\nabla^{(0)}\mu_\alpha$? Both are isothermal, but, whereas the former is under conditions of specified pressure and mole-fraction gradients [cf. Eq. (2.4)], the latter is under conditions of specified concentration gradients. Thus they are related by

$$\nabla^{(0)}\mu_\alpha \equiv \nabla\mu_\alpha - (\partial\mu_\alpha/\partial T)_{c_1,c_s}\nabla T, \tag{4.14}$$

$$= \nabla^T\mu_\alpha - (\bar{v}_\alpha\beta/\beta')\nabla T. \tag{4.15}$$

Next, we specialize the hydrodynamic equation, [Eq. (4.1)], to this equilibrium state, inserting Eq. (4.13) for the external force:

$$-kT\nabla c_\alpha + c_\alpha\bar{\mathbf{F}}_\alpha^{(0)} + c_\alpha\nabla^T\mu_\alpha - (\bar{v}_\alpha\beta/\beta')\nabla T = 0, \tag{4.16}$$

where $\bar{\mathbf{F}}_\alpha^{(0)}$ is the average intermolecular force on an ion of species α under the reference conditions.

Subtracting Eq. (4.16) from Eq. (4.2) yields the required statistical mechanical form of the phenomenological linear law [Eq. (2.13)],

$$\nabla^T\mu_\alpha = \bar{\mathbf{F}}_\alpha^{(1)} - \nabla kT + (\bar{v}_\alpha\beta/\beta')\nabla T, \tag{4.17}$$

$$\bar{\mathbf{F}}_\alpha^{(1)} \equiv \bar{\mathbf{F}}_\alpha - \bar{\mathbf{F}}_\alpha^{(0)}. \tag{4.18}$$

Some of the terms of $\bar{\mathbf{F}}_\alpha^{(1)}$ involve the difference of gradients in the Soret stationary state and the reference state. This difference is equivalent to [c.f. Eq. (4.14)]:

$$\nabla - \nabla^{(0)} = \nabla T(\partial/\partial T)_{c_1,c_s}. \tag{4.19}$$

The single-star part of $\bar{\mathbf{F}}_\alpha^{(1)}$, defined by Eq. (4.9), may be simplified by formally writing the pair concentration in the form

$$c_{\alpha\gamma}^{(2)}(\mathbf{r}_1, \mathbf{r}) = c_\alpha(\mathbf{r}_1)c_\gamma(\mathbf{r}_1 + \mathbf{r})g_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}), \tag{4.20}$$

and dividing the pair correlation function $g_{\alpha\gamma}$ into a reference equilibrium part and a perturbation implicitly proportional to the gradient of T,

$$g_{\alpha\gamma}(\mathbf{r}_1, \mathbf{r}) = g_{\alpha\gamma}^{(0)}(\mathbf{r}_1, \mathbf{r}) + g_{\alpha\gamma}^{(1)}(\mathbf{r}_1, \mathbf{r}). \tag{4.21}$$

It remains only to perform the necessary integrals to complete the derivation of the heat of transport.

V. THE HEAT OF TRANSPORT

In order to find the heat of transport of a simple electrolyte, one must write all of the terms in Eq. (4.17) for

$$\nabla^T\mu_s\Big(= \sum_{\alpha=+,-} \nu_\alpha\nabla^T\mu_\alpha\Big)$$

in a form proportional to $\nabla \ln T$. Using Eqs. (4.19–21) and the definition of $\bar{\mathbf{F}}_\alpha^{(1)}$, we have

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[9] R. J. Bearman, J. Chem. Phys. 28, 662 (1958).

[10] The use of such forces in the present connection dates back at least as far as J. W. Gibbs, *Collected Works* (Yale University Press, New Haven, 1948), Vol. 1, p. 429.

$$
\begin{aligned}
\nabla^T \mu_s = {} & \sum_{\alpha,\gamma=+,-} (\nu_\alpha/c_\alpha)[\partial(\mathfrak{d}_{\alpha\gamma})_V/\partial \ln T]_{c_1,c_s} \cdot \nabla \ln T \\
& + \tfrac{1}{2} \sum_{\alpha,\gamma=+,-} \nu_\alpha c_\gamma \int (z_\alpha z_\gamma e^2/\epsilon r) g_{\alpha\gamma}^{(0)}\, d^3\mathbf{r} \\
& \times (\partial \ln \epsilon/\partial \ln T)_{c_1,c_s} \nabla \ln T \\
& + \sum_{\alpha=+,-} \nu_\alpha \bar{v}_\alpha (T\beta/\beta') \nabla \ln T \\
& - \sum_{\alpha=+,-} \nu_\alpha kT \nabla \ln T \\
& + \tfrac{1}{2} \sum_{\alpha,\gamma=+,-} \nu_\alpha c_\gamma \\
& \times \int (z_\alpha z_\gamma e^2/\epsilon r^2) \mathbf{e}_r [g_{\alpha\gamma}^{(1)} - g_{\gamma\alpha}^{(1)}]\, d^3\mathbf{r} \\
& + \sum_{\alpha=+,-} \nu_\alpha \bar{\mathbf{F}}_{1\alpha}^{(1)} = -Q_s^* \nabla \ln T. \qquad (5.1)
\end{aligned}
$$

Similar to most properties of dilute electrolytes, the heat of transport is given by its infinite dilution value plus a term proportional to the inverse Debye length, κ, that is, proportional to $c_s^{\frac{1}{2}}$. Thus we may write

$$Q_s^* = Q_s^{*0} + \mathcal{S}(Q_s^*)\kappa, \qquad (5.2)$$

where

$$\kappa^2 = 4\pi e^2 \sum_\gamma \frac{c_\gamma z_\gamma^2}{\epsilon kT}. \qquad (5.3)$$

In order to calculate the limiting slope $\mathcal{S}(Q_s^*)$ let us examine the lowest-order κ dependence of each of the terms on the right-hand side of Eq. (5.1).

In the first term, the stresses due to ion–ion interaction, $(\mathfrak{d}_{\alpha\gamma})_V$, may be evaluated using the Debye–Hückel linearized radial distribution function

$$g_{\alpha\gamma} = 1 - (z_\alpha z_\gamma e^2/\epsilon kT)(e^{-\kappa r}/r). \qquad (5.4)$$

One obtains

$$
\begin{aligned}
\text{1st term} = {} & -\left[\sum_\alpha \frac{\nu_\alpha z_\alpha^2 e\kappa}{12\epsilon}\right] \\
& \times \left[1 + 3\left(\frac{\partial \ln \epsilon}{\partial \ln T}\right)_{c_1,c_s}\right] \nabla \ln T. \qquad (5.5)
\end{aligned}
$$

In evaluating this term, the "1" on the right hand side of Eq. (5.4) gives rise to the integral $\int_0^\infty r\, dr$, but this divergent term is multiplied by $\sum_\gamma c_\gamma z_\gamma$ which vanishes by electroneutrality.

In like fashion, the second term, arising from the greater dielectric shielding on the cold, rather than hot side of an ion equals

$$\text{2nd term} = -\sum_\alpha \left[\frac{\nu_\alpha z_\alpha^2 e\kappa}{2\epsilon}\right]\left(\frac{\partial \ln \epsilon}{\partial \ln T}\right)_{c_1,c_s}. \qquad (5.6)$$

The partial molecular volume entering into the third term, which arose from the difference between the gradient of chemical potential in the standard state and in the Soret stationary state, may be evaluated from the Debye–Hückel equilibrium theory:

$$
\begin{aligned}
\sum_{\alpha=+,-} \nu_\alpha \bar{v}_\alpha \equiv \bar{v}_s &= \left(\frac{\partial \mu_s}{\partial P}\right)_{T,x_s} \\
\mu_s &= \mu_s^0(T,P) + \nu kT \ln x_s f_s, \\
\nu &= \sum_{\alpha=+,-} \nu_\alpha, \\
\nu kT \ln f_s &= -\sum_\alpha \nu_\alpha z_\alpha^2 e^2 \kappa/2\epsilon, \\
\bar{v}_s &= \bar{v}_s^0 + \left(\sum_\alpha \frac{\nu_\alpha z_\alpha^2 e^2 \kappa}{4e}\right) \\
& \quad \times \left[3\left(\frac{\partial \ln \epsilon}{\partial P}\right)_{T,x_s} - \beta'\right]. \qquad (5.7)
\end{aligned}
$$

The fourth term, which enters through the kinetic portion of the partial stress, contributes only to the infinite-dilution part of the heat of transport.

The integral in the fifth term, representing the forces due to the asymmetry of the ion atmospheres, can be calculated, in general, only by a more detailed theory, which is now under investigation. However, in the case of the calculation of this paper, namely, the heat of transport of a simple electrolyte, the term vanishes by a simple symmetry argument. Since $c_\alpha = \nu_\alpha c_s$, the summand is obviously antisymmetric with respect to interchange of α and γ, and the sum over both α and γ vanishes.[11]

The final term, representing the contribution of ion-solvent forces other than those accounted for by the dielectric approximation, is the most difficult to discuss. Helfand and Kirkwood[6] estimated the term by an argument in the spirit of the calculation of the electrophoretic contribution to the equivalent conductance, but the derivation had certain unsatisfactory features. They found, however, that the term vanishes if the ionic mobilities are identical and appears to make only negligible contributions to the limiting slope of many 1:1 electrolytes. For the purposes of this article, we will attempt no

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[11] It may be noted that in the calculation of Helfand and Kirkwood,[6] the comparable term which they calculated explicitly for a single ion, also vanishes trivially for the total heat of transport of a simple electrolyte. This follows from the fact that the perturbations in the ion atmosphere, $g_{\alpha\gamma}^{(1)}$, must in their case be proportional to the difference of velocity, $\mathbf{u}_\gamma - \mathbf{u}_\alpha$. For the calculation of the total heat of transport of a simple electrolyte, it is sufficient to consider conditions of zero current, in which case the difference in velocity between the two ions must vanish to maintain electroneutrality.

calculation of the order κ contribution arising from this source, but only note that it may be present.

In combining the terms contributing to the limiting slope of the heat of transport, Eqs. (5.5–7), one must use the thermodynamic identity

$$\left(\frac{\partial \epsilon}{\partial T}\right)_{c_1,c_s} = \left(\frac{\partial \epsilon}{\partial T}\right)_{P,x_s} + \left(\frac{\partial \epsilon}{\partial P}\right)_{T,x_s}\left(\frac{\partial P}{\partial T}\right)_{c_1,c_s}. \qquad (5.8)$$

The result is[12]

$$Q_s^* = Q_s^{*0} + \left(\sum_\alpha \frac{\nu_\alpha z_\alpha^2 e^2}{\epsilon}\right) \times \left[\left(\frac{1}{12}\right) + \frac{3}{4}\left(\frac{\partial \ln \epsilon}{\partial \ln T}\right)_P + \tfrac{1}{4}\beta T\right]\kappa, \qquad (5.9)$$

plus an ion-solvent term. This formula is identical with that obtained by Helfand and Kirkwood by a procedure which bears no outward resemblance to the present calculation. It thus represents an explicit verification of the heat–matter reciprocal relation without directly invoking time-reversal invariance.

VI. DISCUSSION

The heat-of-transport calculation in this paper is based on the relationship of the intermolecular forces arising from the temperature gradient in the nonuniform Soret stationary state to the equilibrium gradient of chemical potential required to maintain the same concentration gradients. Most of these forces have been studied previously,[1,7] but in an electrolytic solution there are also forces arising from the fact that the solvent's dielectric shielding of the ion–ion interaction is lower on the hot than on the cold side. Furthermore, for electrolytes, by employing Debye–Hückel theory, one may explicitly evaluate most of the terms which contribute to the limiting slope of the heat of transport versus square root of concentration.

The only other attempt to calculate the limiting law for the heat of transport of an electrolyte is that of Agar.[13] It is based on the argument that the heat of transport is due to the ion leaving behind it, the solvent polarization entropy as it diffuses. Agar's arguments are closer to those of Helfand and Kirkwood[6] than to the present paper. It is even difficult to draw the parallel between those two theories because of the qualitative nature of the Agar derivation and especially the manner in which he introduces concentration effects. Agar finds that the limiting slope of the heat of transport is proportional only to ($\partial \ln \epsilon/\partial \ln T$). Perhaps this is indicative of the fact that he has not accounted for all of the heat (or entropy) transport mechanisms. For example, one might inquire whether the ion leaves behind the ion atmosphere and its associated entropy. It would be interesting to attempt to put Agar's ideas into more precise terms, and also see if his arguments have an analog from the point of view of the Soret effect.

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[12] In units of kcal per mole, the limiting law for the heat of transport of a simple electrolyte in aqueous solution at 25°C is given by

$$Q_s^* = Q_s^{*0} - 2.56\,|\tfrac{1}{2}z_+z_-\nu|^{3/2} m^{1/2},$$

where m is molality in moles of solvent per kg of solvent. (The coefficient 2.57 in Helfand and Kirkwood is off by rounding errors.)

[13] J. N. Agar *Structure of Electrolytic Solutions*, edited by W. J. Hamer (John Wiley and Sons, New York, 1959), p. 200.

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Structure of the Three-Particle Scattering Operator in Classical Gases

P. RÉSIBOIS*
Université Libre de Bruxelles, Belgique
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It is shown that in all cases where the finite duration of the collision may be neglected, there is a complete equivalence between the 3-particle scattering operator obtained by Prigogine and his co-workers and the corresponding expression derived by Choh and Uhlenbeck using Bogolubov's method. Great emphasis is put on the "irreducible character" of the three-body collision: Only situations in which the three particles are *simultaneously* interacting play a role in both theories.

1. INTRODUCTION

DURING the last few years, Prigogine and his co-workers have developed a general theory of irreversible processes in classical gases.[1] The formalism is based on a systematic analysis of the perturbation solution of the Liouville equation; no extra mechanical assumptions are involved in the study of the dynamics of the system and irreversibility appears as an intrinsic property of those large systems which are such that, at the initial time, no correlations exist between particles that will collide in a sufficiently far off future. In particular, it was recently shown[2] that for a spatially homogeneous system, the kinetics of the approach to equilibrium is essentially determined by a non-Markoffian collision operator. The Laplace transform of this operator, $\psi^+(z)$, has only singularities in the lower half-plane of the complex variable z; this analytical property expresses the fact that a collision process has a finite duration, which cannot generally be neglected. However, the long-time behavior of the system ($t \to \infty$) is entirely determined by the value of $\psi^+(z)$ at the point $z = 0$; the physical meaning of this result is that, in the study of the *asymptotic* time dependence of the distribution functions (H theorem), one is justified in neglecting completely the noninstantaneous character of the collision.[3] Similarly, the operator $\psi^+(0)$ also plays an important role, *although by no means unique*, in the computation of transport coefficients, as was shown by Balescu.[4]

On the other hand, various other methods have been developed for studying irreversible processes in classical gases. We cite the work of Bogolubov,[5] Kirkwood and his co-workers,[6] and Green.[7] The equivalence of these approaches is now rather well established[8] and we do not intend to discuss them here in detail. It is however, very important to realize that they all make the assumption, explicitly or implicitly, that the duration of the collision is negligible. As was pointed out in I (see also the paper of Van Hove[9] for the quantum case), they can thus correctly describe no nonequilibrium process in which the finite duration of the collision must be taken into account.

From what has been said before, it is expected that the operator $\psi^+(0)$ (which corresponds to the instantaneous collision approximation in Prigogine's theory) is identical to the corresponding scattering operator in the other group of approaches. However, the proof of the identity between these two expressions is far from trivial. Indeed, in the latter methods all the calculations are performed in ordinary phase space, and constant use is made of formal exact n-particle propagators describing the motion of a subgroup of n particles interacting only with each other. On the contrary, the former technique is developed in the Fourier space associated with the configurational coordinates and is based on a perturbation expansion in power of the coupling constant between the molecules.

In a previous paper,[10] we have shown that the collision operator $i\psi^{+(2)}(0)$ describing two-particle collisions could, indeed, be brought to the usual form of the Boltzmann operator. The aim of the present work is to extend this result to triple col-

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* Chargé de Recherches au Fonds National de la Recherche Scientifique de Belgique.

[1] I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962). This paper will hereafter be referred to as I.

[2] I. Prigogine and P. Résibois, Physica **27**, 629 (1961). This paper will hereafter be referred to as II.

[3] F. Henin, P. Résibois, and F. Andrews, J. Math. Phys. **2**, 68 (1961).

[4] R. Balescu, Physica **27**, 693 (1961).

[5] N. N. Bogolubov, *Problems of a Dynamical Theory in Statistical Physics* (in Russian) Moscow (1947).

[6] See, for instance, S. Rice and H. Frisch, Ann. Rev. Phys. Chem. **11**, 187 (1960).

[7] M. Green, National Bureau of Standards Rept. 3327, (August 1955).

[8] E. Cohen, Physica **27**, 163 (1961).

[9] L. Van Hove, Physica **23**, 441 (1957).

[10] P. Résibois, Physica **25**, 725 (1959).

lisions and to show that the corresponding operator $i\psi^{+(3)}(0)$ is identical with the scattering operator $\Omega^{(3)}(\varphi)$ obtained by Uhlenbeck and Choh using Bogolubov's method[11] in a form derived by M. Green[12]:

$$\Omega^{(3)}(\varphi) = \int dx_2\, dx_3 \theta_{12}[S^{(3)}_{-\infty}(x_1x_2x_3)$$

$$- S^{(2)}_{-\infty}(x_1x_2)S^{(2)}_{-\infty}(x_2x_3) - S^{(2)}_{-\infty}(x_1x_2)S^{(2)}_{-\infty}(x_2x_3)$$

$$+ S^{(2)}_{-\infty}(x_1x_2)]\varphi_1(p_1)\varphi_1(p_2)\varphi_1(p_3) \qquad (I.1)$$

In this formula, we have used the notation of I, but we shall write it more explicitly in the following. The same result was also obtained by Rice, Kirkwood, and Harris.[13]

In Sec. II of this paper, we recall the explicit form of the operator $\psi^{+(3)}(0)$ and show that it describes an "irreducible" collision, in the sense that it contains only contributions of the three-body motion in which these particles are *simultaneously* interacting with each other.

In order to save notations, it is very convenient to employ the diagramatic representation of triple collisions used previously by J. Brocas and the author[14,15] in similar problems. This technique allows a very direct analysis of the mathematical implications of this condition of irreducibility. The identity between $i\psi^{+(3)}(0)$ and $\Omega^{(3)}$ is explicitly proved in Sec. III. It appears very clear that the condition of irreducibility which is automatically implied in the definition of $i\psi^{+}(0)$, is in fact equivalent to the substraction of products of two-particle propagators $S^{(2)}_{-\infty}$ in formula (I-1). Both exclude the successive two-body processes which appear in the description of the three-body motion.

Finally, we remark about the practical use of these two formally identical expressions as starting points for explicit approximate calculations. We also comment on generalizations of the present work to more involved problems.

II. THE STRUCTURE OF THE OPERATOR $\psi^{+}(0)$

In I, it was shown that *if the duration of the collision is neglected*, the generalized master equation takes the following form [see formula I(4–6) which gives, in fact, the long time behavior of the velocity distribution function and includes an operator ${}^{(0)}\Omega(0)$ which takes into account the long-time effect of the finite collision duration. As we are interested in the instantaneous collision approximation, we may replace this operator ${}^{(0)}\Omega$ by unity. Moreover, we notice here that this formula is lacking a factor i]:

$$\partial\rho_0(\{\mathbf{v}\}, t)/\partial t = i\psi^{+}(0)\rho_0(\{\mathbf{v}\}, t). \qquad (II.1)$$

As was mentioned previously, we do not want to discuss here the range of validity of this equation; we shall limit ourselves to prove the identity of Eq. (II.1) with the evolution equation obtained using Bogolubov's and other methods cited above.

We first integrate (II.1) over all particles except particle 1, and we take into account the factorization of the velocity-distribution functions. Moreover we limit ourselves to the contribution of triple collisions; indeed, we have already shown how the two-particle contribution is identical with the Boltzmann collision operator,[10] and the consideration of higher-order processes (quadruple, etc.) would bring no new mathematical feature into the analysis.

We then obtain

$$(\partial\varphi_1(\mathbf{v}_1, t)/\partial t)_{\text{triple coll.}}$$

$$= iN^2 \iint d\mathbf{v}_2\, d\mathbf{v}_3 \psi^{+(3)}(0) \prod_{j=1}^{3} \varphi_1(\mathbf{v}_j, t), \qquad (II.2)$$

with the following expression for the collision operator (in Fourier space):

$$i\psi^{+(3)}(0) = \sum_{n=0}^{\infty} \left\langle 0 \middle| (-i\delta L^{(12)}) \right.$$

$$\left. \times \left[\frac{1}{i(L_0 - i0)}(-i\lambda\delta L)\right]^n \middle| 0 \right\rangle_{\{\mathbf{k}\}\neq 0}, \qquad (II.3)$$

where

$$\delta L = \sum_{i>j} \delta L^{ij}, \qquad ij \in 1, 2, 3.$$

In this expression, particle 3 must appear at least once in the interactions.

The explicit formulas for the matrix elements involved in (II.3) are

$$\langle\{\mathbf{k}\}\, |-i\lambda\delta L^{ij}|\, \{\mathbf{k}'\}\rangle$$

$$= -i\lambda\Omega^{-1} V_{|\mathbf{k}_i-\mathbf{k}_i'|}(\mathbf{k}_i - \mathbf{k}_i')\left(\frac{\partial}{\partial\mathbf{v}_i} - \frac{\partial}{\partial\mathbf{v}_j}\right)$$

$$\times\ \delta^{Kr}(\mathbf{k}_i + \mathbf{k}_j - \mathbf{k}_i' - \mathbf{k}_j')\delta^{Kr}(\mathbf{k}_l - \mathbf{k}_l'),$$

$$i \neq j \neq l \in 1, 2, 3 \qquad (II.4)$$

$$\equiv -\lambda\Omega^{-3} \iiint d\mathbf{r}_i\, d\mathbf{r}_j\, d\mathbf{r}_l \frac{\partial V^{ij}}{\partial\mathbf{r}_{ij}}\left(\frac{\partial}{\partial\mathbf{v}_i} - \frac{\partial}{\partial\mathbf{v}_j}\right)$$

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[11] S. Choh and G. Uhlenbeck, *The Kinetic Theory of Dense Gases* (University of Michigan, Ann Arbor, Michigan, 1958); E. Cohen, *Fundamentals Problems in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), p. 110.

[12] M. Green, Physica **24**, 393 (1958).

[13] S. Rice, J. Kirkwood, and R. Harris, Physica **26**, 717 (1961).

[14] P. Résibois, Physica **27**, 33 (1961).

[15] J. Brocas and P. Résibois, Bull. Classe. Sci. Acad. Roy. Belg. **47**, 226 (1961).

$$\times \exp\left[-i\sum_{s=1}^{3}(\mathbf{k}_s-\mathbf{k}'_s)\mathbf{r}_s\right] \tag{II.4a}$$

$$\langle\{\mathbf{k}\}\,|-i(L_0-i0)^{-1}|\,\{\mathbf{k}'\}\rangle$$
$$= -i\left(\sum_{s=1}^{3}\mathbf{k}_s\mathbf{v}_s - i0\right)^{-1}\prod_{s=1}^{3}\delta^{Kr}(\mathbf{k}_s-\mathbf{k}'_s) \tag{II.5}$$
$$= \Omega^{-3}\int\prod_{s=1}^{3}d\mathbf{r}_s\,d\mathbf{r}'_s\,G(\{\mathbf{r}_s-\mathbf{r}'_s\},\{\mathbf{v}_s\})$$
$$\times \exp -i(\mathbf{k}_s\mathbf{r}_s-\mathbf{k}'_s\mathbf{r}'_s). \tag{II.5a}$$

In this latter expression, we have introduced the three-particle propagator in ordinary space (see reference 10):

$$G(\{\mathbf{r}_s-\mathbf{r}'_s\};\{\mathbf{v}_s\})$$
$$= \int_{\substack{0\\ \epsilon\to 0}}^{\infty} d\tau\prod_{s=1}^{3}\delta(\mathbf{r}_s-\mathbf{r}'_s-\mathbf{v}_s\tau)\exp -\epsilon\tau. \tag{II.6}$$

Although the transport equation (II.3) is valid only in the limit of an infinite system ($N\to\infty$, $\Omega\to\infty$, $N/\Omega = C =$ finite), we have (formally) written all the expressions in the case of a discrete Fourier space. This will simplify somewhat the mathematical discussion, but there is no essential difficulty in going to the continuous case in any expression written in the following discussion.

The main feature of formula (II.3) is that it represents an *irreducible diagonal fragment*, i.e., all intermediate states must have nonvanishing $\mathbf{k}_i$ wave vectors. We return later to the physical meaning of this condition. However, from a purely mathematical point of view, we can see immediately that this requirement of irreducibility forbids us to perform a Fourier inversion of the operator $\psi^{+(3)}(0)$ and to express it directly in configurational space. Consider the following simple example; suppose $A(\mathbf{r})$ and $B(\mathbf{r})$ to be two real functions, the Fourier coefficients of which are $A_\mathbf{k}$ and $B_\mathbf{k}$, respectively; then by the Parseval formula,[16] we have

$$\frac{1}{\Omega}\sum_{\mathbf{k}}A_kB_{-k} = \int d\mathbf{r}\,A(\mathbf{r})B(\mathbf{r}). \tag{II.7}$$

However, if in the left-hand side of (II.7) we explicitly exclude the point $\mathbf{k} = 0$, either of two cases can occur:

(1) The coefficients A_0 and B_0 *are non singular*; their contribution in the limit of a large volume becomes negligible and formula (II.7) is still valid, or

(2) the coefficients A_0 and B_0 are singular in the limit of a large volume; then formula (II.7) can no longer be applied and we must substract explicitly the contributions coming from this single point. This remark is in fact the keynote to the present calculation; we must analyze carefully the behavior of the points $\mathbf{k} = 0$ in the matrix elements of (II.3); if they give a negligible contribution in the limit of a large system, we are allowed to include them in the expression for $\psi^{+(3)}(0)$, and the Fourier transformation may be performed. However we see that certain contributions do indeed behave singularly and these terms need special considerations before we can transform them back in configurational space.

We follow the following procedure: we first extend the definition of the collision operator $\psi^{+(3)}(0)$ by neglecting provisionally the condition of irreducibility, i.e.,

$$i\psi^{+(3)}_{\text{ext.}}(0)$$
$$= \sum_{n=0}^{\infty}\left\langle 0\left|(-i\lambda\,\delta L^{(12)})\left[\frac{1}{i(L_0-i0)}(-i\lambda\,\delta L)\right]^n\right|0\right\rangle \tag{II.8}$$

(here again, particle 3 must appear at least once in the interaction). We study (II.8) and, in particular, seek the terms which are reducible and which, at the same time, give a finite contribution to the transport equation (II.2). These reducible terms are spurious and must thus be substracted from (II.8). In formula, we set

$$i\psi^{+(3)}(0) = i\psi^{+(3)}_{\text{ext.}}(0)$$
$$- \text{(reducible contributions of order } \Omega^{-2}). \tag{II.9}$$

As the matrix elements appearing in (II.3) are of a rather complicated structure, we shall describe each contribution of $\psi^{+(3)}_{\text{ext.}}(0)$ by means of suitable diagrams. However we want to be able to draw diagrams for both irreducible and reducible contributions. Since the latter are automatically excluded in Prigogine–Balescu notation (or, more properly, they are treated in a different way from irreducible ones), we must use a different technique; the graphs introduced by J. Brocas and the author[14,15] are very convenient for the present purpose.

We draw an horizontal line to describe the complete history of each particle (1, 2, 3); a vertical line between particles i and j ($i, j \in 1, 2, 3$) represents an interaction δL^{ij} between this pair of molecules and these vertical lines are ordered according to their succession in the corresponding contribution of Eq. (II.8). Moreover, the wave

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[16] D. Morse and H. Feschbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953).

vectors of each particle are explicitly indicated for each intermediate state.

As an example, the term

$$\left\langle 0 \left| (-i\lambda\,\delta L^{(12)}) \frac{1}{i(L_0 - i0)} (-i\lambda\,\delta L^{(13)}) \right.\right.$$
$$\times \frac{1}{i(L_0 - i0)} (-i\lambda\,\delta L^{(13)}) \frac{1}{i(L_0 - i0)} (-i\lambda\,\delta L^{(12)} \left| 0 \right\rangle$$

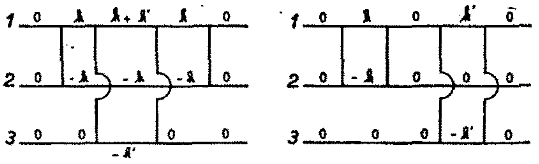
is represented by Fig. 1(a). Using Eqs. (II.4) and (II.5) we get for this term, in the limit of an infinite system ($\sum_{\mathbf{k}} = (\Omega/8\pi^3) \int d\mathbf{k}$),

$$\frac{\lambda^4}{(8\pi^3)^2\Omega^2} \int d\mathbf{k}\, d\mathbf{k}'\, \mathbf{k} V_k \left(\frac{\partial}{\partial \mathbf{v}_1} - \frac{\partial}{\partial \mathbf{v}_2}\right) \pi\delta_-(\mathbf{k}\mathbf{v}_{12})$$
$$\times \mathbf{k}' V_{k'} \left(\frac{\partial}{\partial \mathbf{v}_1} - \frac{\partial}{\partial \mathbf{v}_2}\right) \pi\delta_-[(\mathbf{k} + \mathbf{k}')\mathbf{v}_1 - \mathbf{k}\mathbf{v}_2 - \mathbf{k}'\mathbf{v}_3]$$
$$\times \mathbf{k}' \mathbf{V}_{k'} \left(\frac{\partial}{\partial \mathbf{v}_1} - \frac{\partial}{\partial \mathbf{v}_3}\right) \pi\delta_-(\mathbf{k}\mathbf{v}_{12}) \mathbf{k} V_{-k} \left(\frac{\partial}{\partial \mathbf{v}_1} - \frac{\partial}{\partial \mathbf{v}_2}\right). \tag{II.11}$$

This is irreducible because the contributions coming from the points $\mathbf{k}$, $\mathbf{k}' = 0$ are of order Ω^{-3} (one point in a finite integral) and may thus be neglected in the transport equation (II.4). On the contrary, the diagram of Fig. 1(b) is a typical example of a reducible term; indeed we obtain

$$\frac{\lambda^4}{8\pi^3)\mathbf{V}^2} \lim_{1\to 0} \int' \int' d\mathbf{k}\, d\mathbf{k}'\, \mathbf{k} V_k \left(\frac{\partial}{\partial \mathbf{v}_1} - \frac{\partial}{\partial \mathbf{v}_2}\right)$$
$$\times \pi\delta_-(\mathbf{k}\mathbf{v}_{12}) \mathbf{k} V_{-k} \left(\frac{\partial}{\partial \mathbf{v}_1} - \frac{\partial}{\partial \mathbf{v}_2}\right)$$
$$\times \pi\delta_-(\mathbf{l}\mathbf{v}_{13})(\mathbf{k}' - \mathbf{l}) V_{|\mathbf{k}'-\mathbf{l}|} \left(\frac{\partial}{\partial \mathbf{v}_1} - \frac{\partial}{\partial \mathbf{v}_3}\right)$$
$$\times \pi\delta_-(\mathbf{k}'\mathbf{v}_{13}) \mathbf{k}' V_{-k'} \left(\frac{\partial}{\partial \mathbf{v}_1} - \frac{\partial}{\partial \mathbf{v}_3}\right), \tag{II.12}$$

where, in order to give a meaning to the propagator $\{0\}$ of one of the intermediate states, we have used a limiting procedure which gives a unique answer as is shown, in the next section. This term contributes a finite amount to the transport equation, although one of its intermediate states has vanishing wave vectors, and it is thus an example of terms which must be substracted from $\psi^{+(3)}_{\mathrm{ext.}}(0)$ in order to obtain the correct collision operator. However, here we may also neglect the special situations where $\mathbf{k}$, $\mathbf{k}' = 0$ because, as in the previous example, they correspond to one point in a finite integral.



(a) (b)

FIG. 1. (a) An irreducible contribution. (b) A reducible contribution.

Let us now consider the general nth-order term in Eq. (II.8). We have $3(n - 1)$ summations over the wave vectors (one wave vector for each particle at each intermediate state). Each δL introduces two conservation conditions [see (II.4)], one of which (at the last vertex) is automatically satisfied. We are thus left, for an arbitrary nth-order term, with $n - 2$ independent summations. As each interaction δL also introduces a factor Ω^{-1}, it is obvious that any diagram describing one possible sequence of interactions will be of the order Ω^{-2}. In the transport equation (II.2), for every diagram we obtain a contribution of order $(N/\Omega)^2 = C^2$. This could be expected on a physical basis and is simply a restatement in this particular case, of the general rules given by Prigogine and Balescu.[17] However, we can now proceed much further and observe these $n - 2$ independent summations. In fact, we are able to choose arbitrarily the exchange of wave vector between the pair of interacting particles (i, j) at each vertex, *except*:

(1) for the last interaction, in which particles 1 and 2 necessarily return to the state of zero wave vector (see Fig. 1). This latter limitation is trivial because, whatever the reducible or irreducible character of the diagram, the final state must be $\{0\}$;

(2) for the last vertex where particle 3 interacts; here again the wave vectors must be choosen such that the wave vector for particle 3 vanishes [see Fig. 1(a) and 1(b)].

This last condition is the central point in the distinction between reducible and irreducible diagrams. If, as in the example of Fig. 1(b), the condition that $\mathbf{k}_3 = 0$ at the last vertex involving particle 3 automatically implies that the two other wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are also vanishing, we get a reducible contribution which must be substracted according to (II.9). However, in the general case, a typical example of which is given in Fig. 1(a), $\mathbf{k}_1$ and $\mathbf{k}_2 = -\mathbf{k}_1$ will be nonvanishing and the diagram is irreducible.

From this argument, we see that all non-negligible reducible contributions will be obtained by collecting all terms in which the intermediate state following the last interaction involving particle 3 has identically vanishing wave vectors.

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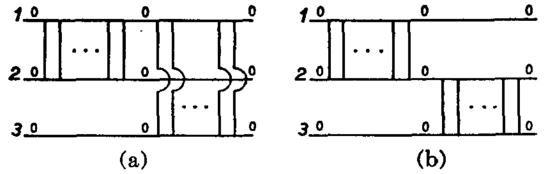
[17] I. Prigogine and R. Balescu, Physica 25, 281 (1959).



(a) (b)

FIG. 2. The most general reducible diagrams.

This class of terms is very easy to obtain: it is given by all diagrams such that there is first an arbitrary number of interactions 1–3 (or alternatively an arbitrary number of interactions 2–3) followed by an arbitrary number of interactions 1–2. The most general graphs of this type are shown in Fig. 2(a) and 2(b).

The proof of this property is done in two steps:

1) It is clear from what we have said previously that all these diagrams are non-neglibible reducible contributions.

(2) they are unique. Indeed, taking any other diagram, there exists, before the last interaction involving particle 3, one or a series of intermediate states in which the three particles simultaneously have nonvanishing wave vectors $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 \neq 0$. Now, by the conservation of wave vectors as implied by Eq. (II.4), this has for a consequence the fact that after the last interaction involving 3, (denoted by an asterisk on the diagrams in Fig. 3), particle 1 and 2 have, in general, $\mathbf{k}_1 = -\mathbf{k}_2 \neq 0$. The only exception occurs if we cause these wave vectors to vanish, which in turn implies restrictions on one or more of the free summations we have at our disposal. This however gives a vanishingly small contribution to the transport equation as we have seen in detail in the (II.11).

There exists a last restriction on $\psi^{+(3)}(0)$ and on $\psi^{+(3)}_{\text{ext.}}(0)$ which we wish to eliminate. The definition of these two operators implies that particle 3 must appear at least once in the sequence of interactions δL^{ij}. As we shall see in the next section, it is much simpler to suppress this condition in the definition of the three-body collision operator and to substract the contributions explicitly where only particles 1 and 2 collide with each other, i.e., the term $\psi^{+(2)}(0)$.

Defining a new operator $\bar{\psi}^{+(3)}_{\text{ext.}}$ by Eq. (II.8), but *without* the condition mentioned after this equation, we may thus write finally [see Eq. (II.9)]:

$$i\psi^{+(3)}(0) = i\bar{\psi}^{+(3)}_{\text{ext.}}(0) - i\psi^{+(2)}(0)$$
$$- i \text{ (contributions of the diagrams in Fig. 2)} \quad \text{(II.13)}$$

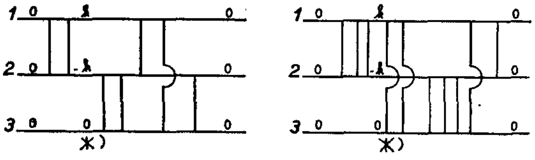


FIG. 3. Examples of irreducible diagrams.

With this last expression, we are now ready to obtain the equation for the 3-particle collision operator in configurational space; this is accomplished in the next section.

III. THE COLLISION OPERATOR IN CONFIGURATIONAL SPACE

The operator $\bar{\psi}^{+(3)}_{\text{ext.}}(0)$ can be Fourier-inverted because it is defined in a way such that no condition appears on any intermediate state. Substituting (II.4a) and (II.5a) into Eq. (II.8), we obtain

$$i\bar{\psi}^{+(3)}_{\text{ext.}} = \Omega^{-3} \sum_{n=1}^{\infty} \lambda^n \int d\{\mathbf{r}\}\, d\{\mathbf{r}'\} \cdots d\{\mathbf{r}^n\}$$
$$\times\, \delta L^{(12)}(\{\mathbf{r}\}) G^{(3)}(\{\mathbf{r} - \mathbf{r}'\}; \{\mathbf{v}\}) \delta L(\{\mathbf{r}'\})$$
$$\times \cdots G^{(3)}(\{\mathbf{r}^{n-1} - \mathbf{r}^n\}; \{\mathbf{v}\}) \delta L(\{r^n\}). \quad \text{(III.1)}$$

In this formula, we have introduced the following compact notation:

$$\{\mathbf{r}\} = \{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3\} \qquad \{\mathbf{v}\} = \{\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3\}, \quad \text{(III.2)}$$

$$\delta L(\{\mathbf{r}\}) = \sum_{i>j} \delta L^{(ij)}(\{\mathbf{r}\})$$
$$= -\sum_{i>j} \frac{\partial V}{\partial \mathbf{r}_{ij}} \left(\frac{\partial}{\partial \mathbf{v}_i} - \frac{\partial}{\partial \mathbf{v}_j} \right), \quad \text{(III.3)}$$

$$G^{(3)}(\{\mathbf{r} - \mathbf{r}'\}; \{\mathbf{v}\})$$
$$= G(\mathbf{r}_1 - \mathbf{r}_1'; \mathbf{r}_2 - \mathbf{r}_2', \mathbf{r}_3 - \mathbf{r}_3'; \{\mathbf{v}\}). \quad \text{(III.4)}$$

It is surprising at first sight that there is a factor Ω^{-3} before this integral, even though we have previously shown that all the contributions to $\bar{\psi}^{+(3)}_{\text{ext.}}(0)$ were proportional to Ω^{-2}. However one should realize that the integrand in (III.1) is invariant with respect to a translation of the mass center of the system, and this gives a supplementary volume factor.

Using the generalization of the two-body scattering theory previously developed by the author,[10] it is a simple matter to write (III.1) in a more compact form.

For the sake of simplicity, let us first operate with $\bar{\psi}^{+(3)}_{\text{ext.}}(0)$ on an initial state of the form

$$\prod_{i=1}^{3} \delta(\mathbf{v}_i - \mathbf{v}_i') = \delta(\{\mathbf{v} - \mathbf{v}'\}), \quad \text{(III.5)}$$

and let us consider the following expression:

$$S^{(3)}(\{\mathbf{r}\}\{\mathbf{v}\} \mid \{\mathbf{v}'\}) = \sum_{n=0}^{\infty} \lambda^n \int d\{\mathbf{r}'\} \cdots d\{\mathbf{r}^n\}$$
$$\times G^{(3)}(\{\mathbf{r} - \mathbf{r}'\}; \{\mathbf{v}\})\delta L(\{\mathbf{r}'\})$$
$$\times \cdots G^{(3)}(\{\mathbf{r}^{n-1} - \mathbf{r}^n\}; \{\mathbf{v}\})\delta(\{\mathbf{v} - \mathbf{v}'\}). \quad \text{(III.6)}$$

This series is the Neumann expansion of the following integral equation:

$$S^{(3)}(\{\mathbf{r}\}\{\mathbf{v}\} \mid \{\mathbf{v}'\}) = \delta(\{\mathbf{v} - \mathbf{v}'\})$$
$$+ \int d\{\mathbf{r}'\}G^{(3)}(\{\mathbf{r} - \mathbf{r}'\}; \{\mathbf{v}\})\delta L(\{\mathbf{r}'\})$$
$$\times S^{(3)}(\{\mathbf{r}'\}\{\mathbf{v}\} \mid \{\mathbf{v}'\}). \quad \text{(III.7)}$$

Noting that $G^{(3)}(\{\mathbf{r} - \mathbf{r}'\}; \{\mathbf{v}\})$ is Green's function of the unperturbed Liouville equation

$$\sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} G^{(3)}(\{\mathbf{r} - \mathbf{r}'\}; \{\mathbf{v}\}) = \delta(\{\mathbf{r} - \mathbf{r}'\}), \quad \text{(III.8)}$$

we may easily verify that this integral equation is identical to the Liouville equation

$$\left(\sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} + \lambda \delta L\right) S^{(3)}(\{\mathbf{r}\}\{\mathbf{v}\} \mid \{\mathbf{v}'\}) = 0 \quad \text{(III.9)}$$

with the limiting condition that for $\lambda \to 0$, $S^{(3)}$ reduces to (III.5).

In this form, the physical meaning of the function $S^{(3)}$ is ascertained. It represents the stationary distribution realized when homogeneous flows of particles with respective velocities $\mathbf{v}_1'$, $\mathbf{v}_2'$ and $\mathbf{v}_3'$ come from infinity and scatter each other. Taking into account that the characteristics of Eq. (III.9) are the trajectories of the three particles, one readily sees that this function is identical to Bogolubov's streaming operator $S_{-\infty}^{(3)}$ acting on the initial distribution (III.5) [see references 5 and 11].

Thus we have finally:

$$i\Psi_{\text{ext.}}^{+(3)}(0)\delta(\{\mathbf{v} - \mathbf{v}'\})$$
$$= \Omega^{-3} \int d\{\mathbf{r}\}\delta L^{(12)}(\{\mathbf{r}\})S^{(3)}(\{\mathbf{r}\}\{\mathbf{v}\} \mid \{\mathbf{v}'\}). \quad \text{(III.10)}$$

We now consider the class of reducible contributions described by Fig. 2(a) [the other class 2(b) is treated similarly]. Keeping in mind the limiting procedure introduced in (II.12), we obtain:

Reducible class 2(a)

$$= \lim_{l \to 0} \Omega^{-4} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \left[\int d\mathbf{r}_1\, d\mathbf{r}_2 \cdots d\mathbf{r}_1^n\, d\mathbf{r}_2^n\right.$$
$$\times \delta L^{(12)}(\{\mathbf{r}\})G^{(1,2)}(\{\mathbf{r} - \mathbf{r}'\}; \{\mathbf{v}\})$$
$$\left.\times \cdots G^{(1,2)}(\{\mathbf{r}^{n-1} - \mathbf{r}^n\}\{\mathbf{v}\})\delta L^{(12)}(\{\mathbf{r}^n\})\right]$$

$$\times \left[\int d\mathbf{r}_1\, d\mathbf{r}_3 \cdots d\mathbf{r}_1^{m+1}\, d\mathbf{r}_3^{m+1} \exp -i\mathbf{l}(\mathbf{r}_1 - \mathbf{r}_3)\right.$$
$$\times G^{(1,3)}(\{\mathbf{r} - \mathbf{r}'\}; \{\mathbf{v}\})\delta L^{(13)}(\{\mathbf{r}'\})$$
$$\times \cdots G^{(1,3)}(\{\mathbf{r}^m - \mathbf{r}^{m+1}\}\{\mathbf{v}\})$$
$$\left.\times \delta L^{(1,3)}(\{\mathbf{r}^{m+1}\})\right]\delta(\{\mathbf{v} - \mathbf{v}'\}). \quad \text{(III.11)}$$

In this form, it is clear that the limiting procedure $l \to 0$ gives a perfectly well defined value to this expression. Moreover, we have used an obvious notation for the two particle free propagators $G^{(1,2)}$ and $G^{(1,3)}$. Here again the Ω^{-4} dependence is apparent only because each bracketed integrand is a translational invariant and results in an extra volume factor.

Using the same procedure as for (III.6), we may write the second bracket of (III.8) in a compact form as:

$$\int d\mathbf{r}_1\, d\mathbf{r}_3 \left[S^{(2)}(\mathbf{r}_1\mathbf{r}_3, \mathbf{v}_1\mathbf{v}_3 \mid \mathbf{v}_1', \mathbf{v}_3')\delta(\mathbf{v}_2 - \mathbf{v}_2')\right.$$
$$\left. - \delta(\{\mathbf{v} - \mathbf{v}'\})\right], \quad \text{(III.12)}$$

where the function $S^{(2)}$ is defined exactly as $S^{(3)}$ [see Eq. (III.7)], but for the pair of particles (1, 3) only.

As this expression (III.12) does not depend on the coordinates of any of the three particles, the same procedure can be applied once more to the first bracket and we obtain:

Reducible class 2(a)

$$= \Omega^{-4} \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{v}_1''\, d\mathbf{v}_2''\, d\mathbf{v}_3''\; \delta L^{(12)}(\mathbf{r}_{12})$$
$$\times S^{(2)}(\mathbf{r}_1\mathbf{r}_2\mathbf{v}_1\mathbf{v}_2 \mid \mathbf{v}_1''\mathbf{v}_2'')\delta(\mathbf{v}_3 - \mathbf{v}_3'') \int d\mathbf{r}_1'\, d\mathbf{r}_3'$$
$$\times \left[S^{(2)}(\mathbf{r}_1'\mathbf{r}_3'\mathbf{v}_1''\mathbf{v}_3'' \mid \mathbf{v}_1'\mathbf{v}_3')\delta(\mathbf{v}_2'' - \mathbf{v}_2')\right.$$
$$\left. - \prod_{i=1}^{3} \delta(\mathbf{v}_i'' - \mathbf{v}_i')\right]. \quad \text{(III.13)}$$

A similar formula is obtained for the reducible class 2(b), and the body collision operator is given by[10]

$$i\psi^{+(2)}(0)\delta(\{\mathbf{v} - \mathbf{v}'\})$$
$$= \Omega^{-2} \int d\mathbf{r}_1\, d\mathbf{r}_2\; \delta L^{(12)}(\mathbf{r}_{12})$$
$$\times S^{(2)}(\mathbf{r}_1\mathbf{r}_2\mathbf{v}_1\mathbf{v}_2 \mid \mathbf{v}_1'\mathbf{v}_2')\delta(\mathbf{v}_3 - \mathbf{v}_3'). \quad \text{(III.14)}$$

All the contributions to $\psi^{+(3)}(0)$ are now expressed in configurational space. We substitute (III.10), (III.13), and (III.14) into (II.13) and introduce this result into (II.2). Taking into account explicitly that the S functions depend only on the relative coordinates, we obtain

$$(\partial\varphi_1/\partial t)_{\text{t.c.}} = C^2 \int d\mathbf{v}_2\, d\mathbf{v}_3 \int d\mathbf{r}_{12}\; \delta L(\mathbf{r}_{12})$$

$$\times \int d\{\mathbf{v}'\}\, d\mathbf{r}_3 \Big\{ S^{(3)}(\{\mathbf{r}\}\{\mathbf{v}\} \mid \{\mathbf{v}'\})$$

$$- \int d\mathbf{v}_2''\; S^{(2)}(\mathbf{r}_1\mathbf{r}_2\mathbf{v}_1\mathbf{v}_2 \mid \mathbf{v}_1'\mathbf{v}_2'')S^{(2)}(\mathbf{r}_2\mathbf{r}_3\mathbf{v}_2''\mathbf{v}_3 \mid \mathbf{v}_2'\mathbf{v}_3')$$

$$- \int d\mathbf{v}_1''\; S^{(2)}(\mathbf{r}_1\mathbf{r}_2\mathbf{v}_1\mathbf{v}_2 \mid \mathbf{v}_1''\mathbf{v}_2')S^{(2)}(\mathbf{r}_1\mathbf{r}_3\mathbf{v}_1''\mathbf{v}_3 \mid \mathbf{v}_1'\mathbf{v}_3')$$

$$+ S^{(2)}(\mathbf{r}_1\mathbf{r}_2\mathbf{v}_1\mathbf{v}_2 \mid \mathbf{v}_1'\mathbf{v}_2')\,\delta(\mathbf{v}_3 - \mathbf{v}_3')\Big\} \prod_{i=1}^{3} \varphi_1(\mathbf{v}_i', t). \quad \text{(III.15)}$$

This is, in full notation, the expression (I.1) of Choh and Uhlenbeck[11] for the 3-particle collision operator.

IV. DISCUSSION

We are now in a position allowing us to discuss in detail the significance of irreducibility. Indeed, we have seen that the operator $\bar{\psi}^{+(3)}_{\text{ext.}}(0)$, where the condition of irreducibility was dropped, results in the term (III.10), involving the whole three-body motion $S^{(3)}$. In this latter operator, some contributions arise from separate two-body collisions in which, for instance, particles 1 and 3 collide first in a binary interaction, particle 1 then interacting with particle 2. However such a sequence of two-body collisions has already been taken into account in the usual two-particle Boltzmann operator and must thus be eliminated. This is achieved by the "reducible part" [see Eq. (III.13)] which indeed involves products of $S^{(2)}$ operators. The contribution to $S^{(3)}$ resulting from a simple two-body interaction in which particle 3 completely ignores the other two must also be substracted, and this results in the term (III.14). In the final result, the only effective part thus corresponds to irreducible collisions in which the three particles simultaneously interact with one another.

How this condition of irreducibility is automatically satisfied in the definition of the operator $i\psi^{+}(0)$—as given by (II.3)—appears very clear if we remember the relationship between space variables and their corresponding wave vectors:

$$\mathbf{kr} \simeq 1. \quad \text{(IV.1)}$$

The condition that $\{\mathbf{k}\} \neq$ zero at every intermediate state, eliminates all physical situations for which the three particles would be temporarily infinitely separated from one another in some of these intermediate states.

Keeping these remarks in mind, one realizes that although it appears compact, Eq. (III.15) is very difficult to handle for any practical calculations. Indeed the integrals appearing in this formula are, strictly speaking, defined for an infinite system. However in this limit, when taken separately, each of these integrals diverges! This will be best illustrated if we consider the binary correlation function defined from (III.15)[11] by

$$(\partial\varphi_1/\partial t)_{\text{t.c.}} \equiv C^2 \int d\mathbf{v}_2\, d\mathbf{v}_3$$

$$\times \int d\mathbf{r}_{12}\; \delta L(\mathbf{r}_{12}) f^{(3)}(\mathbf{r}_{12}; \mathbf{v}_1, \mathbf{v}_2; t). \quad \text{(IV.2)}$$

If we evaluate this expression for the only case where the calculations can be done directly (i.e., for an equilibrium velocity distribution function!), and dropping unimportant normalization and velocity dependent factors we obtain from (III.15):

$$f^{(3)}(\mathbf{r}_{12}; \mathbf{v}_1, \mathbf{v}_2) \propto \exp\left[-\beta V(\mathbf{r}_{12})\right]$$

$$\times \int d\mathbf{r}_3 \,\{\exp\left[-\beta(V[\mathbf{r}_{12}] + V[\mathbf{r}_{13}])\right]$$

$$- \exp\left[-\beta V(\mathbf{r}_{13})\right] - \exp\left[-\beta V(\mathbf{r}_{23})\right] + 1\}, \quad \text{(IV.3)}$$

where each of the factors is in a one to one correspondance with a term of Eq. (III.15). We thus see that expression (IV.2) involves the nonequilibrium equivalent of the binary correlation function *as expressed in terms of Boltzmann factors*, each of which diverges for a large system. That the total result is finite and gives the correct equilibrium distribution, is readily verified by reorganizing Eq. (IV.3) in terms of Mayer's factor $f_{ij} = \exp\left[-\beta V_{ij} - 1\right]$, which gives the well-known result

$$f^{(3)}(\mathbf{r}_{12}; \mathbf{v}_1, \mathbf{v}_2) \propto \exp\left[-\beta V(\mathbf{r}_{12})\right] \int d\mathbf{r}_3 f_{13}(\mathbf{r}_{13}) f_{23}(\mathbf{r}_{23}).$$

Such a difficulty is completely avoided in the formulation (II.3); as was previously shown by F. Henin, F. Andrews, and the author,[3,18] the corresponding expression for the binary correlation function is directly expressed in terms of *irreducible* (and finite) quantities.

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[18] F. Andrews, Physica **27**, 1054 (1961).

The advantage of the formulation in Fourier space could be of great help in an approximate evaluation of the three body cross sections, an exact calculation of which remains beyond the power of our present mathematical techniques. Indeed, if one begins from (III.14), the greatest care should be taken at each step to ensure that the approximations are made in a consistent way, such that the improper integrals in this equation always give a total final result. Moreover, it seems somewhat difficult to introduce the characteristic features (if any!) of the three-body collision in Green's function $S^{(3)}$ because this function also involves spurious two-body motion contributions.

If, however, no such problem arises in the formalism of Prigogine's group, it should be recognized that the whole theory is based upon the use of infinite perturbation expansions in the coupling constant, and some partial resummation procedure is needed for treating realistic hard-core forces.

Finally, we should mention that the generalization of the present calculation to higher order collisions (quadruple, etc.) offers no difficulty. Along the same line, it is possible to prove—to any order in the concentration—that the operator $i\psi^{+}(0)$ is identical with the corresponding collision operator derived independently by E. Cohen[19] and H. Green[20] [see also reference 13] in recent work. We shall give this general proof in a separate publication.

In conclusion we may say that the present work establishes the bridge between Prigogine and his co-workers' theory and what we may call the Bogolubov–Kirkwood types of approach. This link was already indicated briefly in a previous publication[2] where it was stressed that the equivalence was valid only whenever the duration of the collision could be completely neglected. The validity of this latter condition must be analyzed carefully for each particular problem studied. However, one can say that in general this is *not* the case and that the complete diagonal operator $\psi^{+}(z)$ is needed for all values of z. The second group of theory is then incorrect and the more general approach is necessary, as developed in references 1, 2, and 4.

ACKNOWLEDGMENT

We would like to express our gratitude to Professor I. Prigogine for his interest in this work.

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[19] E. Cohen, Communication at the I.C.P.A.P., (Brown University, Providence, Phode Island, 1962); Physica **28**, 1025 (1962).

[20] M. Green, Communication at the I.C.P.A.P., (Brown University, Providence, Rhode Island, 1962).

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Stochastic Liouville Equations

RYOGO KUBO
Department of Physics, University of Tokyo
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When a dynamical system has a perturbation which is considered as a stochastic process, the Liouville equation for the system in the phase space or the space of quantum-mechanical density operators is a sort of stochastic equation. The ensemble average of its formal integral defines the relaxation operator $\Phi(t)$ of the system. By the definition $\Phi(t) = \exp K(t)$, the cumulant function $K(t)$ may be introduced. Some general properties are first discussed for a simple example of an oscillator with random frequency modulation and then, concepts of slow and fast modulation are considered. These concepts can be generalized to more general types of stochastic Liouville equations. It is shown that by various possibilities of defining generalized exponential functions, this approach may be useful to understand some essential features of the problem from an unified point of view.

1. INTRODUCTION

ONE of the most fundamental problems in statistical mechanics is the logical foundation of transport equations. Great efforts have been made in recent years to derive such equations from basic dynamical equations, making a minimum number of assumptions, using various refined, mathematical tools.[1]

The present paper deals essentially with the same kind of problem but uses a less refined tool and takes slightly different standpoints from those taken in the previous theories. The author only wishes to throw a light on certain general features of the problem, of which many investigators may have been aware, but do not seem to have been discussed very clearly.

Take a very simple example of an oscillator whose natural frequency ω is modulated randomly by a certain disturbance.[2,3] Its equation of motion may be written as

$$\dot{x} = i\omega(t)x, \tag{1.1}$$

where $\omega(t)$ is regarded as a stochastic process. Now, an ensemble of such oscillators are irradiated by electromagnetic waves and the absorption spectrum is observed. The question is how the line shape is related to the modulation $\omega(t)$. This is the sort of problem one meets in magnetic resonance phenomena and also in some communication technology. It turns out that the spectrum depends on the relative magnitude of the amplitude of the modulation and on the speed of the modulation. If the modulation is slow, the coherence of perturbation remains and the line shape directly reflects the distribution of modulated frequencies. If the modulation is fast, the coherence is lost and the spectral line is narrowed. This narrowing and incoherence may be, in a sense, compared with the irreversibility which is realized in transport phenomena.

2. THE RELAXATION FUNCTION OF A RANDOMLY MODULATED OSCILLATOR

Equation (1.1) is integrated to

$$x(t) = \exp\left\{i\omega_0 t + \int_0^t \nu(t')\,dt'\right\}, \tag{2.1}$$

where ω_0 is the unperturbed frequency and $\nu(t)$ is the frequency modulation

$$\nu(t) = \omega(t) - \omega_0, \tag{2.2}$$

which is averaged to zero:

$$\langle \nu(t) \rangle = 0. \tag{2.3}$$

We assume the process $\nu(t)$ is stationary and ergodic, so that an ensemble average denoted by bracket may be considered as a long-time average. The function

$$\Phi(t) = \left\langle \exp i \int_0^t \nu(t')\,dt' \right\rangle \tag{2.4}$$

will be called the *relaxation function*, which may be generalized to a functional of $\xi(t)$,

$$\Phi(t, [\xi]) = \left\langle \exp\left\{ i \int_0^t \xi(t')\nu(t')\,dt' \right\}\right\rangle. \tag{2.5}$$

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[1] M. Bogoloubov, J. Phys. (USSR) **10**, 265 (1946); L. Van Hove, Physica **21**, 517, 901 (1955); **22**, 342 (1956); **23**, 441 (1957); I. Prigogine and P. Resibois, *ibid.* **27**, 629 (1961).

[2] R. Kubo, "Some Aspects of the Statistical-Mechanical Theory of Irreversible Processes," in *Lectures in Theoretical Physics I.*, edited by W. E. Brittin and L. G. Dunham (Interscience Publishers, Inc., New York, 1959).

[3] R. Kubo, "A Stochastic Theory of Line-Shape and Relaxation," A lecture at the Scottish Universities Summer School at Newbattle Abbey, 1961 [to be published as *Fluctuation, Relaxation and Resonance in Magnetic Systems*, edited by ter Haar, (Oliver and Boyd, Edinburgh, 1962)].

Thus, we may write

$$\Phi(t) \equiv \Phi(t, [1]).$$

The functional $\Phi(t, [\xi])$ is the *characteristic functional* for the process $\nu(t)$. By the fluctuation-dissipation theorem the spectral distribution $I(\omega - \omega_0)$ of an ensemble of these oscillators is given by

$$I(\omega - \omega_0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Phi(t) e^{-i(\omega-\omega_0)t}\, dt. \tag{2.6}$$

Let us now introduce the *cumulant function* $K(t)$ by

$$\Phi(t) = \exp K(t). \tag{2.7}$$

By a theorem which has been previously discussed by the author,[4] this may be expressed as

$$K(t) = \left\langle \exp\left(i \int_0^t \nu(t')\, dt'\right) - 1 \right\rangle_c \tag{2.8a}$$

$$\begin{aligned} &\equiv i \int_0^t dt_1\, \langle \nu(t_1) \rangle + i^2 \int_0^t dt_1 \int_0^t dt_2\, \langle \nu(t_1)\nu(t_2) \rangle_c \\ &\quad + \cdots + i^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \\ &\quad \times \langle \nu(t_1)\nu(t_2) \cdots \nu(t_n) \rangle_c + \cdots \end{aligned} \tag{2.8b}$$

$$\begin{aligned} &= -\int_0^t dt_1 \int_0^{t_1} dt_2\, \langle \nu(t_1)\nu(t_2) \rangle \\ &\quad + i^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3\, \langle \nu(t_1)\nu(t_2)\nu(t_3) \rangle_c \\ &\quad + \cdots, \end{aligned} \tag{2.8c}$$

where the brackets with the suffix c are the "cumulant averages" defined, for example, by

$$\begin{aligned} \langle X_1 \rangle_c &= \langle X_1 \rangle, \\ \langle X_1 X_2 \rangle_c &= \langle X_1 X_2 \rangle - \langle X_1 \rangle \langle X_2 \rangle, \\ \langle X_1 X_2 X_3 \rangle_c &= \langle X_1 X_2 X_3 \rangle - \langle X_1 \rangle \langle X_2 X_3 \rangle \\ &\quad - \langle X_2 \rangle \langle X_1 X_3 \rangle - \langle X_3 \rangle \langle X_1 X_2 \rangle \\ &\quad + 2 \langle X_1 \rangle \langle X_2 \rangle \langle X_3 \rangle. \end{aligned} \tag{2.9}$$

The cumulant averages are generally defined by

$$\left\langle \exp\left(\sum_i^N \xi_i X_i\right)\right\rangle = \exp\left\{\sum \prod \frac{\xi_i^{m_i}}{m_i!} \langle X_1^{m_1} \cdots X_N^{m_N} \rangle_c \right\}. \tag{2.10}$$

One sees easily that a cumulant average vanishes identically if any of the variables in it is statistically independent from the others.[4]

This property of cumulant averages has an important consequence on the convergence of the series (2.8). We shall not go into any mathematical discussion of this convergence here, but shall content ourselves with less rigorous qualitative arguments. Suppose that the process $\nu(t)$ has a finite correlation time τ_c which may be defined by

$$\tau_c = \int_0^{\infty} \langle \nu(0)\nu(t) \rangle\, dt / \Delta^2, \tag{2.11}$$

where

$$\Delta = \langle \nu^2 \rangle^{1/2} \tag{2.12}$$

measures the amplitude of modulation. Now let us consider the short-time and long-time behavior of $\Phi(t)$ or $K(t)$.

For a small $t (\ll \tau_c)$, the temporal change of $\nu(t)$ may be ignored so that (2.4) will be approximated by

$$\Phi(t) \sim \langle \exp i\nu t \rangle = \int e^{i\nu' t} P(\nu')\, d\nu' \equiv \Phi_0(t), \tag{2.13}$$

where $P(\nu')$ is the probability density of the frequency modulation ν, and so $\Phi_0(t)$ is nothing but the characteristic function of $P(\nu')$. Higher approximations to $\Phi(t)$ may be obtained similarly by taking account of the distributions of $\dot{\nu}$, $\ddot{\nu}$ and so on.

For a long-time $t (\gg \tau_c)$, $K(t)$ will be shown to have the asymptotic form

$$K(t) \sim -(at + b) \equiv -(\gamma - i\delta)t - b, \tag{2.14}$$

which is equivalent to

$$\begin{aligned} \mathfrak{K}(s) &\equiv \int_0^{\infty} e^{-st} K(t)\, dt \\ &= -\frac{a}{s^2} - \frac{b}{s} + \cdots \quad (s \sim 0). \end{aligned} \tag{2.15}$$

Then the relaxation function $\Phi(t)$ will behave as

$$\Phi(t) \sim \exp\{-at - b\} \equiv \Phi_\infty(t) \tag{2.16}$$

$(t \gg \tau_c)$ and it may be described asymptotically by the differential equation

$$d\Phi/dt = -a\Phi \qquad (t \gg \tau_c). \tag{2.17}$$

By the nature of cumulant averages, the nth term in (2.8) may be estimated as

$$\int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n\, \langle \nu(t_1) \cdots \nu(t_n) \rangle_c \sim tO(\Delta^n \tau_c^{n-1}) + O(\Delta^n \tau_c^n),$$

if $t \gg n\, \tau_c$. Therefore, for a sufficiently large t, in

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[4] R. Kubo, J. Phys. Soc. Japan, 17, 1100 (1962).

(2.14), a and b have such structures as

$$a = O(\Delta^2\tau_c) + O(\Delta^3\tau_c^2) + \cdots$$
$$b = O(\Delta^2\tau_c^2) + O(\Delta^3\tau_c^3) + \cdots . \qquad (2.18)$$

A simple example may be useful for illustration. If we assume that

$$\langle \nu(t_1)\nu(t_2) \cdots \nu(t_n)\rangle_c = \Delta^n\psi(t_1 - t_2)\psi(t_2 - t_3) \cdots \psi(t_{n-1} - t_n)$$
$$(t_1 > t_2 > \cdots > t_n, n \geq 2), \qquad (2.19)$$

we find

$$\mathfrak{K} = \int_0^\infty e^{-st}K(t)\,dt = \frac{(i\Delta)^2}{s^2}\frac{g(s)}{1 - i\Delta g(s)}, \qquad (2.20)$$

where

$$g(s) = \int_0^\infty e^{-st}\psi(t)\,dt = \frac{\tau_c}{1 + s\tau_c}.$$

For example, if ψ in Eq. (2.19) is simply assumed to be

$$\psi(t) = \exp(-\tau/\tau_c), \qquad (2.21)$$

then Eq. (2.20) becomes

$$\mathfrak{K} = -\frac{\Delta^2\tau_c}{s^2}\frac{1}{1 - i\Delta\tau_c + s\tau_c}, \qquad (2.22)$$

which, in fact, is in accordance with (2.15). The cumulant function $K(t)$ is then found to be

$$K(t) = -\frac{\Delta^2\tau_c}{1 - i\Delta\tau_c}t - \frac{\Delta^2\tau_c^2}{(1 - i\Delta\tau_c)^2} \times \left[1 - \exp\left\{-(1 - i\Delta\tau_c)\frac{t}{\tau_c}\right\}\right]. \qquad (2.23)$$

3. SLOW OR FAST MODULATION. NARROWING CONDITIONS

We have obtained two limiting approximations for $\Phi(t)$, one for short time and the other for long time. Which of these is better? The question can be answered by the following criterion[3]:

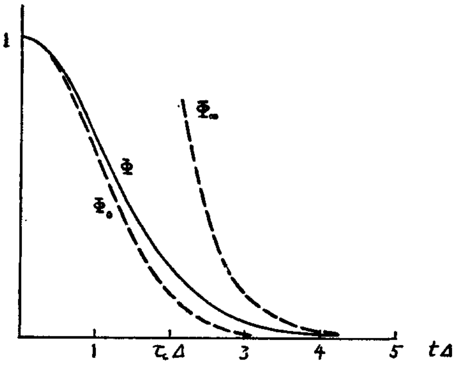

FIG. 1. Relaxation function $\Phi(t)$ in slow modulation case. $\Phi(t)$, $\Phi_0(t)$, and $\Phi_\infty(t)$ are calculated by Eqs. (4.1b), (4.3), and (4.4), respectively, $\psi(t)$ being assumed as $\psi(t) = \exp(-t/\tau_c)$. $\tau_c\Delta$ is taken as 2.0.

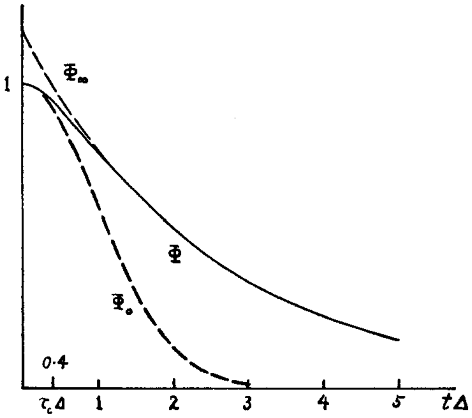

FIG. 2. Relaxation function $\Phi(t)$ in fast modulation case. The curves are calculated in the same way as in Fig. 1. $\tau_c\Delta$ is taken as 0.4.

Case a. Slow modulation

$$\Phi_0(\tau_c) \ll 1 \quad \text{or} \quad \Phi_\infty(\tau_c) \ll 1, \qquad (3.1)$$

Case b. Fast modulation

$$\Phi_0(\tau_c) \sim 1. \quad \text{or} \quad \Phi_\infty(\tau_c) \sim 1, \qquad (3.2)$$

or

$$a\tau_c + b \ll 1. \qquad (3.3)$$

In the case a, the relaxation function $\Phi(t)$ looks like Fig. 1. It is essentially represented by $\Phi_0(t)$ because it becomes very small in the region $t > \tau_c$ where the short-time approximation fails. This means persistence of *coherence* over the period which is practically important. The spectral distribution (2.6) is then identical with the distribution of modulated frequency, namely,

$$I(\omega - \omega_0) = P(\omega - \omega_0). \qquad (3.4)$$

The condition for this slow modulation may be also roughly expressed by

$$\tau_c\Delta \gg 1 \qquad (3.5)$$

which means that the speed of modulation (measured by $1/\tau_c$) is slow compared with the modulation amplitude Δ.

In case b, on the other hand, $\Phi_\infty(t)$ represents $\Phi(t)$ quite well except in the neighborhood of $t \sim 0$ $(t < \tau_c)$ where $\Phi_\infty(t)$ definitely deviates from $\Phi(t)$. (See Fig. 2). The graph of $\Phi(t)$ must be horizontal at $t = 0$ as is easily proved by the stationary property of $\nu(t)$. $\Phi_\infty(t)$ does not satisfy this condition, but this region is only a small part of the whole domain of t where $\Phi(t)$ has significant values. The line shape (2.6) is obtained as

$$I(\omega - \omega_0) = \frac{1}{\pi}\operatorname{Re}\frac{e^{-b}}{a + i(\omega - \omega_0)}$$

$$= \frac{1}{\pi}\frac{\gamma \operatorname{Re} e^{-b}}{(\omega - \omega_0 - \delta)^2 + \gamma^2} + \frac{1}{\pi}\frac{(\omega - \omega_0 - \delta)\operatorname{Im} e^{-b}}{(\omega - \omega_0 - \delta)^2 + \gamma^2} \qquad (3.6a)$$

$$\sim \frac{1}{\pi}\frac{\gamma}{(\omega - \omega_0 - \delta)^2 + \gamma^2} \text{ (if } b \ll 1\text{)}, \qquad (3.6b)$$

which is essentially a Lorentzian form but with a slight skewness represented by the second term of (3.6a). The width γ,

$$\gamma = \operatorname{Re} a, \qquad (3.7)$$

is *smaller* than Δ. Therefore, the spectrum is *narrowed*. If, further, the condition

$$\tau_c \Delta \ll 1 \qquad (3.8)$$

is satisfied, the width γ is approximately given by

$$\gamma = \tau_c \Delta^2. \qquad (3.9)$$

Thus the condition (3.3) may be called the narrowing condition and the condition (3.9) the strong narrowing condition since it is more stringent than (3.3).

When the narrowing condition is satisfied, the coherence of modulation is essentially lost and the modulation simply appears as *incoherent* interruption of oscillations. Correspondingly, the relaxation function $\Phi(t)$ shows a simple exponential decay.

The Lorentzian form (3.6) does not prescisely describe the spectral form at far wings. If $\Phi_0(t)$ is analytic in t at $t = 0$, the moments should be convergent in every order. Therefore, the intensity distribution should decrease at wings much faster than the Lorentzian curve. But this discrepancy is not very significant since the intensity there is very weak if the narrowing has occurred.

At this point it may be worth pointing out the following. It is true that the relaxation function $\Phi(t)$ follows Eq. (2.17) quite generally at large $t(\gg \tau_c)$. This may be regarded as the characteristic of an irreversible process. The physical significance of this statement depends, however, on what we are observing. This may be significant if we are just concerned with such long-time behavior of $\Phi(t)$. But if the spectrum $I(\omega - \omega_0)$ itself is really what matters, then this statement is meaningful only when the narrowing condition is satisfied.

4. GAUSSIAN AND POISSON MODULATIONS

A simple example is provided by a Gaussian modulation $\omega(t)$. In this case the cumulants terminate at the second, so that the relaxation function becomes

$$\Phi(t) = \exp\left\{-\int_0^t dt_1 \int_0^{t_1} dt_2\, \Delta^2 \psi(t_1 - t_2)\right\} \qquad (4.1a)$$

$$= \exp\left\{-\Delta^2 \int_0^t (t - \tau)\psi(\tau)\, d\tau\right\}, \qquad (4.1b)$$

where

$$\psi(t) = \langle \nu(t_1 + t)\nu(t_1)\rangle / \langle \nu^2 \rangle \qquad (4.2)$$

is the correlation function of the modulation $\nu(t)$, for which

$$\langle \nu(t) \rangle = 0$$

is assumed. For $t \ll \tau_c$ (4.1) is approximated by

$$\Phi(t) \sim \Phi_0(t) = \exp(-\tfrac{1}{2}\Delta^2 t^2), \qquad (4.3)$$

which reflects the Gaussian nature of modulation, and for $t \gg \tau_c$

$$\Phi(t) \sim \Phi_\infty(t) = \exp\{-\Delta^2 \tau_c t + b\}, \qquad (4.4)$$

where

$$\tau_c = \int_0^\infty \psi(t)\, dt, \qquad b = \Delta^2 \int_0^\infty t\psi(t)\, dt.$$

The narrowing condition in this case is exactly given by (3.8). This has been discussed by Anderson and Weiss[5] as a model of exchange narrowing in paramagnetic resonance.

Another instructive example is a Poisson modulation. Suppose the modulation $\nu(t)$ consists of random pulses with an average duration τ_d, the average interval $\tau_i(\gg \tau_d)$, and the average height ν_p. Then for $t \gg \tau_d$ the relaxation function is easily found to be[3]

$$\Phi(t) = \exp\{(t/\tau_i)\langle e^{i\alpha} - 1\rangle\} \qquad (4.5)$$

where α is the phase shift during a pulse, i.e.,

$$\alpha = \int_{-\infty}^{\infty} \nu_{\text{pulse}}(t)\, dt. \qquad (4.6)$$

The narrowing condition here is

$$(\tau_d/\tau_i)(1 - \langle \cos \alpha \rangle) \ll 1 \qquad (4.7)$$

which is less stringent then $\omega\tau_d \ll 1$ or even than $\tau_d \ll \tau_i$. The Poisson modulation represents a model of spectral broadening in dilute gases. It also cor-

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[5] P. W. Anderson and P. J. Weiss, Rev. Mod. Phys. **25**, 269 (1953).

responds to kinetic models of rarefied gases or nearly free electrons.

Generally speaking, the narrowing condition can be regarded as a condition for a perturbational treatment. If the strong narrowing condition (3.8) is satisfied, the perturbation $\nu(t)$ is weak (compared with $1/\tau_c$). The Gaussian modulation is a limiting case where the crudest (Born) approximation becomes correct, because it really occurs when a number of very weak perturbations are present. If a non-Gaussian modulation $\nu(t)$ satisfies (3.8), a and b in Eq. (2.14) can be calculated by perturbational series (2.18).

A Poisson process, on the other hand, represents the situation where local interactions are present. Such a local perturbation may be so strong that each perturbation has to be taken into full account. Still the locality allows the narrowing condition (4.7). In dilute particle systems, each collision has to be calculated by an exact scattering matrix, but with this in mind the whole process can be treated in a perturbational way.

5. STOCHASTIC LIOUVILLE EQUATION. RELAXATION OPERATOR

We consider a dynamical system, the Hamiltonian of which has the form

$$H = H_0 + V(t), \tag{5.1}$$

$$\frac{\partial f}{\partial t} = \sum \left(\frac{\partial H}{\partial q}\frac{\partial}{\partial p} - \frac{\partial H}{\partial p}\frac{\partial}{\partial q}\right) f = [L_0 + L_1(t)]f, \tag{5.2}$$

L_0 and L_1 being Liouville operators corresponding to H_0 and V. In the interaction representation

$$g(t) = e^{-L_0 t} f(t), \qquad g(0) = f(0), \tag{5.3}$$

Equation (5.2) becomes

$$\partial g/\partial t = e^{-L_0 t} L_1(t) e^{L_0 t} g \equiv \Omega(t) g. \tag{5.4}$$

This equation is formally integrated with the use of an ordered exponential to

$$\begin{aligned} g(t) &= \exp_0 \left(\int_0^t \Omega(t')\,dt'\right) f(0) \\ &= \left[1 + \int_0^t dt_1\,\Omega(t_1) + \int_0^t dt_1 \int_0^{t_1} dt_2\,\Omega(t_1)\Omega(t_2)\right. \\ &\quad + \cdots + \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \\ &\quad \left.\times\ \Omega(t_1)\Omega(t_2)\cdots\Omega(t_n) + \cdots\right] f(0). \end{aligned} \tag{5.5}$$

Now, we may look at Eq. (5.4) as a stochastic equation similar to (1.1). If $V(t)$, (5.1), is in fact a random perturbation from outside, this correspondence is obvious. Then the expression (5.5) is averaged over the ensemble of the stochastic process $V(t)$, to give

$$\begin{aligned} \langle g(t)\rangle &= \Phi(t) g(0) \\ &\equiv \left\langle \exp_0 \int_0^t \Omega(t')\,dt' \right\rangle g(0), \end{aligned} \tag{5.6}$$

and so we have

$$\langle f(t)\rangle = e^{L_0 t}\Phi(t) f(0). \tag{5.7}$$

$\Phi(t)$ defined by Eq. (5.6) may be called the *relaxation operator* for the process $\Omega(t)$.

If the initial distribution $f(0)$ is a delta function in the phase space,

$$f(0) = \delta(p - p_0)\delta(q - q_0),$$

the expression (5.7) gives the *transition probability* from (p_0, q_0) to (p, q) in the time interval t. This may be written as the matrix element of the operator $\exp(L_0 t)\Phi(t)$ in (5.7), namely,

$$\begin{aligned} f(pqt \mid p_0 q_0 0) &= (pq \,|e^{L_0 t}\Phi(t)|\, p_0 q_0) \\ &= \iint (pq\,|e^{L_0 t}|\,p'q')\,dp'\,dq'\,(p'q'\,|\Phi(t)|\,p_0 q_0), \end{aligned} \tag{5.8}$$

where the matrix element of $\Phi(t)$ is the transition probability in the coordinate system moving in the unperturbed motion.

In some cases, the perturbation V is a constant interaction within the system, but we may take the interaction representation as before, while transferring ourselves to the moving system defined by H_0. Then the equation of motion becomes (5.4) again, and is integrated to (5.5). The perturbation $\Omega(t)$ may be regarded as stochastic if our observation is restricted to a certain subspace of the original phase space. Let us assume that

$$f(0) = f_1(P, Q \mid 0) f_0(p, q), \tag{5.9}$$

and

$$L_0 f_0(p, q) = 0, \quad \text{or} \quad e^{L_0 t} f_0(p, q) = f_0(p, q), \tag{5.10}$$

where (P, Q) represents the variables in the subspace Γ_1 under observation and (p, q) those in Γ_0 which are dropped out from observation. The distribution $f_0(p, q)$ is invariant with respect to the unperturbed motion of the system by the assumption (5.10) and is normalized to

$$\int d\,\Gamma_0 f_0(p, q) = 1. \tag{5.11}$$

The expression (5.5) is integrated in Γ_0 to give

$$g_1(P, Q \mid t) = \int d\,\Gamma_0 \exp_0\left\{\int_0^t \Omega(t')\,dt'\right\} \times f_1(P, Q \mid 0) f_0(p, q) = \left\langle \exp_0 \int_0^t \Omega(t')\,dt \right\rangle f_1(P, Q \mid 0), \quad (5.12)$$

where the average $\langle\ \rangle$ is defined by this equation. The assumption (5.10) assures

$$\langle \Omega(t_1 + t) \cdots \Omega(t_n + t)\rangle = \langle \Omega(t_1) \cdots \Omega(t_n)\rangle.$$

The process $\Omega(t')$ in (5.12) may now be regarded as a stationary stochastic process. Therefore its relaxation operator $\Phi(t)$ is defined in the same way as before, by (5.6), and the matrix elements in (5.8) give the transition probabilities.

The above can be immediately extended to quantum-mechanical cases. Instead of Eq. (5.2), we have the equation of motion for the density matrix

$$\partial\rho/\partial t = (1/i\hbar)[H, \rho] \equiv (L_0 + L_1)\rho. \quad (5.13)$$

In the interaction representation,

$$\sigma = e^{-L_0 t}\rho = e^{iH_0 t/\hbar}\rho e^{-iH_0 t/\hbar}. \quad (5.14)$$

Equation (5.13) is transformed into

$$\begin{aligned} \partial\sigma/\partial t &= \Omega(t)\sigma \\ &\equiv (1/i\hbar)[e^{iH_0 t/\hbar} v e^{-iH_0 t/\hbar}, \sigma] \\ &= (1/i\hbar)[\tilde{V}(t), \sigma], \end{aligned} \quad (5.15)$$

and is integrated to

$$\sigma(t) = \exp_0\left\{\int_0^t \Omega(t')\,dt'\right\}\rho(0) \quad (5.16)$$

as before. If the perturbation $V(t)$ is a random process, (5.16) is averaged over the ensemble of the stochastic process. If V is originally an interaction inside the system and some dynamical variables are now dropped out from observation, we assume that

$$\rho = \rho_1\rho_0 \quad (5.17)$$

and take trace over the part ρ_0. If ρ_0 is invariant under transformation by H_0, this will define

$$\left\langle \exp_0 \int_0^t \Omega(t')\,dt' \right\rangle \rho_1 = \mathrm{Tr}_0 \exp_0\left\{\int_0^t \Omega(t')\,dt'\right\}\rho_1\rho_0, \quad (5.18)$$

by which $\Omega(t')$ is now considered as a stationary stochastic process. The arguments are parallel to the classical arguments.

6. RELAXATION OPERATOR AND GENERALIZED CUMULANT FUNCTION

Similarly to (2.7), the cumulant function $K(t)$ can be introduced by the definition

$$\begin{aligned} \Phi(t) &= \left\langle \exp_0 \int_0^t \Omega(t')\,dt' \right\rangle \\ &= 1 + \int_0^t dt_1\,\langle\Omega(t_1)\rangle \\ &\quad + \cdots + \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \\ &\quad \times \langle \Omega(t_1) \cdots \Omega(t_n)\rangle + \cdots \\ &= \exp_P\left\{\int_0^t dt_1\,\langle\Omega(t_1)\rangle_c \right. \\ &\quad + \int_0^t dt_1 \int_0^{t_1} dt_2\,\langle\Omega(t_1)\Omega(t_2)\rangle_c \\ &\quad + \cdots + \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \\ &\quad \left. \times \langle\Omega(t_1) \cdots \Omega(t_n)\rangle_c + \cdots \right\} \\ &= \exp_P K(t). \end{aligned} \quad (6.1)$$

Since $\Omega(t)$'s are operators which are not generally commutable, the cumulant K is a complex operator. The cumulants involve products of $\Omega(t)$'s, and the expansion of $\exp_P K(t)$ in series is a fairly complicated matter. The suffix P specifies a prescription for the ordering of Ω's and cumulants.

As is discussed in more detail by the author in a previous paper,[4] it is possible to generalize the concept of moments and cumulants to noncummuting q-number variables and to generalized exponentials. The important point is that a cumulant $\langle\Omega(t_1) \cdots \Omega(t_n)\rangle_c$ in (6.1) can be expressed by a sum of certain products of lower moments or cumulants and the moment of the same order and so every cumulant can be successively defined. The concept that the operators are "connected" to give nonvanishing cumulants depends on the definition of average and the prescription of ordering. Any cumulant will vanish if any one of the operators in it is unconnected with the others in the proper meaning of the word "connected." To give a few examples, the lower-order cumulants in (6.1) may be explicitly written as

$$\langle\Omega(t)\rangle_c = \langle\Omega(t)\rangle$$

$$\langle\Omega(t_1)\Omega(t_2)\rangle_c = \langle\Omega(t_1)\Omega(t_2)\rangle - P\langle\Omega(t_1)\rangle\langle\Omega(t_2)\rangle$$

$$\begin{aligned}\langle\Omega(t_1)\Omega(t_2)\Omega(t_3)\rangle_c &= \langle\Omega(t_1)\Omega(t_2)\Omega(t_3)\rangle \\ &\quad - P\{\langle\Omega(t_1)\rangle\langle\Omega(t_2)\Omega(t_3)\rangle_c \\ &\quad + \langle\Omega(t_2)\rangle\langle\Omega(t_1)\Omega(t_3)\rangle_c \\ &\quad + \langle\Omega(t_3)\rangle\langle\Omega(t_1)\Omega(t_2)\rangle_c\} \\ &\quad - P\langle\Omega(t_1)\rangle\langle\Omega(t_2)\rangle\langle\Omega(t_3)\rangle, \end{aligned} \tag{6.2}$$

where P is a certain prescription for the product of lower-order cumulants. Such prescription may be chosen in various ways. Let us give here a few important examples.

a. The chronological ordering 0 in (5.5) is followed for the ordering P. For instance, if the moments have the form

$$\begin{aligned}\langle\Omega(t_1)\cdots\Omega(t_n)\rangle &= A(t_1)\cdots A(t_n)\psi(t_1,\cdots t_n) \\ &\qquad t_1 > t_2 > \cdots > t_n (n \geqq 2),\end{aligned} \tag{6.3}$$

where $A(t_1)\cdots A(t_n)$ are q numbers and $\psi(t_1\cdots t_n)$ is a c-number function, the relaxation operator Φ is written as

$$\begin{aligned}\Phi(t) = \exp_0\Big\{&\int_0^t dt_1 \int_0^{t_1} dt_2\, A(t_1)A(t_2)\psi(t_1, t_2) \\ &+ \cdots + \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n\, A(t_1)\cdots A(t_n) \\ &\times \psi_c(t_1\cdots t_n) + \cdots\Big\}.\end{aligned} \tag{6.4}$$

The ordering 0 means chronological ordering of $A(t)$'s and $\psi_c(t_1, \cdots t_n)$ is the nth cumulant constructed from the moments $\psi(t_1\cdots t_m)$ $(m \leq n)$.

b. A generalized exponential with different ordering F may be defined by

$$d\Phi(t)/dt = F(t)\Phi(t), \tag{6.5}$$

or

$$\begin{aligned}\Phi(t) &= \exp_F \int_0^t F(t')\,dt' \\ &= \exp_F \int_0^t dt'\,\{F_1(t') + F_2(t') + \cdots\},\end{aligned} \tag{6.6}$$

which means the chronological ordering in F's. The third cumulant, for instance, becomes

$$\begin{aligned}\int_0^t F_3(t')\,dt' = \int_0^t dt_1 &\int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\ &\times [\langle\Omega(t_1)\Omega(t_2)\Omega(t_3)\rangle \\ &- \langle\Omega(t_1)\rangle\{\langle\Omega(t_2)\Omega(t_3)\rangle - \langle\Omega(t_2)\rangle\langle\Omega(t_3)\rangle\} \\ &- \{\langle\Omega(t_1)\Omega(t_3)\rangle - \langle\Omega(t_1)\rangle\langle\Omega(t_3)\rangle\}\langle\Omega(t_2)\rangle \\ &- \{\langle\Omega(t_1)\Omega(t_2)\rangle - \langle\Omega(t_1)\rangle\langle\Omega(t_2)\rangle\}\langle\Omega(t_3)\rangle \\ &- \langle\Omega(t_1)\rangle\langle\Omega(t_2)\rangle\langle\Omega(t_3)\rangle].\end{aligned} \tag{6.7}$$

c. We assume that

$$\frac{d\Phi(t)}{dt} = \int_0^t G(t, t')\,dt'\,\Phi(t'), \tag{6.8}$$

and integrate this as

$$\begin{aligned}\Phi(t) &= 1 + \int_0^t dt_1 \int_0^{t_1} dt'\, G(t_1, t_1')\Phi(t_1') \\ &= 1 + \int_0^t dt_1 \int_0^{t_1} dt_1'\, G(t_1, t_1') + \cdots \\ &\qquad + \cdots + \int_0^t dt_1 \int_0^{t_1} dt_1' \int_0^{t_1'} dt_2 \\ &\qquad \times \int_0^{t_2} dt_2' \cdots \int_0^{t'_{n-1}} dt_n \int_0^{t_n} dt_n' \\ &\quad G(t_1, t_1')G(t_2, t_2')\cdots G(t_n, t_n') + \cdots \\ &= \exp_G\left\{\int_0^t dt_1 \int_0^{t_1} dt_1'\, G(t_1, t_1')\right\}.\end{aligned} \tag{6.9}$$

This defines another kind of exponential with the prescription G, which means time ordering and elimination of those terms in the expansion which have overlapped intervals (t_i, t_i')'s. If

$$\langle\Omega(t)\rangle = 0$$

is assumed, one sees easily that the equation

$$\begin{aligned}&\left\langle \exp_0 \int_0^t \Omega(t')\,dt' \right\rangle \\ &\qquad = \exp_G\left[\int_0^t dt_1 \int_0^{t_1} dt_1'\,\{G_2(t_1, t_1') \right. \\ &\qquad\qquad \left. + G_3(t_1, t_1') + \cdots\}\right]\end{aligned} \tag{6.10}$$

defines the cumulants G's successively. For instance,

$$\begin{aligned}\langle\Omega(t_1)\Omega(t_2)\Omega(t_3)\rangle_c &= \langle\Omega(t_1)\Omega(t_2)\Omega(t_3)\rangle \\ \langle\Omega(t_1)\Omega(t_2)\Omega(t_3)\Omega(t_4)\rangle_c &= \langle\Omega(t_1)\Omega(t_2)\Omega(t_3)\Omega(t_4)\rangle \\ &\quad - \langle\Omega(t_1)\Omega(t_2)\rangle\langle\Omega(t_3)\Omega(t_4)\rangle.\end{aligned} \tag{6.11}$$

The cumulants are obtained by applying the principle seen in the example (6.2). They always vanish if the variables in them are uncorrelated.

Equation (6.8) takes a simple form if we have the condition

$$G(t, t') = G(t - t'), \tag{6.12}$$

which is fulfilled if the process $\Omega(t)$ is stationary. Then the Laplace transformation of this equation gives

$$\int_0^\infty e^{-st}\Phi(t)\,dt = \frac{1}{s - \mathfrak{G}(s)}, \tag{6.13}$$

where

$$\mathfrak{G}(s) = \int_0^\infty e^{-st}G(t)\,dt$$
$$= s^2\mathfrak{K}(s), \qquad (6.14)$$

$\mathfrak{K}(s)$ being the cumulant function defined by Eq. (6.10).

If the relaxation operator $\Phi(t)$ is obtained in such a form as (6.6), its long-time behavior is described by

$$d\Phi/dt \sim F(\infty)\Phi(t), \qquad (6.15)$$

or

$$\Phi(t) \sim \exp\,[tF(\infty)], \qquad (6.16)$$

which corresponds to (2.14) for the relaxation of a modulated oscillator. The operator $F(\infty)$ determines the long-time relaxation process.

If $\Phi(t)$ is obtained in the form (6.9), with the *cumulant kernel* $G(t_1 - t_1')$, Eq. (6.13) immediately gives the important admittance function

$$\int_0^\infty e^{-i\omega t}\Phi(t)\,dt = \frac{1}{i\omega + 0 - \mathfrak{G}(i\omega + 0)}. \qquad (6.17)$$

In particular, the static admittance is determined by $\mathfrak{G}(0)$, which is generally different from $F(\infty)$. Only when some condition similar to the narrowing condition is satisfied, do they coincide with each other. This is in accordance with the results obtained by Prigogine and Résibois[1] and Balescu.[6]

An operator process $\Omega(t)$ may be called *Gaussian* if the relaxation function $\Phi(t)$ has the form

$$\Phi(t) = \exp_P\left\{\int_0^t dt_1\,\langle\Omega(t_1)\rangle + \int_0^t dt_1 \int_0^{t_1} dt_2\,\langle\Omega(t_1)\Omega(t_2)\rangle_c\right\}, \qquad (6.18)$$

namely, if the cumulant terminates at the second. The definition of cumulants depends on the ordering prescription P, so does the concept of a Gaussian process in this generalized sense. For instance, if $\Omega(t)$ has the form

$$\Omega(t) = A(t)\omega(t), \qquad (6.19)$$

where $\omega(t)$ is simply a c-number Gaussian process, $\Phi(t)$ as defined by (6.4) becomes, in fact,

$$\Phi(t) = \exp_0\left\{\int_0^t dt_1\int_0^{t_1} dt_2\,A(t_1)A(t_2)\psi(t_1, t_2)\right\}. \qquad (6.20)$$

The ordering 0 prescribes full chronological ordering of $A(t)$'s if they are not commutable. This ordering can be changed into other kinds of ordering such as (6.6) or (6.9). Then the transformed cumulants are no longer so simple.

When a certain system A, a system of electrons for instance, is in contact with harmonic oscillators, the interaction V may be of the form

$$V = \textstyle\sum_q (A_q b_q + A_q^* b_q^*), \qquad (6.21)$$

where the b_q's and b_q^*'s are the annihilation and creation operators of oscillators and A_q and A_q^* are variables for the system A representing its coupling to the oscillator q. If the oscillator system is assumed to be in thermal equilibrium, (6.21) gives a stochastic perturbation $V(t)$ to the system A. Because of harmonicity of the oscillators this provides an example of a Gaussian process.

A Poisson process $\Omega(t)$ may be defined in the same way as (4.5). Its relaxation function can be written as

$$\Phi(t) = \exp\,\{(t/\tau_i)\langle e^{iA} - 1\rangle\}, \qquad (6.22)$$

where A is defined by

$$e^{iA} = \exp_0\left\{\int_{-\infty}^{\infty} \Omega_{\text{pulse}}(t)\,dt\right\}. \qquad (6.23)$$

Such examples are provided by scattering process of a particle by short-range scatterers which are distributed randomly in space. The master equation for a dilute gas system can also be considered in this way. It is, of course, possible to extend the Poisson limit (6.22) to include higher-order corrections by a sort of cluster or virial expansion as used in the Mayer theory of imperfect gases. At the same time, it becomes necessary to take account of finite duration of each collision.

If a strong narrowing condition is fulfilled, the cumulant expansion in (6.1) may be terminated at the second, and furthermore, the long-time approximation of $\Phi(t)$ gives a good approximation. This means that the random perturbation is weak and effectively incoherent. Then Eq. (5.7) can be transformed into

$$(d/dt)\langle f(t)\rangle = \{L_0 + \Gamma\}\langle f(t)\rangle, \qquad (6.24)$$

where

$$\Gamma = \int_0^\infty \langle L_1(t)e^{L_0(t-t')}L_1(t')e^{-L_0(t-t')}\rangle\,dt'. \qquad (6.25)$$

This can be seen either by (6.6) or (6.10). Γ here naturally coincides with the familiar result of the perturbational calculation in the second order. It contains the transition probability in this approximation and the self-energy part. It also has other

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[6] R. Balescu, Physica **27**, 693 (1961).

parts which often are just ignored but may become important under certain circumstances. Thus, (6.23) gives, in particular, the well-known transport equation of electrons in metals, the Bloch equation of magnetic spins[7] and many other kinetic equations commonly used.

7. SIMPLE EXAMPLES

A few simple examples may be added just for the purpose of illustration.

a. If the velocity $u(t)$ is regarded as a stochastic process, the equation

$$\partial f/\partial t = -u(t)(\partial/\partial x)f \tag{7.1}$$

is a stochastic Liouville equation. Thus the relaxation function is given by

$$\Phi(t) = \left\langle \exp\left\{-\int_0^t u(t')\,dt'\,\frac{\partial}{\partial x}\right\}\right\rangle. \tag{7.2}$$

If, for simplicity, $u(t)$ is assumed to be Gaussian, (7.2) becomes

$$\Phi(t) = \exp\left\{-\langle u^2\rangle \int_0^t d\tau\,(t-\tau)\psi(\tau)\,\frac{\partial^2}{\partial x^2}\right\}, \tag{7.3}$$

where $\psi(\tau)$ is the correlation function of $u(t)$. If the narrowing condition

$$\langle u^2\rangle^{\frac{1}{2}}\tau_c \ll \delta x \tag{7.4}$$

is satisfied, (7.3) is equivalent to the diffusion equation

$$\partial\langle f\rangle/\partial t = D(\partial^2/\partial x^2)\langle f\rangle \tag{7.5}$$

with the diffusion constant

$$D = \langle u^2\rangle \int_0^\infty \psi(\tau)\,d\tau. \tag{7.6}$$

In (7.4) δx is the precision in observing the position of the Brownian particle. One sees easily that the frequency modulation problem (1.1) can be treated also by (7.1), in which x is replaced by the phase angle $\theta(t)$ and u by $\omega(t)$.

b. When a Brownian particle is interacting with a system of scatterers, which is assumed for simplicity to consist of free particles, the Liouville equation is written as

$$\frac{\partial f}{\partial t} = -\left\{\frac{\mathbf{P}}{M}\frac{\partial}{\partial \mathbf{X}} + \sum_i \frac{\mathbf{p}_i}{m}\frac{\partial}{\partial \mathbf{x}_i} - \frac{\partial V}{\partial \mathbf{X}}\frac{\partial}{\partial \mathbf{P}} - \sum_i \frac{\partial V}{\partial \mathbf{x}_i}\frac{\partial}{\partial \mathbf{p}_i}\right\}f. \tag{7.7}$$

In the interaction representation we have the time-dependent Liouville operator,

$$\Omega(t) = \sum_{i=1}^N \int d\mathbf{q}\,\phi(\mathbf{q}) \times \exp\left\{i\mathbf{q}\cdot\left(\mathbf{X} + \frac{\mathbf{P}}{M}t - \mathbf{x}_i - \frac{\mathbf{p}_i}{m}t\right)\right\} \times iq\cdot\left(\frac{\partial}{\partial \mathbf{P}} - \frac{\partial}{\partial \mathbf{p}_i}\right), \tag{7.8}$$

where $\phi(\mathbf{q})$ is the Fourier component of the interaction potential for the wavenumber $\mathbf{q}$. If the scatterers are assumed to be in thermal equilibrium at the temperature $T = 1/k\beta$, $\Omega(t)$ in (7.8) is regarded as a stationary stochastic process. For simplicity we consider here only the Brownian motion of the particle in the momentum space. If the scattering potential is assumed to be weak enough, the narrowing-limit equation (6.23) can be easily calculated. Obviously it becomes a Fokker–Planck equation

$$\frac{\partial}{\partial t}\langle f\rangle = \frac{\partial}{\partial \mathbf{P}}\left\{D\left(\frac{\partial}{\partial \mathbf{P}} + \beta\frac{\mathbf{P}}{M}\right)\right\}\langle f\rangle. \tag{7.9}$$

The calculation is rather straightforward and so is omitted here. The condition to allow (7.9) is

$$(l^3/a^3)\phi^2 \ll (kT/m)(\delta P)^2, \tag{7.10}$$

where ϕ is the scattering potential, l the force range, and a the average distance between the scatterers.

c. The magnetization vector M of a spin system follows an equation of motion of the form[3]

$$\begin{aligned} dM_x/dt &= -\omega M_y + F_x, \\ dM_y/dt &= \omega M_x + F_y, \end{aligned} \tag{7.11}$$

where M_x and M_y are the components in the x–y plane, which is perpendicular to the direction of a constant magnetic field. Its Larmor frequency

$$\omega_0 = \gamma H_0$$

is modulated to

$$\omega = \omega_0 + \nu(t), \qquad \nu(t) = \gamma H'(t) \tag{7.12}$$

by a fluctuating field H'. The Liouville equation is

$$\frac{\partial f}{\partial t} = \left[\omega\left(M_y\frac{\partial}{\partial M_x} - M_x\frac{\partial}{\partial M_y}\right) - F_x\frac{\partial}{\partial M_x} - F_y\frac{\partial}{\partial M_y}\right]f. \tag{7.13}$$

If $\omega(t)$ and $(F_x(t), F_y(t))$ are regarded as stochastic

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[7] F. Bloch, Phys. Rev. **102**, 104 (1056).

processes, Eq. (7.13) can be treated along the general line discussed in Sec. 5. The simplest case is where certain narrowing conditions are satisfied, when we obtain

$$\frac{\partial}{\partial t}\langle f\rangle = \left[\omega_0 L_z + AL_z + B\left(\frac{\partial^2}{\partial M_x^2} + \frac{\partial^2}{\partial M_y^2}\right)\right]\langle f\rangle \quad (7.14)$$

as the diffusion equation in the (M_x–M_y) plane. Here,

$$L_z = M_y\, \partial/M_x - M_x\, \partial/\partial M_y \equiv \partial/\partial\theta$$

is the "angular momentum" operator in the (M_x-M_y) plane. The diffusion constants A and B are given by

$$A = \langle\nu^2\rangle\tau_c = \int_0^\infty \langle\nu(0)\nu(t)\rangle\, dt,$$

$$B = \int_0^\infty \langle F_x(0)F_x(t)\rangle \cos\omega_0 t\cdot dt$$

$$= \int_0^\infty \langle F_y(0)F_y(t)\rangle \cos\omega_0 t\cdot dt. \quad (7.15)$$

Equation (7.14) may be approximated by

$$\frac{\partial}{\partial t}\langle f\rangle = \left[\omega_0\frac{\partial}{\partial\theta} + \left(A + \frac{B}{M}\right)\frac{\partial^2}{\partial\theta^2} + \frac{B}{M}\frac{\partial}{\partial M}M\frac{\partial}{\partial M}\right]\langle f\rangle. \quad (7.16)$$

The "adiabatic modulation" $\nu(t)$ gives rise only to diffusional motion in θ, whereas the "nonadiabatic" perturbation (F_x, F_y) obviously induces additional diffusion in θ and variation in the amplitude M.

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On the Kinetic Theory of Dense Gases

E. G. D. Cohen
Instituut voor Theoretische Fysica, Universiteit van Amsterdam, Amsterdam, Netherlands

(Received 22 June 1962)

A statistical mechanical theory of a dense gas that is not in equilibrium is presented, which is completely analogous to the well known theory of a dense gas in equilibrium. In particular, an expansion of the pair distribution function in powers of the density for a gas not in equilibrium is given, corresponding with that in equilibrium to all orders in the density, that can be represented by the same diagrams. The expansion can be reduced to that derived by Bogolubov, Uhlenbeck, and Choh from a solution of the *B-B-G-K-Y* hierarchy. The conditions for the validity of the expansion are, for an infinite system at not too high density, and after the lapse of some time after $t = 0$: (1) a statistical assumption at $t = 0$; (2) some conditions on the interaction potential; (3) coarse-grained distribution functions. A simple generalization of the Boltzmann equation to general order in the density is included. Also, the connection with a Master equation for a spatially homogeneous system is discussed.

I. INTRODUCTION

A systematic statistical mechanical theory of dense gases has already been developed by Bogolubov, Uhlenbeck and Choh.[1] They consider special solutions of the *B–B–G–K–Y* hierarchy where the second- and all higher-order distribution functions are functionals of the first distribution function as far as their time dependence is concerned. By expanding in powers of the density, these functionals can be determined in successive approximation. Due to the rapidly increasing complexity of the coefficients belonging to increasing powers of the density, the general structure of these coefficients is not clear. The theory is based on two assumptions: (1) For a large class of initial conditions after a time considered long when compared with the duration of a collision τ_0, the second- and higher-order distribution functions become functionals of the first distribution function as far as their time dependence is concerned; (2) an asymptotic or boundary condition is postulated for the form of the above-mentioned functionals.

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[1] N. N. Bogolubov, J. Phys. U.S.S.R. **10**, 265 (1946); *Studies in Statistical Mechanics* I, (North-Holland Publishing Company, Amsterdam 1962, G. E. Uhlenbeck, Higgins Lectures, Princeton University (1954); S. T. Choh, and G. E. Uhlenbeck, "The kinetic theory of dense gases," University of Michigan (1958); E. G. D. Cohen, *Fundamental Problems in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), p. 110.

processes, Eq. (7.13) can be treated along the general line discussed in Sec. 5. The simplest case is where certain narrowing conditions are satisfied, when we obtain

$$\frac{\partial}{\partial t}\langle f\rangle = \left[\omega_0 L_z + AL_z + B\left(\frac{\partial^2}{\partial M_x^2} + \frac{\partial^2}{\partial M_y^2}\right)\right]\langle f\rangle \quad (7.14)$$

as the diffusion equation in the $(M_x\text{–}M_y)$ plane. Here,

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In this paper we present a different derivation of a density expansion of the pair distribution function for a gas not in equilibrium, this derivation employing the same cluster expansions that are used for a gas in equilibrium. Under a number of conditions that are given below, this procedure leads, in a straightforward and simple fashion, to a density expansion of the pair distribution function for a gas not in equilibrium. The first three terms of such an expansion are derived explicitly, while the generalization to the general term is indicated. The first two terms of the expansion, in the spatially homogeneous case, have already been derived by Green[2] using cluster expansions in a different way.

In Sec. III, the correlation with the results of Bogolubov, Uhlenbeck and Choh as well as with those obtained by Lewis[3] on the basis of the hierarchy, is discussed. In Sec. IV, some remarks about the derivation and generalization of a master equation are made.

II. EXPANSION OF THE PAIR DISTRIBUTION FUNCTION

We first introduce the basic D functions in terms of which we want to expand the first as well as the second, (or pair) distribution function. These functions are defined as solutions of the Liouville equations,

$$\frac{\partial D_s(x_1 \cdots x_s;t)}{\partial t} = \{H_s(x_1 \cdots x_s),\, D_s(x_1 \cdots x_s;t)\},$$

or

$$\frac{\partial D_s(x_1 \cdots x_s;t)}{\partial t} + \mathcal{H}_s(x_1 \cdots x_s) D_s(x_1 \cdots x_s;t) = 0, \qquad (s = 1, 2, \cdots, N), \tag{1}$$

and can be written in the form

$$D_s(x_1 \cdots x_s;t) = S_{-t}^{(s)}(x_1 \cdots x_s) D_s(x_1 \cdots x_s;0) \tag{2}$$

for a given initial condition $D_s(x_1 \cdots x_s;0)$.

Here the Hamilton functions $H_s(x_1 \cdots x_s)$ are defined as

$$H_s(x_1 \cdots x_s) = \sum_{i=1}^{s} \frac{\mathbf{p}_i^2}{2m} + \sum\sum_{\substack{i<j\\1}}^{s} \phi(r_{ij}), \tag{3}$$

where $x_i \equiv \mathbf{q}_i, \mathbf{p}_i$ $(i = 1, 2, \cdots, s)$ and the "Hamilton operators" $\mathcal{H}_s(x_1 \cdots x_s)$ as

$$\mathcal{H}_s(x_1 \cdots x_s) = \sum_{i=1}^{s} \frac{\mathbf{p}_i}{m}\cdot\frac{\partial}{\partial \mathbf{q}_i} - \sum\sum_{\substack{i<j\\1}}^{s} \theta_{ij}, \tag{4a}$$

where

$$\theta_{ij} = \frac{\partial \phi(r_{ij})}{\partial \mathbf{q}_i}\cdot\frac{\partial}{\partial \mathbf{p}_i} + \frac{\partial \phi(r_{ij})}{\partial \mathbf{q}_j}\cdot\frac{\partial}{\partial \mathbf{p}_j}, \tag{4b}$$

and the streaming operators by

$$S_{-t}^{(s)}(x_1 \cdots x_s) = \exp\,[-t\mathcal{H}_s(x_1 \cdots x_s)]. \tag{5}$$

The solutions of Eq. (1) are normalized such that

$$\int \cdots \int D_{N-s}(x_1 \cdots x_{N-s};t)\, dx_1 \cdots dx_{N-s} = \frac{1}{V^s}, \tag{6}$$

where V is the volume of the system. The D functions take the place of the Boltzmann factors in equilibrium. They are, however, normalized in a different way. To the D functions, we introduce U functions in the same way as in equilibrium through the relations

$$D_s(x_1 \cdots x_s;t) = \sum_{\text{div}} \prod_{l} U_l(x_1 \cdots x_l;t), \tag{7}$$

so that

$$U_s(x_1 \cdots x_s;t) = \sum_{\text{div}} (-1)^{k-1}(k-1)! \prod_{l} D_l(x_1 \cdots x_l;t). \tag{8}$$

In Eq. (7), the D functions are written as a sum of products of U functions by dividing the group of molecules in all possible ways into subgroups and by taking the corresponding product of U-functions for each division. In Eq. (8) the same rule applies; a coefficient $(-1)^{k-1}(k-1)!$ must be added, however, to every division into k groups.

After the introduction of the basic D and U functions for isolated groups of particles, we now define the distribution (F) functions, for groups of particles in the system of N particles:

$$F_s(x_1 \cdots x_s;t) = V^s \int \cdots \int D_N(x_1 \cdots x_N;t)\, dx_{s+1} \cdots dx_N. \tag{9}$$

To the F functions we introduce G functions through the relations

$$F_s(x_1 \cdots x_s;t) = \sum_{\text{div}} \prod_{l} G_l(x_1 \cdots x_l;t), \tag{10}$$

so that

$$G_s(x_1 \cdots x_s;t) = \sum_{\text{div}} (-1)^{k-1}(k-1)! \prod_{l} F_l(x_1 \cdots x_l;t). \tag{11}$$

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[2] M. S. Green, J. Chem. Phys. **25**, 836 (1956); Physica **24**, 393 (1958).

[3] R. J. Lewis, J. Math. Phys. **2**, 222 (1961).

We now derive an expansion of the F functions in terms of the D functions, and in order to do this, we first expand the G functions in terms of the U functions. This leads, for an *infinite system* (N, $V \to \infty$, $n = N/V =$ constant), to[4]

$$n^s G_s(x_1 \cdots x_s; t) = \sum_{l=s}^{\infty} b_l(x_1 \cdots x_s; t) n^s, \tag{12}$$

where

$$b_l(x_1 \cdots x_s; t) = \frac{1}{(l-s)!}$$
$$= \int \cdots \int dx_{s+1} \cdots dx_l \, U_l(x_1 \cdots x_l; t), \tag{13}$$

so that in particular we have for $s = 1$,

$$\begin{aligned} nF_1(x_1; t) = nG_1(x_1; t) &= U_1(x_1; t)n \\ &+ \int dx_2 \, U_2(x_1x_2; t)n^2 \\ &+ \frac{1}{2!}\int dx_2 \int dx_3 \, U_3(x_1x_2x_3; t)n^3 + \cdots, \end{aligned} \tag{14}$$

and for $s = 2$,

$$\begin{aligned} n^2G_2(x_1x_2; t) &= U_2(x_1x_2; t)n^2 \\ &+ \int dx_3 \, U_3(x_1x_2x_3; t)n^3 + \cdots. \end{aligned} \tag{15}$$

These expansions are analogous to the activity expansions in the equilibrium case.

We now want to derive from these expansions, in terms of D_s functions ($s = 1, 2, \cdots$), an expansion for the first and second distribution function in terms of D_1 functions alone. In order to do this, we first transform the U functions occurring in Eqs. (14) and (15) from time t to time $t = 0$. Then we make a statistical assumption about the D functions at $t = 0$. This assumption, together with two others, enables us to express F_1 and F_2 in terms of D_1 functions. Elimination of the D_1 functions between F_2 and F_1 will lead ultimately to an expansion of the pair distribution function F_2 at time t in terms of the first distribution function F_1 at time t.

Transforming then, with Eqs. (8) and (2), the U functions occurring in the right-hand side of Eq. (14) and (15) to $t = 0$, one obtains

$$U_1(x_1; t) = S^{(1)}_{-t}(x_1)D_1(x_1; 0);$$
$$\begin{aligned} U_2(x_1x_2; t) &= S^{(2)}_{-t}(x_1x_2)D_2(x_1x_2; 0) \\ &- S^{(1)}_{-t}(x_1)S^{(1)}_{-t}(x_2)D_1(x_1; 0)D_1(x_2; 0); \end{aligned}$$

$$\begin{aligned} U_3(x_1x_2x_3; t) &= S^{(3)}_{-t}(x_1x_2x_3)D_3(x_1x_2x_3; 0) \\ &- S^{(2)}_{-t}(x_1x_2)S^{(1)}_{-t}(x_3)D_2(x_1x_2; 0)D_1(x_3; 0) \\ &- S^{(2)}_{-t}(x_1x_3)S^{(1)}_{-t}(x_2)D_2(x_1x_3; 0)D_1(x_2; 0) \\ &- S^{(2)}_{-t}(x_2x_3)S^{(1)}_{-t}(x_1)D_2(x_2x_3; 0)D_1(x_1; 0) \\ &+ 2S^{(1)}_{-t}(x_1)S^{(1)}_{-t}(x_2)S^{(1)}_{-t}(x_3) \\ &\times D_1(x_1; 0)D_1(x_2; 0)D_1(x_3; 0). \end{aligned} \tag{16}$$

Assuming:

(1) Repulsive intermolecular potential of finite range σ;
(2) At $t = 0$, the $D_s(x_1 \cdots x_s; 0)$'s show a product property whenever the group of molecules $1 \cdots s$ can be divided into two or more groups such that the distance between at least two of them is larger than a correlation length of the order of σ;
(3) Distribution functions are considered in a coarse-grained sense;

then for $t \gg \tau_0$, (the duration of a collision), one can replace Eq. (16) by

$$\bar{U}_1(x_1; t) = S^{(1)}_{-t}(x_1)D_1(x_1; 0),$$
$$\begin{aligned} \bar{U}_2(x_1x_2; t) &= [S^{(2)}_{-t}(x_1x_2) - S^{(1)}_{-t}(x_1)S^{(1)}_{-t}(x_2)] \\ &\times D_1(x_1; 0)D_1(x_2; 0), \end{aligned}$$
$$\begin{aligned} \bar{U}_3(x_1x_2x_3; t) &= [S^{(3)}_{-t}(x_1x_2x_3) - S^{(2)}_{-t}(x_1x_2)S^{(1)}_{-t}(x_3) \\ &- S^{(2)}_{-t}(x_1x_3)S^{(1)}_{-t}(x_2) - S^{(2)}_{-t}(x_2x_3)S^{(1)}_{-t}(x_1) \\ &+ 2S^{(1)}_{-t}(x_1)S^{(1)}_{-t}(x_2)S^{(1)}_{-t}(x_3)] \\ &\times D_1(x_1; 0)D_1(x_2; 0)D_1(x_3; 0). \end{aligned} \tag{17}$$

Substituting Eq. (17) in Eqs. (14) and (15), and transforming back again from $t = 0$ to t, one obtains the following expansions for F_1 and G_2 in terms of $D_1(t)$:

$$\begin{aligned} nF_1(x_1; t) &= \bar{U}_1(x_1; t)n + \int dx_2 \, \bar{U}_2(x_1x_2; t)n^2 \\ &+ \frac{1}{2!}\int dx_2 \int dx_3 \, \bar{U}_3(x_1x_2x_3; t)n^3 + \cdots, \end{aligned} \tag{18}$$

$$\begin{aligned} n^2G_2(x_1x_2; t) &= \bar{U}_2(x_1x_2; t)n^2 \\ &+ \int dx_3 \, \bar{U}_3(x_1x_2x_3; t)n^3 + \cdots, \end{aligned} \tag{19}$$

where

$$\bar{U}_1(x_1; t) = U_1(x_1; t) = D_1(x_1; t),$$
$$\bar{U}_2(x_1x_2; t) = [\mathcal{S}^{(2)}_t(x_1x_2) - 1]D_1(x_1; t)D_1(x_2; t), \tag{20}$$
$$\begin{aligned} \bar{U}_3(x_1x_2x_3; t) &= [\mathcal{S}^{(3)}_t(x_1x_2x_3) - \mathcal{S}^{(2)}_t(x_1x_2) \\ &- \mathcal{S}^{(2)}_t(x_1x_3) - \mathcal{S}^{(2)}_t(x_2x_3) + 2] \\ &\times D_1(x_1; t)D_1(x_2; t)D_1(x_3; t), \end{aligned}$$

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[4] E. G. D. Cohen, Physica **28**, 1025, 1045, 1060 (1962).

with

$$\mathcal{S}_t^{(s)}(x_1 \cdots x_s) = S_{-t}^{(s)}(x_1 \cdots x_s) \cdot \prod_{i=1}^{s} S_t^{(1)}(x_i). \tag{21}$$

In order to obtain an expansion of F_2 in terms of F_1, we convert the D_1 expansion (19) of G_2 into an F_1 expansion by eliminating $D_1(x;\,t)$ between Eqs. (18) and (19). This elimination procedure corresponds to the elimination of the activity z between the z expansions of the corresponding equations in equilibrium viz. the z expansions of the density n and the pair correlation function $G_2(r) = g(r)$ in equilibrium which results in a density expansion of $g(r)$. For the first few terms, this can be done by solving Eq. (18) for $D_1(x_1;\,t)$ in successive approximation, leading to

$$D_1(x_1;\,t) = F_1(x_1;\,t) - n \int dx_2$$
$$\times\, [\mathcal{S}_t^{(2)}(x_1x_2) - 1]F_1(x_1;\,t)F_1(x_2;\,t) + \cdots, \tag{22}$$

so that for G_2, one obtains the expansion

$$n^2G_2(x_1x_2;\,t) = n^2[\mathcal{S}_t^{(2)}(x_1x_2) - 1]F_1(x_1;\,t)F_1(x_2;\,t)$$
$$+\, n^3 \int dx_3\, [\mathcal{S}_t^{(3)}(x_1x_2x_3) - \mathcal{S}_t^{(2)}(x_1x_2)\cdot\mathcal{S}_t^{(2)}(x_1x_3)$$
$$- \mathcal{S}_t^{(2)}(x_1x_2)\cdot\mathcal{S}_t^{(2)}(x_2x_3) + \mathcal{S}_t^{(2)}(x_1x_2)]$$
$$\times\, F_1(x_1;\,t)F_1(x_2;\,t)F_1(x_3;\,t) + \cdots. \tag{23}$$

Clearly the parameter n is used throughout for ordering. This implies that in addition to the assumptions listed above, it is always assumed that the density is sufficiently low so that the evolution of the system proceeds in first approximation through binary collisions!

The general term in the F_1 expansion of G_2 can be obtained in the following way. We see that the U functions can be written in the form of an operator $\mathcal{U}_l(x_1 \cdots x_l;\, t)$ operating on a product of D_1 functions:

$$U_l(x_1 \cdots x_l;\,t) = \mathcal{U}_l(x_1 \cdots x_l;\,t) \prod_{i=1}^{l} D_1(x_i;\,t). \tag{24}$$

We remark that the $\mathcal{U}$ operators are related to the $\mathcal{S}$ operators in the same way as the U functions are related to the D functions.

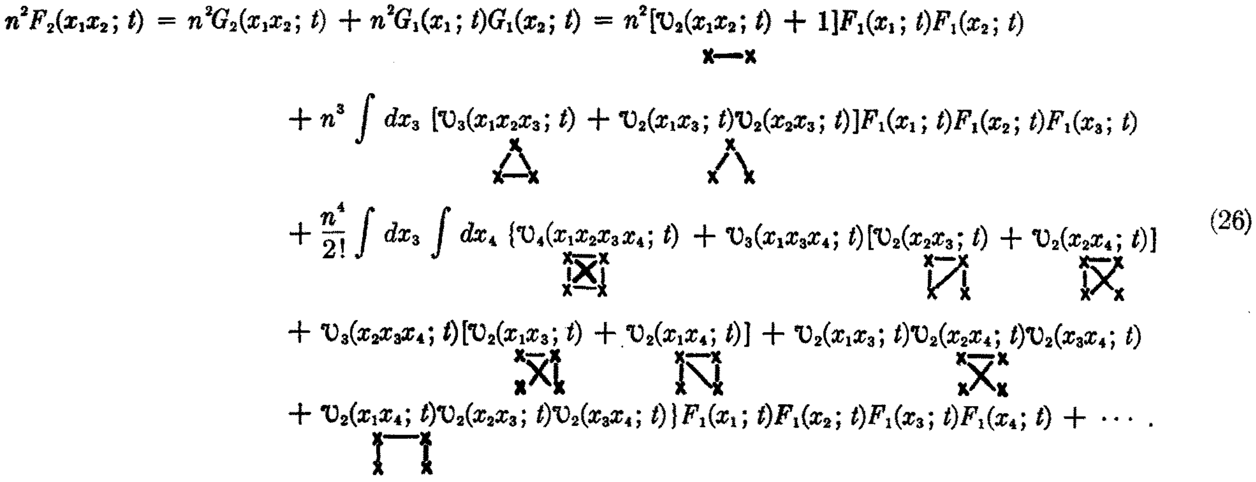
We now introduce to the $\mathcal{U}$ operators a new set of operators, $\mathcal{V}$ operators that are related to the $\mathcal{U}$ operators in the same way as the Husimi functions are related to the U functions in the theory of gases in equilibrium:

$$\mathcal{U}_2(x_1x_2;\,t) = \mathcal{V}_2(x_1x_2;\,t); \tag{25}$$

$$\mathcal{U}_3(x_1x_2x_3;\,t) = \mathcal{V}_3(x_1x_2x_3;\,t) + \mathcal{V}_2(x_1x_2;\,t)\mathcal{V}_2(x_1x_3;\,t) + \mathcal{V}_2(x_1x_2;\,t)\mathcal{V}_2(x_2x_3;\,t) + \mathcal{V}_2(x_1x_3;\,t)\mathcal{V}_2(x_2x_3;\,t).$$

In (25) we have represented the various $\mathcal{U}$ and $\mathcal{V}$ operators by graphs; the $\mathcal{U}$ operators by graphs consisting of lines connecting closed points, the $\mathcal{V}$ operators by graphs consisting of lines connecting open points. The $\mathcal{V}$-operator expansion can best be defined in terms of its graphical representation. The $\mathcal{V}$ operators are defined then by writing the $\mathcal{U}$ operators as a sum of products of $\mathcal{V}$ operators, which when the $\mathcal{U}_l$ operator is represented by l points, then by connecting these l points in all possible ways by lines, triangles, etc., a connected graph results.

A difference with the equilibrium case should be noted in that unlike the Husimi functions, the $\mathcal{V}$ operators do not commute. Therefore, a standard order should always be kept in which the $\mathcal{V}$ operator containing the lowest-labeled molecule precedes those with higher-labeled molecules. For a discussion of these $\mathcal{V}$ operators, the reader is refered elsewhere.[4] Introduction of the $\mathcal{V}$ operators with (25) and (24) into the expansion (18) and (19), leads to an expansion of F_1 and G_2 with $\mathcal{V}$ operators, the various terms of which can be represented by the same graphs as used in (25). The elimination of the D_1 functions between (18) and (19) can now be effected by restricting oneself in the $\mathcal{V}$ expansion of G_2 to a subset of all graphs (viz. the 1, 2-irreducible $\mathcal{V}$ graphs[4]) and then by replacing the D_1 functions, on which the corresponding $\mathcal{V}$ operators act, by F_1 functions. Then using (10), the following expansion is obtained for the pair distribution function in terms of the first distribution function:



$$
\begin{aligned}
n^2F_2(x_1x_2;t) &= n^2G_2(x_1x_2;t) + n^2G_1(x_1;t)G_1(x_2;t) = n^2[\mathcal{V}_2(x_1x_2;t)+1]F_1(x_1;t)F_1(x_2;t)\\
&\quad + n^3\int dx_3\,[\mathcal{V}_3(x_1x_2x_3;t)+\mathcal{V}_2(x_1x_3;t)\mathcal{V}_2(x_2x_3;t)]F_1(x_1;t)F_1(x_2;t)F_1(x_3;t)\\
&\quad + \frac{n^4}{2!}\int dx_3\int dx_4\,\{\mathcal{V}_4(x_1x_2x_3x_4;t)+\mathcal{V}_3(x_1x_3x_4;t)[\mathcal{V}_2(x_2x_3;t)+\mathcal{V}_2(x_2x_4;t)]\\
&\quad + \mathcal{V}_3(x_2x_3x_4;t)[\mathcal{V}_2(x_1x_3;t)+\mathcal{V}_2(x_1x_4;t)]+\mathcal{V}_2(x_1x_3;t)\mathcal{V}_2(x_2x_4;t)\mathcal{V}_2(x_3x_4;t)\\
&\quad + \mathcal{V}_2(x_1x_4;t)\mathcal{V}_2(x_2x_3;t)\mathcal{V}_2(x_3x_4;t)\}F_1(x_1;t)F_1(x_2;t)F_1(x_3;t)F_1(x_4;t)+\cdots.
\end{aligned}
\tag{26}
$$

Here the 1, 2-irreducible graphs are written underneath the various terms. The crosses indicate that they act on F_1 functions instead of on D_1 functions. If one now makes the additional assumption that the interaction potential is such that repeated collisions between the same particles can be neglected, if $t \to \infty$, then the $\mathcal{S}_t^{(s)}$ operators can be replaced by the time-independent $\mathcal{S}^{(s)}$ operators:

$$\mathcal{S}^{(s)}(x_1\cdots x_s) = \lim_{t\to\infty}\mathcal{S}_t^{(s)}(x_1\cdots x_s), \tag{27}$$

and the $\mathcal{V}$ operators occurring in (26) become independent of the time t. Then the whole time dependence of F_2 is through F_1 alone, and F_2 has become a functional $F_2(x_1x_2 \mid F_1(;t))$ of F_1 as far as time dependence is concerned.

Using Eqs. (27), (26), (25), (24), and (20), the following expansion is obtained for the functional $F_2(x_1x_2 \mid F_1(;t))$ in powers of the density:

$$
\begin{aligned}
F_2(x_1x_2 \mid F_1) &= F_2^{(0)}(x_1x_2 \mid F_1)\\
&\quad + nF_2^{(1)}(x_1x_2 \mid F_1) + n^2F_2^{(2)}(x_1x_2 \mid F_1)+\cdots,
\end{aligned}
\tag{28}
$$

where[4]

$$F_2^{(0)}(x_1x_2 \mid F_1) = \mathcal{S}^{(2)}(x_1x_2)F_1(x_1;t)F_1(x_2;t);$$

$$
\begin{aligned}
F_2^{(1)}(x_1x_2 \mid F_1) &= \int dx_3\,[\mathcal{S}^{(3)}(x_1x_2x_3)\\
&\quad - \mathcal{S}^{(2)}(x_1x_2)\mathcal{S}^{(2)}(x_1x_3) - \mathcal{S}^{(2)}(x_1x_2)\mathcal{S}^{(2)}(x_2x_3)\\
&\quad + \mathcal{S}^{(2)}(x_1x_2)]F_1(x_1;t)F_1(x_2;t)F_1(x_3;t);
\end{aligned}
\tag{29}
$$

$$
\begin{aligned}
F_2^{(2)}(x_1x_2 \mid F_1) &= \frac{1}{2!}\int dx_3\int dx_4\,(\mathcal{S}^{(4)}(x_1x_2x_3x_4) - \mathcal{S}^{(3)}(x_1x_2x_3)[\mathcal{S}^{(2)}(x_1x_4)+\mathcal{S}^{(2)}(x_2x_4)+\mathcal{S}^{(2)}(x_3x_4)+2]\\
&\quad - \mathcal{S}^{(3)}(x_1x_2x_4)[\mathcal{S}^{(2)}(x_1x_3)+\mathcal{S}^{(2)}(x_2x_3)+\mathcal{S}^{(2)}(x_3x_4)+2] - \mathcal{S}^{(2)}(x_1x_2)\{[\mathcal{S}^{(3)}(x_1x_3x_4) - \mathcal{S}^{(2)}(x_1x_3)\mathcal{S}^{(2)}(x_1x_4)\\
&\quad - \mathcal{S}^{(2)}(x_1x_3)\mathcal{S}^{(2)}(x_3x_4)] + [\mathcal{S}^{(3)}(x_2x_3x_4) - \mathcal{S}^{(2)}(x_2x_3)\mathcal{S}^{(2)}(x_2x_4) - \mathcal{S}^{(2)}(x_2x_3)\mathcal{S}^{(2)}(x_3x_4)] - \mathcal{S}^{(2)}(x_1x_3)\mathcal{S}^{(2)}(x_1x_4)\\
&\quad - \mathcal{S}^{(2)}(x_1x_3)\mathcal{S}^{(2)}(x_2x_4) - \mathcal{S}^{(2)}(x_2x_3)\mathcal{S}^{(2)}(x_2x_4) - \mathcal{S}^{(2)}(x_1x_4)\mathcal{S}^{(2)}(x_2x_3) - \mathcal{S}^{(2)}(x_1x_4)\mathcal{S}^{(2)}(x_3x_4)\\
&\quad - \mathcal{S}^{(2)}(x_2x_4)\mathcal{S}^{(2)}(x_3x_4) + \{2\mathcal{S}^{(2)}(x_1x_3) + 2\mathcal{S}^{(2)}(x_2x_3) + 2\mathcal{S}^{(2)}(x_1x_4) + 2\mathcal{S}^{(2)}(x_2x_4)\\
&\quad + \mathcal{S}^{(2)}(x_3x_4)\} + 2\mathcal{S}^{(2)}(x_1x_2))F_1(x_1;t)F_1(x_2;t)F_1(x_3;t)F_1(x_4;t).
\end{aligned}
$$

This expansion for $F_2(\ \mid F_1)$ when introduced for $F_2(x_1x_2;t)$ into the right-hand side of the first hierarchy equation for $F_1(x_1;t)$, leads to the following equation for F_1:

$$
\begin{aligned}
&\frac{\partial F_1(x_1;t)}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\frac{\partial F_1(x_1;t)}{\partial \mathbf{q}_1}\\
&= n\int dx_2\,\theta_{12}[F_2^{(0)}(x_1x_2 \mid F_1)\\
&\quad + nF_2^{(1)}(x_1x_2 \mid F_1) + n^2F_2^{(2)}(x_1x_2 \mid F_1)+\cdots].
\end{aligned}
\tag{30}
$$

This equation, with (29), *constitutes a generalization of the Boltzmann equation to general order in the density, where the contributions of n particle collisions are given by the* $F_2^{(n-2)}(x_1x_2 \mid F_1)$, *which is characterized by all* 1,2-*irreducible graphs of n points.*

III. DISCUSSION

In the preceding section, an expansion (26) for the pair distribution was derived which can be established under the following conditions: (a)

TABLE I

Equilibrium	Nonequilibrium
β	t
$H_s(x_1 \cdots x_s)$	$\mathcal{H}_s(x_1 \cdots x_s)$
$\exp[-\beta H_s(x_1 \cdots x_s)]$	$S_{-t}^{(s)}(x_1 \cdots x_s)$
$\exp[-\beta \Phi_s(\mathbf{q}_1 \cdots \mathbf{q}_s)]$	$\mathcal{S}_t^{(s)}(x_1 \cdots x_s)$
n	$nF_1(x_1; t)$

density low enough so that the time development of the system proceeds in first approximation through binary collisions; (b) $t \gg \tau_0$; (c) infinite system; (d) statistical assumption at $t = 0$; (e) some conditions on the intermolecular potential a.o. repulsive; (f) coarse-grained distribution functions.

We would now like to discuss the relation of the expansions (26) and (29) with the results obtained in a different manner by Bogolubov, Uhlenbeck and Choh[1] and by Lewis.[3]

Bogolubov, Uhlenbeck and Choh also obtain an expansion of the pair distribution as a functional of the first distribution function from a solution of the *B-B-G-K-Y* hierarchy. It can be shown that their expansion is identical with our expansion (29). This can be demonstrated explicitly for the first few terms of the expansions by transforming their expressions for $F_2^{(0)}(x_1x_2 \mid F_1)$, $F_2^{(1)}(x_1x_2 \mid F_1)$, $F_2^{(2)}(x_1x_2 \mid F_1)$ into those presented here. A proof of the identity of the general terms in the expansions cannot be given in this way because the general term in the expansion for $F_2(x_1x_2 \mid F_1)$ cannot be written explicitly. Therefore one must proceed in a different fashion for which we refer the reader elsewhere.[4]

Lewis has obtained from the *B-B-G-K-Y* hierarchy, a density expansion of the fine-grained distribution functions F_s at time t in terms of their values at time $t = 0$.

Under the same conditions as listed above, especially with condition (d), these expansions, and in particular those of the first and second distribution functions, can be expressed in terms of the $F_1(x_1; 0)$. Elimination of $F_1(x_1; 0)$ between the expansions of $F_1(x_1; t)$ and $F_2(x_1x_2; t)$ in terms of $F_1(x_1; 0)$ leads again to our expansion (26).

We would like to make a final remark concerning the close correspondence between the cluster expansions used in Sec. II for a gas not in equilibrium and those well known from the theory of gases in equilibrium. In fact, one can write down the basic nonequilibrium expansion (26) for F_2 immediately from the known expansion of the $g(r)$ function in equilibrium:

$$n^2 g(r_{12}) = e^{-\beta\Phi_2(\mathbf{q}_1\mathbf{q}_2)} n^2 + \int d\mathbf{q}_3 \, [e^{-\beta\Phi_3(\mathbf{q}_1\mathbf{q}_2\mathbf{q}_3)} - e^{-\beta[\Phi_2(\mathbf{q}_1\mathbf{q}_2)+\Phi_2(\mathbf{q}_1\mathbf{q}_3)]} - e^{-\beta[\Phi_2(\mathbf{q}_1\mathbf{q}_2)+\Phi_2(\mathbf{q}_2\mathbf{q}_3)]} + e^{-\beta\Phi_2(\mathbf{q}_1\mathbf{q}_2)}] n^3 + \cdots, \tag{31}$$

where

$$\Phi_3(\mathbf{q}_1\mathbf{q}_2\mathbf{q}_3) = \phi(r_{12}) + \phi(r_{13}) + \phi(r_{23}), \tag{32a}$$

and

$$\Phi_2(\mathbf{q}_1\mathbf{q}_2) = \phi(r_{12}), \tag{32b}$$

if Table I is used.[4] Similarly the nonequilibrium expansions (18) and (19) for $nF_1(x_1; t)$ and $n^2F_2(x_1x_2; t)$ in terms of D_1 functions, reduce to the activity expansions for n and $n^2g(r)$ in equilibrium respectively by using the Table II.

TABLE II

Equilibrium	Nonequilibrium
$z^s \exp[-\beta\Phi_s(\mathbf{q}_1 \cdots \mathbf{q}_s)]$	$n^s D_s(x_1 \cdots x_s; t)$
z	$nD_1(x_1; t)$

IV. MASTER EQUATION IN SPATIALLY HOMOGENEOUS CASE

Several attempts have been made[5,6] to derive and generalize the Boltzmann equation from a Master equation. The central problem is to derive a Master equation from the Liouville equation in a systematic way, taking into account, successively, the effect of collisions between groups of an increasing number of molecules; binary collisions, ternary collisions, etc. Brout[6] has obtained a Master equation including only the effect of binary collisions, partly by using the classical analogue of the techniques which Van Hove employed in a derivation of a master equation for a quantum mechanical system.[7] By using similar cluster expansions as in Sec. II, one can obtain a generalization of the master equation derived by Brout, to general order in the density:

$$\partial W_N(\mathbf{p}_1 \cdots \mathbf{p}_N; t)/\partial t = \Omega_N W_N(\mathbf{p}_1 \cdots \mathbf{p}_N; t). \tag{33}$$

Here,

$$W_N(\mathbf{p}_1 \cdots \mathbf{p}_N; t) = \int d\mathbf{q}_1 \cdots \int d\mathbf{q}_N \, D_N(x_1 \cdots x_N; t)$$

is the over-all, coordinates-integrated N-particle distribution function. The operator Ω_N is given by

$$\Omega_N = \sum_{(1\,2)} \Omega_2(\mathbf{p}_1\mathbf{p}_2) + \sum_{(1\,2\,3)} \Omega_3(\mathbf{p}_1\mathbf{p}_2\mathbf{p}_3) + \cdots, \tag{34}$$

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[5] M. Kac, *Lectures in Applied Mathematics* I (Interscience Publishers, Inc., New York, 1959), p. 109.

[6] R. Brout, Physica **22**, 509 (1956).

[7] L. Van Hove, Physica **21**, 517 (1955).

where the summations are carried out over all pairs of molecules (1 2), all triples of molecules (1 2 3), etc. Furthermore,

$$\Omega_l(\mathbf{p}_1 \cdots \mathbf{p}_l) = \int \cdots \int \left[\frac{d}{dt} V_l(x_1 \cdots x_l;\, t)\right]_{t\to\infty} d\mathbf{q}_2 \cdots d\mathbf{q}_l / V^{l-1}, \tag{35}$$

so that

$$\Omega_2(\mathbf{p}_1\mathbf{p}_2) = \frac{1}{V} \int d\mathbf{q}_2\ \theta_{12} S_{-\infty}^{(2)}(x_1x_2) \tag{36a}$$

contains the contribution of binary collisions, and

$$\begin{aligned}\Omega_3(\mathbf{p}_1\mathbf{p}_2\mathbf{p}_3) = \frac{1}{V^2} \int d\mathbf{q}_2 \int d\mathbf{q}_3 \\ \times [(\theta_{12} + \theta_{13} + \theta_{23}) S_{-\infty}^{(3)}(x_1x_2x_3) \\ - \theta_{12} S_{-\infty}^{(2)}(x_1x_2) S_{-\infty}^{(2)}(x_1x_3) \\ - S_{-\infty}^{(2)}(x_1x_2)\, \theta_{13} S_{-\infty}^{(2)}(x_1x_3) \\ - \theta_{12} S_{-\infty}^{(2)}(x_1x_2) S_{-\infty}^{(2)}(x_2x_3) \\ - S_{-\infty}^{(2)}(x_1x_2)\, \theta_{23} S_{-\infty}^{(2)}(x_2x_3) \\ - \theta_{13} S_{-\infty}^{(2)}(x_1x_3) S_{-\infty}^{(2)}(x_2x_3) \\ - S_{-\infty}^{(2)}(x_1x_3)\, \theta_{23} S_{-\infty}^{(2)}\ x_2x_3) \\ + \theta_{12} S_{-\infty}^{(2)}(x_1x_2) + \theta_{13} S_{-\infty}^{(2)}(x_1x_3) \\ + \theta_{23} S_{-\infty}^{(2)}(x_2x_3)]\end{aligned} \tag{36a}$$

contains the contributions of triple collisions, etc.

Conditions under which the Eq. (33) can be established are: (a) density low enough that the time development of the gas proceeds in first approximation through binary collisions, (b) $t \gg \tau_0$; (c) a very large system; (d) a strong assumption of spatial homogeneity; (e) some conditions on the intermolecular potential; (f) coarse-grained distribution function.

By integrating Eq. (33) over all momenta but one, the generalized Boltzmann equation (30) for the special case of a spatially homogeneous system can be obtained if, in addition to the above mentioned assumptions, a factorization of all distribution functions into single-particle distribution functions is assumed.

A Master equation of the form (33) does not seem to exist for a spatially inhomogeneous system.

It is interesting to note that the approach sketched in this section corresponds to a well-known procedure followed in equilibrium statistical mechanics: the expansion of the configurational partition function in powers of the density. Using Table I and the correspondence of $Q_N(\beta)$ and $W_N(\mathbf{p}_1 \cdots \mathbf{p}_N;\, t)$, one has, for the equation corresponding to (33), in the case of equilibrium [one must replace $S_{-\infty}^{(s)}$ by $\mathcal{S}_t^{(s)}$ in (33), and drop $t \to \infty$ in (35)],

$$\partial Q_N(\beta)/\partial\beta = -E_N(\beta) Q_N(\beta), \tag{37}$$

where the thermodynamic energy $E_N(\beta)$ can be written in the form

$$E_N(\beta) = \sum_{(1\,2)} E_2(12;\, \beta) + \sum_{(1\,2\,3)} E_3(123;\, \beta) + \cdots,$$

with

$$E_l(12 \cdots l;\, \beta) = \int \cdots \int \left[\frac{d}{d\beta} V_l(\mathbf{q}_1 \cdots \mathbf{q}_l;\, \beta)\right] d\mathbf{q}_2 \cdots d\mathbf{q}_l / V^{l-1},$$

where $V_l(\mathbf{q}_1 \cdots \mathbf{q}_l)$ is the Husimi function for l particles.

It is interesting to note that the close analogy between equilibrium and nonequilibrium theories which has been established here on the basis of cluster expansions, can also be discussed on the basis of the *B–B–G–K–Y* hierarchy. One must use in equilibrium, however, a β hierarchy that is derived from the Bloch equation, instead of the usual equilibrium hierarchy derived from the Liouville equation.

This close analogy between equilibrium and nonequilibrium theories is ultimately attributable to (1) the analogy between the Bloch equation in equilibrium and the Liouville equation in nonequilibrium, and (2) to the fact that at infinite temperature ($\beta = 0$) in equilibrium and at the initial instant of time ($t = 0$) in nonequilibrium, the distribution functions have, in both cases, a product property[3]; the physical quantities that characterize the system in equilibrium as well as the nonequilibrium system, are the same viz. the range of the intermolecular forces and the average distance between the molecules.

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Thermal Fluctuations in Nonlinear Systems

N. G. VAN KAMPEN
Instituut voor Theoretische Fysica der Rijksuniversiteit, Utrecht, Netherlands
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The simple physical assumptions on which the familiar linear fluctuation theory is based do not carry over to the nonlinear case. In order to treat this case, one has to start from the master equation, and expand it in reciprocal powers of a suitable parameter (roughly speaking, the size of the system). The successive powers yield first the phenomenological law, next the linear fluctuation theory, and subsequently the influence of nonlinearity in successive approximations. The coefficients in the expansion are connected with each other by relations of the same type as the fluctuation-dissipation theorem in the linear theory. Whether or not these relations are sufficient to uniquely determine the coefficients from phenomenological data is not known at present.

I. FORMULATION OF THE PROBLEM

CONSIDER the simple electric circuit[1] of Fig. 1. The Ohmic resistance R is in contact with a heat bath T. The macroscopic, phenomenological law for the potential difference V is, of course,

$$dV/dt = -V/RC. \tag{1}$$

Since this phenomenological equation is linear, we shall call this the *linear case*. Fluctuations are not taken into account by the phenomenological law; the symbol V has meaning only if fluctuations are neglected or averaged out.

In order to describe the fluctuations about this average behavior, one adds a "random electromotive force" $\kappa(t)$,

$$dV/dt = -V/RC + \kappa(t). \tag{2}$$

(Langevin equation). $\kappa(t)$ is due to the thermal fluctuations in the resistor and is pictured as a very rapidly and irregularly varying function of time. Such functions can only be described by their stochastic properties. For $\kappa(t)$ one *assumes* the properties

$$\langle\kappa(t)\rangle = 0 \quad \text{and} \quad \langle\kappa(t)\kappa(t')\rangle = c\,\delta(t - t'). \tag{3}$$

Here $\langle\ \rangle$ denotes the average over a time interval that is long compared to the fluctuations in $\kappa(t)$ but short compared to the macroscopic RC time of the circuit. More conveniently one may think of it as the average over an ensemble of circuits. c is a constant, independent of t or V. The delta function is actually a peaked function, whose width is the auto-correlation time of $\kappa(t)$.

From Eqs. (2) and (3) follows immediately for

$$(d/dt)\langle V\rangle = -(1/RC)\langle V\rangle,$$

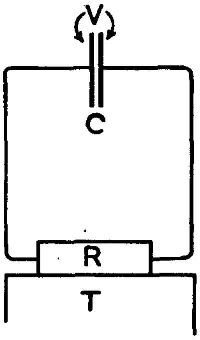

FIG. 1.

the average value of V, which is identified with the phenomenological equation (1). The solution is, of course,

$$\langle V\rangle_t = \langle V\rangle_0 e^{-t/RC}.$$

One also finds from Eqs. (2) and (3), by means of the usual calculation of Uhlenbeck and Ornstein,[2]

$$\langle V^2\rangle_t = \langle V^2\rangle_0 e^{-2t/RC} + \tfrac{1}{2}cRC(1 - e^{-2t/RC}).$$

Since the equilibrium value of $\langle V^2\rangle$ is known to be kT/C one must have

$$c = 2kT/RC^2. \tag{4}$$

The fact that the coefficient c (which only shows up in the fluctuations) is fully determined by the macroscopic properties of the system, is the foundation of the Einstein relation for Brownian movement, the Nyquist relation, and the fluctuation-dissipation theorem (see Sec. III).

Now suppose the linear resistance is replaced by a device with a *nonlinear* $I - V$ characteristic. Then the phenomenological law has the form

$$dV/dt = (1/C)g(V). \tag{5}$$

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[1] First studied in connection with nonlinear fluctuations by D. K. C. MacDonald, Phil. Mag. **45**, 63 (1954). See also D. Polder, Phil. Mag. **45**, 69 (1954) and reference 3.

[2] G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 823 (1930). [*Selected Papers on Noise and Stochastic Processes*, edited by N. Wax, (Dover Publications, Inc., New York, 1954).]

The function $g(V)$ characterizes the properties of the resistor and will be called the *response function.* Suppose one now tries again to take fluctuations into account by adding a random emf,

$$dV/dt = -(1/C)g(V) + \kappa(t), \qquad (6)$$

where $\kappa(t)$ has again the properties (3). One then finds on averaging

$$(d/dt)\langle V\rangle = -(1/C)\langle g(V)\rangle. \qquad (7)$$

This can *not* be identified with Eq. (5), because $\langle g(V)\rangle \neq g(\langle V\rangle)$.

One might try to adjust this by using a slightly different g in (7) than is used in (5), but it is easily seen that this does not work. For, one derives from Eq. (7):

$$(d/dt)\langle V\rangle = -(1/C)\{g(\langle V\rangle) + \tfrac{1}{2}(\langle V^2\rangle - \langle V\rangle^2)g''(\langle V\rangle) + \cdots\},$$

which shows that, unless g is a linear function, the rate of change of $\langle V\rangle$ depends not only on $\langle V\rangle$ itself, but also on the variance $\langle V^2\rangle - \langle V\rangle^2$ and on higher moments. The physical explanation is that the fluctuations take V to different points along the characteristic, each of which corresponds to a slightly different resistance (Fig. 2).

An analogous situation prevails if one tries to use the Fokker–Planck equation as a starting point for the generalization from the linear to the nonlinear case. In the linear case the fluctuations may also be described by the linear Fokker–Planck equation

$$\frac{\partial P(V,t)}{\partial t} = \frac{1}{RC}\frac{\partial}{\partial V}VP + \frac{c}{2}\frac{\partial^2 P}{\partial V^2}, \qquad (8)$$

which is mathematically equivalent with the Langevin equation (2) together with Eq. (3). Here $P(V, t)$ is the probability distribution of V at time t. The correct value, Eq. (4) for c is again found *a posteriori*, by demanding that the known equilibrium distribution

$$P^{eq}(V) = (2\pi CkT)^{-1/2}\exp[-CV^2/2kT] \qquad (9)$$

be a solution of Eq. (8).

Once again one finds from Eq. (8) immediately,

$$\frac{d}{dt}\langle V\rangle = \int V\frac{\partial P}{\partial t}dV = -\frac{1}{RC}\langle V\rangle.$$

This suggests that one should describe the nonlinear process [Eq. (5)] by a nonlinear Fokker–Planck equation

$$\frac{\partial P(V,t)}{\partial t} = \frac{\partial}{\partial V}g(V)P + \frac{1}{2}\frac{\partial^2}{\partial V^2}f(V)P. \qquad (10)$$

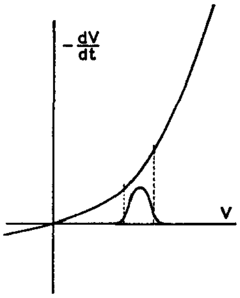

FIG. 2.

However, it is again true that from this equation, follows Eq. (7), which is not identical with (5). [In fact (10) is mathematically equivalent to Eq. (6) together with

$$\langle\kappa(t)\rangle = 0 \quad\text{and}\quad \langle\kappa(t)\kappa(t')\rangle = \tfrac{1}{2}f(V)\,\delta(t-t'),$$

and is therefore equally unsatisfactory. Moreover, if one determines $f(V)$ from the condition that P^{eq} must be a solution, it becomes too complicated to be reliable.[3]]

Summary

In the linear case it was possible to include fluctuations by a simple and plausible guess concerning the stochastic properties of the random emf. There is no simple and straightforward manner in which to make a similar guess for nonlinear systems.

Various guesses have been made by several authors.[3,4] It appeared that the result does depend on the specific guess made, whereas there was no theoretical basis for preferring one guess to the other, nor is there experimental evidence. Consequently one has to search for a firmer and more fundamental starting point. This was found to be the well-known "master equation". At first it was used to compute the fluctuations in a number of specific models, but it now seems possible to give a general method.

Of course, the master equation cannot be mathematically derived from first principles, but this problem is of quite a different nature than the problem of finding the correct description of nonlinear fluctuations. In fact, there are models (viz. the diode[5] and the Rayleigh particle[6] for which the master equation is clearly obeyed, and yet the

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[3] D. K. C. MacDonald, Phys. Rev. **108**, 540 (1957).

[4] N. G. van Kampen, Phys. Rev. **110**, 319 (1958); R. O. Davies, Physica **24**, 1055 (1958); M. Lax, Rev. Mod. Phys. **32**, 25 (1960).

[5] C. T. J. Alkemade, Physica **24**, 1029 (1958); N. G. van Kampen, Physica **26**, 585 (1960), and J. Math. Phys. **2**, 592 (1961).

[6] Lord Rayleigh, Phil. Mag. **32**, 424 (1891) [*Scientific Papers* **3**, Cambridge University Press, New York, 1902)] 473; F. Zernike, **3**, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1929) 419; A. Siegel, J. Math. Phys. **1**, 378 (1960).

treatment of their fluctuations has been the subject of controversy. This controversy has now been resolved.

II. EXPANSION OF THE MASTER EQUATION[7]

The master equation, from which we start, is

$$\frac{\partial P(V,t)}{\partial t} = \int_{-\infty}^{+\infty} \{W(V \mid V')P(V',t) - W(V' \mid V)P(V,t)\}\, dV'. \qquad (11)$$

Clearly this integro-differential equation for $P(V, t)$ is a much more elaborate description of the process than the simple differential equation for V [Eq. (5)]. The first question is: How is it possible for an equation describing the behavior of the probability distribution $P(V, t)$ to give rise to a phenomenological law for V itself? The next question is how to extract useful information from Eq. (11) concerning the fluctuations. We shall answer these questions by giving *a systematic approximation method for solving Eq.* (11), *which yields to lowest order, the phenomenological law* (*the next order gives the linear fluctuation theory*), *while the higher orders describe the influence of the nonlinearity on the fluctuations in successive approximations.*

There exists a well-known expansion of the master equation (11), namely the Kramers–Moyal expansion[8]

$$\frac{\partial P(V,t)}{\partial t} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \left(\frac{\partial}{\partial V}\right)^n \{\alpha_n(V)P(V,t)\}, \qquad (12)$$

where the $\alpha_n(V)$ are the successive moments of the magnitude of the jump ("derivate moments")

$$\alpha_n(V) = \int (V' - V)^n W(V' \mid V)\, dV'.$$

If the jumps are small, i.e., if $W(V' \mid V)$ decreases rapidly with increasing $|V - V'|$, the successive $\alpha_n(V)$ will decrease in size, so that Eq. (12) looks reasonable as an expansion. Yet it is not a *systematic* expansion, because it is not a power series in parameter. Our task is, therefore, to find a suitable expansion parameter.

Consider the electric circuit of Fig. 1. The irregular motion of the electrons in the resistor gives rise to random fluctuations of the charge Q on the condenser, and hence also of the potential V. The magnitude of these fluctuations may be estimated from their known equilibrium values:

$$\langle(\Delta Q)^2\rangle^{eq} = CkT, \qquad \langle(\Delta V)^2\rangle^{eq} = kT/C.$$

This suggests that if C is large, the probability distribution $P(V, t)$ is sharply peaked, so that it is possible to ascribe a pretty well defined unique value to V. Consequently, it is reasonable to use $1/C$ as our expansion parameter. The result will show that this actually leads to a systematic power series expansion.

A similar parameter can be found in other cases. One always has an intensive and an extensive variable, and the ratio between the two is something like the size of system (in this case, the size of the condenser). If this size is large, the fluctuations in the intensive parameters are small. Hence the reciprocal of this ratio is the appropriate expansion parameter. In the case of the Rayleigh particle, the particle velocity is the intensive parameter, its momentum is the extensive parameter, the expansion parameter is their ratio, i.e., the reciprocal of the mass.

Next we have to find how the various quantities in (11) depend on C. As the individual jumps in Q will be of the order of an electron charge e, the jumps in V are of the order e/C. Hence $W(V' \mid V)$ will fall off rapidly for $|V - V'| > e/C$, so that one has $\alpha_n(V) \sim (e/C)^n$. Accordingly we write

$$\alpha_n(V) = C^{-n}\beta_n(V).$$

Furthermore, the equilibrium distribution, Eq. (9), shows that when dealing with equilibrium fluctuations, one has to treat V as a quantity of order $C^{-\frac{1}{2}}$. It is therefore convenient to introduce a normalized variable

$$x = C^{1/2}V. \qquad (13)$$

On the other hand, in nonequilibrium situations, V consists of a macroscopic value Φ, plus fluctuations; accordingly we write

$$V = \Phi + C^{-1/2}x. \qquad (14)$$

Φ will presently be chosen as a suitable function of time. Finally, in order to allow for the increase of the RC time of the system, we increase the time scale by writing

$$t = C\tau. \qquad (15)$$

This finishes our task of making the dependence on C explicit.

Inserting all this in the Kramers–Moyal equation, (12), and collecting the successive powers of C one obtains an equation for the probability distribution $P(x, \tau)$ of x, viz.,

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[7] N. G. van Kampen, Can. J. Phys. **39**, 551 (1961).

[8] H. A. Kramers, Physica **7**, 284 (1940) [Collected Scientific Papers, p. 754 (Amsterdam 1956)]; J. E. Moyal, J. Roy. Stat. Soc. B **11**, 150 (1949).

$$\frac{\partial P(x,\tau)}{\partial \tau} - C^{1/2}\frac{d\Phi}{d\tau}\frac{\partial P}{\partial x} = C^{1/2}\beta_1(\Phi)\frac{\partial P}{\partial x}$$
$$+\sum_{m=2}^{\infty}\frac{C^{-(m-2)/2}}{m!}\sum_{n=1}^{m}\binom{m}{n}\beta_n^{(m-n)}(\Phi)\left(-\frac{\partial}{\partial x}\right)^n x^{m-n}P. \quad (16)$$

Here $\beta_n^{(m-n)}(\Phi)$ denotes the $(m-n)$th derivative of $\beta_n(V)$ taken at the value $V = \Phi$.

It is now possible to study the behavior for large C. First one must have

$$d\Phi/d\tau = -\beta_1(\Phi), \quad (17)$$

which determines Φ as a function of time. To show that this equation has exactly the form that one would expect for the phenomenological law, it is sufficient to note that from Eq. (12) follows

$$(d/dt)\langle V\rangle = -\langle\alpha_1(V)\rangle,$$

which for negligible fluctuations is identical with Eq. (17). Thus $\beta_1(V)$ is to be identified with the phenomenological response function $g(V)$ in (5),

$$\beta_1(V) \equiv g(V). \quad (18)$$

The remaining terms of Eq. (16) describe the fluctuations of V about the value Φ. We shall here only consider the fluctuations in the equilibrium state, so that we may take $\Phi = 0$. The first two terms of (16) are

$$\frac{\partial P}{\partial \tau} = -\frac{\partial}{\partial x}\,[\beta_1' x + \tfrac{1}{2}C^{-1/2}\beta_1'' x^2]P$$
$$+\frac{1}{2}\frac{\partial^2}{\partial x^2}\,[\beta_2 + C^{-1/2}\beta_2' x]P$$
$$-\frac{1}{3!}\frac{\partial^3}{\partial x^3}\,[C^{-1/2}\beta_3]P + O(C^{-1}). \quad (19)$$

The β_1', β_1'', β_2, are the values of the functions $\beta_n(V)$ and their derivatives at $V = 0$. The lowest-order terms in (19) reproduce the linear Fokker–Planck equation (8); they constitute the familiar linear theory of fluctuations. Indeed, β_1' is nothing but the coefficient of the linear term in the phenomenological response function, see (18).

The next order takes into account the coefficient β_1'', which describes the curvature of the $I - V$ characteristic. However, at the same time the third-order derivative of P enters into the equations. Hence *it is inconsistent to use a nonlinear Fokker–Planck equation* (10) *for describing the equilibrium fluctuations.*

Summary

The nonlinear case can be treated by expanding the master equation in powers of a suitable parameter (in the present case $1/C$). For large C, one finds first the phenomenological law, then the linear theory of fluctuations, and subsequently the influence of nonlinearity in successive orders.

III. THE CONNECTION BETWEEN FLUCTUATIONS AND DISSIPATION

Equation (19) is not of much use if the coefficients β are not known. The coefficients on the first line, β_1', β_1'', β_1''', $\cdots$, are the expansion coefficients of the phenomenological response function g, and may therefore be determined by macroscopic measurements. But the coefficients, β_2, β_2', β_3 etc., are not directly connected with macroscopic experiments. In principle they might be determined by more subtle experiments, in which the fluctuations themselves are observed and measured. However, it was first noticed by Einstein (for the case of linear Brownian movement), and later by Nyquist, that there must exist a relation between the magnitude of the fluctuations and the phenomenological law. The idea is that the equilibrium distribution results from a balance between fluctuations on the one hand, which try to move V away from the value 0, and dissipation on the other hand, which tends to move V towards 0. Because the resulting equilibrium distribution is known from ordinary equilibrium statistical mechanics, this provides a relation between fluctuations and dissipation. Nowadays, this is referred to as the fluctuation–dissipation theorem. Similarly, it appears that in our nonlinear case, there exist relations between the β's, such that at least many of them can be computed once the β_1', β_1'', β_1''', $\cdots$ are known. As these relations again connect the properties of the fluctuations with the function $\beta_1(V) \equiv g(V)$, which determines the macroscopic dissipation, they constitute the proper generalization of the fluctuation—dissipation theorem of the linear theory.

In order to derive relations of this type between the β's we note that

$$P^{eq}(x) = (2\pi kT)^{-1/2}\exp\,[-x^2/2kT]$$

must be a solution of Eq. (19), for any value of C. Thus one has

$$(d/dx)[-\beta_1' x\exp(-x^2/2kT)$$
$$+\tfrac{1}{2}\beta_2(d/dx)\exp(-x^2/2kT)] = 0,$$

which yields

$$\beta_2 = 2kT(-\beta_1').$$

This is the familiar relation (4) of the linear theory. [Indeed, on comparing (19) with (8), and taking into account (13) and (15), one finds $-\beta_1' = 1/R$ and $\beta_2 = C^2c$].

For the nonlinear terms in (19), i.e., the terms of order $C^{-\frac{1}{2}}$, one finds in this way two relations:

$$\beta_3 + 3kT\beta_2' + 6(kT)^2\beta_1'' = 0, \tag{20}$$

and

$$\beta_3 + 3kT\beta_2' = 0. \tag{21}$$

These two relations do not determine β_3 and β_2', but they assert that the phenomenological coefficient $\beta_1'' = 0$, which certainly cannot be universally true. The answer to this paradox is that there is an additional complication, which I have not mentioned so far. It has been tacitly assumed that the $\alpha_n(V)$ are not merely of order C^{-n}, but actually proportional to C^{-n}, so that the $\beta_n(V)$ are independent of C. This is only correct in simple cases.

In general one must expect $\beta_n(V)$ to contain higher orders as well;

$$\beta_n(V) = \beta_{n,0}(V) + C^{-1}\beta_{n,1}(V) + C^{-2}\beta_{n,2}(V) + \cdots .$$

In particular $\beta_1(V)$ may be of this form. Hence it can no longer be identified with the phenomenological function $g(V)$, since we arrived at this identification by taking $C = \infty$. Rather, one has now instead of (18),

$$g(V) \equiv \beta_{1,0}(V).$$

The next term, involving $\beta_{1,1}$, turns up in (19), with the result that (21) changes to

$$\beta_{3,0} + 3kT\beta_{2,0}' + 6(kT)^2\beta_{1,0}'' + 6kT\beta_{1,1} = 0.$$

The only effect of this equation is now to determine, together with (20), the new coefficient $\beta_{1,1}$:

$$\beta_{1,1} = -kT\beta_{1,0}''.$$

The consequences of this complication are serious. The terms of order $C^{-\frac{1}{2}}$ in the equation for $P(x, t)$ now involve *three* unknown coefficients $\beta_{3,0}$, $\beta_{2,0}'$, $\beta_{1,1}$, whereas substitution of $P^{eq}(x)$ leads to only *two* relations. It is therefore no longer possible to determine all three of them from the known phenomenological coefficients. On the other hand we can replace the condition that P^{eq} must satisfy the master equation, by a stronger one. This stronger condition is the principle of microscopic reversibility or detailed balance, which states that $W(V \mid V')$ must have the symmetry property

$$W(V \mid V')P^{eq}(V') = W(V' \mid V)P^{eq}(V).$$

[This formulation only applies to the case that V is an even variable and that the Hamiltonian is invariant for time reversal.] It has been shown for a rather general model, suggested by D. K. C. MacDonald, that with the aid of this principle it is possible to determine all three coefficients from the phenomenological law.[9] It is somewhat doubtful, however, if this still remains true in higher approximations.

Summary

In linear approximation, the fluctuations are fully determined by the phenomenological law. Whether or not this is still true for the general nonlinear case has not yet been decided. The study of a model, however, shows that the principle of microscopic reversibility permits one to determine many, if not all coefficients in the equation governing the fluctuations.

In the linear case it is easy to compute from Eq. (8), the auto-correlation function of V and hence the spectral density of the equilibrium fluctuations. As c is given by Eq. (4), the resulting expression depends only on the specific properties of the resistor through the phenomenological coefficient R. This is the Nyquist relation or fluctuation–dissipation theorem. It has been asserted by Bernard and Callen[10] that the spectral density is not affected by the non-linearity. However, the exact treatment of the model of the diode[5] shows that their result cannot be correct. In other words, *the specific formula of the fluctuation–dissipation theorem is confined to the linear approximation, but the general idea that there is a connection between fluctuations and dissipation remains true in the nonlinear case.* It has not yet been decided whether or not this connection is sufficient to determine completely the noise spectrum from the phenomenological dissipation law.

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[9] D. K. C. MacDonald, N. G. van Kampen and C. T. J. Alkemade, Proc. Roy. Soc. (London) **A271**, 449 (1963).

[10] W. Bernard and H. B. Callen, Phys. Rev. **118**, 1466 (1960).

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Hydrodynamics of a Superfluid Condensate*

EUGENE P. GROSS
Brandeis University, Waltham, Massachusetts
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The theory of the condensate of a weakly interacting Bose gas is developed. The condensate is described by a wavefunction $\psi(\mathbf{x}, t)$ normalized to the number of particles. It obeys a nonlinear self-consistent field equation. The solution in the presence of a rigid wall with the boundary condition of vanishing wavefunction involves a de Broglie length. This length depends on the mean potential energy per particle. The self-consistent field term keeps the density uniform except in localized spatial regions. In the hydrodynamical version, a key role is played by the quantum potential. A theory of quantized vortices and of general potential flows follows immediately. In contrast to classical hydrodynamics, the cores of vortices are completely determined by the de Broglie length and all energies are finite. Nonstationary disturbances of the condensate correspond to phonons, rotons, vortex waves etc. They can exchange momentum with rigid boundaries. This is compatible with the vanishing of the wavefunction at a boundary. This condition fully determines the dynamics of the system. These points are illustrated by considering the motion of a foreign ion in a Bose gas, a rotating container of fluid, and the Landau criterion for superfluidity.

I. INTRODUCTION

A SUGGESTION by Onsager, "Vortices in a superfluid are presumably quantized; the quantum of circulation is h/m, where m is the mass of a single molecule" occurs as a footnote to a paper[1] dealing with classical vortex theory and with the theory of turbulence. In the literature, mention is also made of an unpublished remark by Onsager at a conference held at Shelter Island the previous year. In view of the tremendous significance of the idea in the subsequent experimental research on liquid helium, we have here almost a record for the ratio of significance of a contribution to its length.[2] The notion of quantized vortices was later proposed independently by Feynman,[3] who pointed out in detail its importance in bringing order into the wealth of experimental data on the flow properties of liquid helium. The experiments of Hall, Vinen, Andronikashvili, and others to hunt down vortex lines and to observe their behavior, represents a brilliant chapter in recent experimental physics.[4]

It is a very difficult task, and far from complete at present, to give a reasonably unified treatment of the properties of actual liquid helium from first principles. On the other hand one can make considerably more progress with the theory of a system of weakly interacting Bose particles or of a dilute gas of hard spheres. These systems have been studied intensively in recent years. In the present paper, we outline the picture that has emerged by sketching the derivations for the model of a weakly interacting gas of bosons.

Our starting point is the considerations of London,[5] who called attention to the relevance to the helium problem of the Einstein consideration of an ideal Bose gas: The ideal Bose gas shows a condensation as the temperature is lowered. Below a temperature $T_c = 2.18°\mathrm{K}$, (for particles of helium mass), there is a finite fraction of all the particles in a single quantum state. The fraction is $(1 - T/T_c)^{\frac{3}{2}}$, and at absolute zero all particles are in the same state. For a system enclosed in a volume Ω with periodic boundary conditions, this is the one-particle state $(1/\Omega^{\frac{1}{2}})$ i.e., a plane wave of wave vector zero. One can then speak of a long-range momentum ordering. Now as one lowers the temperature, liquid helium exhibits the transitions gas–ordinary liquid–superfluid. London conjectured that the second transition was like the ideal Bose gas transition. He was encouraged to pursue the gas analogy because the "ordinary" liquid helium I has an unusually large interatomic spacing as a consequence of the large

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[1] L. Onsager, Nuovo Cimento Suppl. **6**, 2, 249 (1949).

[2] E. Montroll and L. Onsager pointed out to me that a more detailed development of the idea was given in response to questions, and is given in the report of the discussion following the paper of Gorter at the same conference.

[3] R. P. Feynman, *Progress in Low Temperature Physics*, (North-Holland Publishing Company, Inc., Amsterdam, 1955), Vol. I, Chap. II; Physica Suppl. **24**, 18 (1958).

[4] W. F. Vinen, "Vortex Lines in Liquid Helium II," in *Progress in Low Temperature Physics*, edited by C. J. Gorter, (North Holland Publishing Company, Amsterdam, 1961), Vol. III, p. 1; E. L. Andronikashvili, *et al.*, Soviet Physics–Usp., July, 1961; K. R. Atkins, *Liquid Helium* (Cambridge University Press, Cambridge, England, 1961); C. T. Lane, *Superfluid Physics* (McGraw-Hill Book Company, Inc., New York, 1962).

[5] F. London, *Superfluids*, (John Wiley & Sons, Inc., New York, 1954), Vol. 2.

zero-point energy and weak interatomic forces, and because it exhibits a gas-like temperature dependence of its viscosity.

These considerations are well known. London's associated idea that in liquid helium we have a fascinating example of a system in which quantum phenomena are manifested on a macroscopic scale, has been taken far less seriously. The genesis of the idea is that the state into which condensation takes place in an ideal gas depends on the boundary conditions; whether one has rigid walls, a cylindrical or irregularly shaped container, etc. By manipulating the boundary externally we can adiabatically change the quantum state. Actually, this idea needs a certain refinement when interparticle forces are considered. However, in giving precision to the London idea, one is led to consider spatially inhomogeneous condensates (or single-particle states), and almost immediately to a theory of quantized vortices. The central importance of spatially inhomogeneous condensates is illuminated by the study of problems such as the rotation of a Bose gas or the motion of a foreign ion in a system of bosons.

These ideas played an essential role in the two-fluid hydrodynamics of Tisza,[6] where the condensate appears as a zero-entropy component. The striking prediction of second sound as a coupled oscillation of super and normal fluids, the explanation of the fountain and thermomechanical affects by this formulation gave clear guidance to attempts to provide microscopic explanations of the properties of helium. Landau's introduction of phonons[7] corrected the chief inadequacy of the London–Tisza approach. His discussion of the criterion for superfluidity in terms of the quasiparticle spectra of a system, removed the mystery of how superfluidity was to be understood on a microscopic basis.

The work of Bogolyubov[8] on the theory of a weakly interacting Bose gas which was insufficiently appreciated when it first appeared, was an important step in harmonizing the correct elements of the preceding theories. The superfluid condensate idea plays an essential part in his mathematical formulation of the many-boson problem in the quantized wave formalism. The condensate is described by giving special consideration to one basis function in the expansion of a quantized field operator in a complete orthonormal set, or alternatively by splitting off a c-number part of the quantized field. The quasiparticle transformation that yields the phonon–roton spectrum is a linear transformation of creation and annihilation operators. This formalism lends itself admirably to generalization to the case of spatially inhomogeneous condensates. The key question is what to choose for the condensate wavefunction. After this has been decided, the machinery of Bogolyubov can be brought into action.

Here we attack this problem for a system of weakly interacting particles by starting with the self-consistent field approximation to determine the condensate wavefunction. This formulation provides one precise mathematical theory that embodies the London idea. It removes the unphysical behavior of the ideal Bose gas. It should be emphasized that the results do not contradict the point of view of Landau, Onsager, Feynman, Hall, and Vinen, concerning the behavior of liquid helium. Indeed no really new ideas are involved. What we have is a simple model which permits a unified, deductive approach to the enormous range of phenomena displayed by a quantum fluid. The conjectures advanced in the case of helium can be examined explicitly and the analysis pushed to consider more complex modes of motion. We have a model of a fluid which from the mathematical point of view is more satisfactory than that of classical fluid dynamics. It is suitable for the study of large-amplitude disturbances, boundary layer phenomena, and turbulence theory. One of the purposes of the present exposition is to bring this model to the attention of mathematical physicists. The model also serves to bring to the fore, the important but inadequately studied question of the relations between the classical and quantum treatments of a nonlinear wave theory.

A number of almost trivial observations play an important role. They are all connected with the adequacy of the usual quantum mechanical boundary condition on a wavefunction $\Psi(\mathbf{x}_1, \cdots \mathbf{x}_N, t)$ to yield a theory of superfluids. Here these conditions are applied to a wavefunction $\psi(\mathbf{x}, t)$ obeying a Hartree equation. One point is the key role played by a de Broglie wavelength which determines the "healing" of the wavefunction and the size of vortex cores. A second point is that a nonstationary disturbance of the condensate can exchange momentum with a boundary in spite of the condition $\psi = 0$ at the boundary. This is identical with the behavior of wave packets in elementary quantum mechanics. All disturbances are motions of the condensate. Failure to fully appreciate these points has prevented wider understanding of the present conception of the nature of superfluidity.

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[6] L. Tisza, Nature (London), **141**, 913 (1938).
[7] L. D. Landau, J. Phys. (U. S. S. R.) **5**, 71 (1941).
[8] N. Bogolyubov, J. Phys. (U. S. S. R.) **11**, 23 (1947).

II. THE SELF-CONSISTENT FIELD APPROXIMATION

We begin with the remark that the noninteracting Bose gas is an overidealized system that leads to highly nonphysical situations. If such a system is in a box of length L with rigid walls so that the boundary condition is that the wavefunction vanishes at the walls, the lowest energy state is (in one dimension)

$$\Psi(x_1, \cdots x_N, t) = \prod_{i=1}^{N} \left(\sin \frac{\pi x_i}{L}\right) \times \left(\frac{2}{L}\right)^{N/2} \exp\left[-i \frac{E_G t}{\hbar}\right],$$

$$E_G = N \frac{\hbar^2}{2M} \left(\frac{\pi}{L}\right)^2. \tag{2.1}$$

This solution, in which all the particles are "condensed" in a single-particle state, $(2/L)^{\frac{1}{2}} \sin (\pi x/L)$, possesses the absurd feature of exhibiting an enormous density near the center of a macroscopic container. It is clear that virtually any kind of interparticle repulsions would result in a ground state of uniform density everywhere except near the walls. The ideal Bose gas is oversensitive to boundary conditions.

A model which treats interparticle forces is therefore needed. We take as the one most amenable to analysis, the case of particles interacting by weak, repulsive two-body forces. Our approach will be based on taking self-consistent field theory as the first approximation. To be on the safe side we suppose the range of the force to be several times the average interparticle spacing, so that the rapidly fluctuating forces on a particle are less important than the smoothly varying average force. Under these conditions one has confidence in starting the analysis with the Hartree approximation. We write

$$\Psi(\mathbf{x}_1, \cdots \mathbf{x}_N, t) \approx \prod_{i=1}^{N} g(\mathbf{x}_i, t)$$
$$\int |g(\mathbf{x}, t)|^2 \, d^3x = 1, \tag{2.2}$$

where g is a normalized single-particle state. If $g(\mathbf{x}, t)$ is separable,

$$g(\mathbf{x}, t) = g(\mathbf{x}) \exp [-iEt/\hbar],$$

it is a candidate for an approximate stationary state of the many-body Hamiltonian

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2M} + \tfrac{1}{2} \sum_{i \neq j} V(\mathbf{x}_i - \mathbf{x}_j). \tag{2.3}$$

It is more convenient to introduce the function $\psi = (N)^{\frac{1}{2}} g$ with $\int |\psi|^2 \, d^3x = N$ so that $|\psi(\mathbf{x}, t)|^2$ is the density of a fluid. In terms of $\psi(\mathbf{x}, t)$ the time-dependent self-consistent field equation is

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2M} \nabla^2 \psi + \psi(x) \int |\psi(y)|^2 \, V(\mathbf{x} - \mathbf{y}) \, d^3y, \tag{2.4}$$
$$\int |\psi(\mathbf{x}, t)|^2 \, d^3x = N.$$

The energy of a stationary state is

$$\mathcal{E} = \frac{\hbar^2}{2M} \int \nabla \psi^+ \cdot \nabla \psi \, d^3x + \frac{1}{2} \int |\psi(\mathbf{x})|^2 \, V(\mathbf{x} - \mathbf{y}) \, |\psi(\mathbf{y})|^2 \, d^3x \, d^3y. \tag{2.5}$$

The complex function $\psi(\mathbf{x}, t)$ will be seen to govern the behavior of the superfluid condensate of a weakly interacting Bose gas.[9] In general the analysis is considerably simpler if we replace $V(\mathbf{x} - \mathbf{y})$ by $V \cdot \delta(\mathbf{x} - \mathbf{y})$. This does not alter the general nature of the results for a phenomenon whose characteristic length is larger than the range of the force. We will often work with the simpler equation

$$i\hbar(\partial \psi/\partial t) = (-\hbar^2/2M)\nabla^2 \psi + V\psi \, |\psi|^2. \tag{2.6}$$

We now proceed to examine some special solutions of this equation appropriate to the description of stationary states of the many-body problem. (The solutions for the case of rigid walls were given by Ginsburg and Pitaevski[10] and also by Wu.[11] The vortex solution is also presented by Ginsburg and Pitaevski who point out that the same equation occurs in the phenomenological theory of superconductivity.[12] Vortex solutions in that theory were found by Abrikosov.[13] The work embodying the present physical application is presented by Pitaevski[14] and Gross.[15]

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[9] E. P. Gross, Ann. Phys. **4**, 57 (1958); **9**, 292 (1960).

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[12] V. L. Ginzburg and L. D. Landau, Soviet Phys.—JETP **20**, 1064 (1950).

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[14] L. P. Pitaevski, J. Exptl. Theoret. Phys. (U.S.S.R.) **13**, 451 (1961); [translation: Soviet Phys—JETP **40**, 646 (1961)].

[15] E. P. Gross, Nuovo Cimento **20**, 454 (1961).

Ground State for a Periodicity Box of Volume Ω

The solution is:

$$\psi = (N/\Omega)^{1/2} \exp\,[-iEt/\hbar],$$

$$\mathcal{E} = \frac{NE}{2} = \frac{N}{2}\frac{(N-1)}{\Omega}\int V(y)\,dy \equiv \frac{N}{2}\,\rho_0 V. \quad (2.7)$$

The density $\rho_0 = N/\Omega$ is constant and the energy per particle is the average potential energy.

Ground State of a System with Rigid Walls

The solution, $\psi = (\rho_0)^{1/2} \tanh\,(x/a) \exp\,[-iEt/\hbar]$ with $E = V\rho_0$, $a = \hbar/(2ME)^{1/2}$, represents a semi-infinite system bounded by a rigid wall at $x = 0$. The density rises from zero at $x = 0$ to its uniform value in a distance of the order of the de Broglie wavelength a.

The occurrence of this "healing length" is a general feature of Eq. (2.6). Since it is central to the construction of vortices in the condensate, we present an elementary discussion of how it appears. The basic equation may be written as

$$\{E - V\,|\psi|^2\}\psi = (-\hbar^2/2M)\nabla^2\psi.$$

The constant E is fixed as V times the asymptotic uniform density ρ_0. Near a boundary, where one requires that $\psi \to 0$, the term $V\,|\psi|^2\cdot\psi$ is negligible and ψ obeys the free-particle Schrödinger equation. Thus $\psi \sim \sin\,(x[(2ME)^{1/2}/\hbar])$, where E has already been fixed. The two asymptotic solutions match near the first maximum of the sine function. This explains the occurrence of this de Broglie length.

It is easy to find the exact solution in terms of elliptic functions for a one-dimensional system confined between rigid walls.[10,11] There is healing behavior at both walls. If we have the condition that there are N particles in a region of length L, then the density in the uniform region differs from $\rho_0 = N/L$ by a term of order $1/L$. The same is true of E. The physical interpretation is clear. The deficiency of particles in a healing layer (or order $a\rho_0$) requires a slight excess spread over the entire container. On the other hand, if the distance between the walls is comparable to the healing length, the behavior is quite different. The solution has been used to describe the limitations on superfluidity in thin helium films.

Vortex Line Solutions

We look next for cylindrically symmetric solutions

$$\psi(r, \nu, z, t) = f(r)e^{i\mu\nu} \exp\,[-iE_\nu t/\hbar], \quad (2.8)$$

where μ is an integer and

$$\int |f(r)|^2\, 2\pi r\, dr\, dz = N.$$

The equation allows the separation of variables, and it only remains to prove that there are suitable solutions of the radial equation for $f(r)$. Before doing this let us discuss the physical interpretation of the wavefunction. We note that $|f|^2$ is the particle-number density. The angular momentum is $N\hbar\mu$. The expectation value of the current density at $\mathbf{x}$ is

$$\mathbf{j}(\mathbf{x}) = \frac{1}{2}\int \Psi^* \sum_{i=1}^{N} \{\mathbf{p}_i\,\delta(\mathbf{x}_i - \mathbf{x}) + \delta(\mathbf{x}_i - \mathbf{x})\mathbf{p}_i\}\Psi\, d\tau \quad (2.9)$$

$$= \frac{\hbar}{2i}\int (\psi^+\nabla\psi - \psi\nabla\psi^+)\, d^3x.$$

We will define the velocity at a point in the fluid as the ratio of two expectation values, the current density and number density. We have then

$$v_\nu = \frac{1}{\psi^+\psi}\frac{\hbar}{2Mi}\left(\psi^+\frac{1}{r}\frac{\partial\psi}{\partial\nu} - \frac{1}{r}\frac{\partial\psi^+}{\partial\nu}\,\psi\right) = \frac{\hbar\mu}{Mr}. \quad (2.10)$$

This is the characteristic velocity pattern of a line vortex. The definition of an average-velocity field that has been chosen satisfies the correspondence principle. We have avoided attempting to introduce a quantum mechanical velocity operator,[16] as it is not essential. With the velocity equal to $\hbar\mu/\mu r$, the vorticity is

$$w_z \equiv (\mathrm{curl}\,\mathbf{v})_z = \frac{1}{2r}\frac{\partial}{\partial r}(rv_\nu) = 0. \quad (2.11)$$

The vorticity is zero everywhere, except possibly on the singular line $r = 0$. This is quite similar to the classical theory of ideal incompressible fluids, where one speaks of an irrotational fluid as long as there is no volume vorticity, but only singular lines with a circulation about the lines. Here the circulation is

$$\Gamma = \int v_\nu(r\, d\nu) = \frac{h}{M}\,\mu \neq 0, \quad (2.12)$$

and is quantized in units of h/M, as suggested in the quotation from Onsager that introduces this article.

We must still see if the radial equation can be satisfied. The function $f(r)$ satisfies

$$E_\nu f(r) = -\frac{\hbar^2}{2M}\left[\frac{1}{r}\frac{d}{dr}\left(r\frac{d}{dr}\right) - \frac{\mu^2}{r^2}\right]f + Vf\,|f|^2. \quad (2.13)$$

The presence of the centrifugal force term means that $f(r)$ must tend to zero as $r \to 0$ if there is to be

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[16] F. London, Rev. Mod. Phys. **17**, 310 (1945).

a finite energy in a given container. However, if we require $f(r) \to 0$ as $r \to 0$, we are led back to the "healing length" argument. For very small r the term $Vf\,|f|^2$ can be neglected and the solution is

$$f(r) \to A j_\mu[(2ME_v/\hbar^2)^{\frac{1}{2}} r] \quad \text{as} \quad r \to 0. \tag{2.14}$$

But E_v is again given by $E_v = V\rho_0$ and

$$f(r) \to \rho_0^{\frac{1}{2}} \quad \text{as} \quad r \to \infty. \tag{2.15}$$

A first approximation to the solution can be obtained by matching the logarithmic derivatives of the limiting forms. This occurs at a distance $r = a$ given by the zeros of $(dj_\mu/dr)[(2ME_v/\hbar^2)^{\frac{1}{2}} r] = 0$. The result is a "core" size of the order of the healing length. Outside the core, the density is essentially constant as is the case for a vortex in a classical incompressible fluid.

The most important difference between the quantum and classical vortex theories, (apart from the quantization of circulation), is that the structure of the quantum vortex is fully determined. In the present Hartree theory, we have a nonclassical de Broglie length. This means that the energy of a line is finite. To find the energy per unit length of a simple vortex, we insert the solution $f(r)$ into Eq. (2.5). One finds for the delta-function potential

$$\frac{\text{energy}}{\text{length}} = \frac{\hbar^2}{2M}\,\rho_0 \ln\left(\frac{1.46R}{a}\right). \tag{2.16}$$

This result was obtained[14] by numerical integration of the differential equation. It has the same dependence on the outer radius R as does a classical line vortex. In addition to the linear dependence of energy on superfluid density, there is a weak dependence in the logarithm because of the presence of a. The fact that the energy is proportional to the length of vortex line implies a tension when the length is increased and gives rise to the existence of vortex waves. Quantized vortices with $\mu > 1$ are highly unstable.

Hydrodynamic Form for the Self-Consistent Field(15)

The elementary argument involving the healing length is extremely general. We immediately conjecture that any steady hydrodynamic pattern of a classical ideal fluid should be considered as a possible approximate stationary state of the many-body system. Let us write the complex field function ψ in a hydrodynamic form by introducing the density R^2 and the velocity potential S:

$$\psi = R(\mathbf{x}, t) \exp\,[iS(\mathbf{x}, t)/\hbar]. \tag{2.17}$$

We equate real and imaginary parts of the field equations. This yields the continuity equation

$$(\partial/\partial t)R^2 = -\nabla\cdot[R^2(\nabla S/M)], \tag{2.18}$$

and the Bernoulli equation

$$-\frac{\partial S}{\partial t} = \frac{(\nabla S)^2}{2M} + \pi(\mathbf{x}). \tag{2.19}$$

Here the pressure $\pi(x)$ is

$$\pi(\mathbf{x}) = -\frac{\hbar^2}{2M}\frac{\nabla^2 R}{R} + \int V(\mathbf{x} - \mathbf{y})R^2(\mathbf{y})\,d^3y, \tag{2.20}$$

and contains the well-known and peculiar quantum pressure term $(-\hbar^2/2M)$ $(\nabla^2 R/R)$. Taking the gradient of the Bernoulli equation one finds

$$\partial\mathbf{v}/\partial t + (\mathbf{v}\cdot\nabla)\mathbf{v} = \nabla\pi. \tag{2.21}$$

To see the usefulness of the hydrodynamic form, let us glance back at the simple line vortex solution. In the Bernoulli equation, the term $(\nabla S)^2/2M$ is $(\hbar^2\mu^2/2M)(1/r^2)$ and tends to infinity as $r \to 0$. On the other hand, R is the same as the function $f(r)$ and satisfies

$$-\frac{\hbar^2}{2M}\frac{\nabla^2 R}{R} = -\frac{\hbar^2}{2M}\frac{\mu^2}{r^2} + (E_v - VR)R.$$

The second term tends to zero as $r \to 0$, and we see that quantum pressure term cancels $(\nabla S)^2/2M$ as $r \to 0$. This is simply the hydrodynamic version of the healing length argument. On the other hand the continuity equation is

$$\nabla\cdot(R^2\nabla S) = R^2\nabla^2 S + \nabla S\cdot\nabla R^2 = 0.$$

For the line vortex, $\nabla(R^2)$ has only a radial component, which ∇S has only an azimuthal component, so that the two vectors are orthogonal. The velocity potential then satisfies Laplace's equation $\nabla^2 S = 0$. For the elementary line vortex, the solution of the hydrodynamical equations divides neatly into two parts—the solution of Laplace's equation and then the solution for $R(r)$. In the general case the self-consistent field term guarantees that the density R^2 will be constant everywhere except in concentrated spatial regions. Thus by starting with a general solution of Laplace's equation, we fail to satisfy the continuity equation (and the Bernoulli equation) only within a healing length of the lines or surfaces of singularity. On the other hand, in the immediate vicinity of the line or surface of singularity, the self-consistent field term is negligible and we can use the free-particle Schrödinger equation with the condition that the wavefunction vanish on the singular line. For a stationary state we must then satisfy the equation

$$-(\hbar^2/2M)(\nabla^2 R) + R[(\nabla S)^2/2M] = ER,$$

for fixed E as one approaches the singular region. This fixes the way in which the density R^2 approaches zero. While we will not try to supply an existence proof, it seems reasonable that one can develop a solution by iteration. A value of R with the correct limiting behavior is used in the continuity equation to find an improved $S(\mathbf{x})$ etc.

III. MOTION OF AN ION IN A BOSON SYSTEM(17,9)

The problem of the self-energy and effective mass of foreign ion moving through the system of bosons is a striking example of the response of the condensate wavefunction to a disturbance. We will take as the interaction energy between an ion and a Bose particle

$$\begin{aligned} U(r) &= \infty & r < a, \\ &= -\tfrac{1}{2}(\alpha e^2/r^4) & r > a. \end{aligned} \qquad (3.1)$$

Here a is a hard-core radius and α is the polarizability of a boson. The Hamiltonian is

$$H = p^2/2\mu + \sum_{i=1}^{N} (p_i^2/2M) + \sum_{i=1}^{N} U(\mathbf{x}_i - \mathbf{q}) + \tfrac{1}{2} \sum_{i \neq j} V(\mathbf{x}_i - \mathbf{x}_j). \qquad (3.2)$$

Here μ, $\mathbf{q}$, $\mathbf{p}$ are the ion mass, coordinate and momentum respectively.

Consideration of this problem is inspired by the behavior of positive He^4 ions in liquid helium.[18] The effective mass seems to be larger than twenty He^4 masses. This is presumably a consequence of the relatively long-range polarization force, since the effective mass of neutral He^3 atoms is the order of two to three He^4 masses.[19] We will not discuss the case of liquid helium,[20] but again consider the weakly interacting Bose system. The foreign ion induces the distortion of the superfluid state, and there is a finite fraction of atoms in a spatially inhomogeneous state. However, now the inhomogeneity is only relative to the ion, since the actual state should be translationally invariant.

Consider first the lowest state of the system, for which the total momentum $\mathbf{p} + \sum \mathbf{p}_i$ has eigenvalue zero. A crude approximation is given by the wavefunction

$$\Psi = \frac{1}{\Omega^{\frac{1}{2}}} \prod_{i=1}^{N} f(\mathbf{x}_i - \mathbf{q}), \qquad \int |f|^2 \, d^3x = 1, \quad (3.3)$$

where f is real. We use this trial function to calculate the expectation value of the Hamiltonian. Variation of the form of $f(r)$ leads to the self-consistent field equation

$$-\frac{\hbar^2}{2}\left(\frac{1}{M} + \frac{1}{\mu}\right)\nabla^2\psi + U(r)\psi + \psi(\mathbf{x}) \times \int V(\mathbf{x} - \mathbf{y})\psi^2(y) \, d^3y = E_0\psi, \qquad (3.4)$$

where we have introduced $\psi(r) = N^{\frac{1}{2}} f(r)$. The function $p(r) \equiv \psi^2(r)$ is the probability distribution of an atom relative to the ion. We have then an equation for a particle of mass $1/m^* = 1/M + 1/\mu$ moving in the potential $U(r)$. The effect of the other bosons is accounted for by the self-consistent field term. As in our earlier considerations, we require $\psi(r) \rightarrow \rho_0^{\frac{1}{2}}$; this fixes E_0 as

$$E_0 = \rho_0 \int V(\mathbf{y}) \, d^3y.$$

The function ψ is zero at the core $r = a$. It rises more steeply than in the "healing" calculation since the curvature is now determined by $E_0 - U(r)$ and in the situation of interest $|U(r = a)| \gg E_0$. In the intermediate region, $\psi(r)$ is determined by the interplay of three terms in the energy functional. There is first the kinetic energy density

$$\tfrac{1}{2}\hbar^2\left(\frac{1}{M} + \frac{1}{\mu}\right) |\nabla\psi|^2,$$

which must be kept as small as possible, and so acts to prevent rapid changes of ψ over extensive regions. Second, there is the interaction energy density $U(r)\psi^2$, entering with a negative sign, and so favoring as high a density as possible in the region where the polarization potential is appreciable. Finally there is the boson–boson energy density which is a quadratic functional in the particle density—with the delta function interaction it is $\frac{1}{2}V\rho^2$. Even with the total neglect of the kinetic energy contribution the boson–boson term holds the polarization term in check. Minimizing the energy with just these two terms leads to

$$\psi^2 \approx [E_0 - U(r)]/V = \rho_0 - U(r)/V.$$

We define a distance b by $|U(b)| = E_0$; the nature of the solution is critically determined by the ratio of b to the core size a. If $b/a \gg 1$ there is an extended spatial region where $|U(r)| \gg E_0$ and where the density $\sim 1/r^4$. In that case one expects the particle

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[17] E. P. Gross, Ann. Phys. (to be published).

[18] G. Careri, Progr. Low Temp. Phys. **3**, 58 (1961).

[19] R. P. Feynman, Phys. Rev. **94**, 262 (1954).

[20] K. R. Atkins, Phys. Rev. **116**, 1339 (1959).

density to rise from zero at $r = a$ to a large value in a distance small compared to b, to turn over and to fall off as does $1/r^4$, until near b it approaches ρ_0.

To treat the case of a moving ion we look for states of the form

$$\Psi(\mathbf{k}) = \frac{1}{\Omega^2} \exp(i\mathbf{k}\cdot\mathbf{q}) \prod_{i=1}^{N} f_k(\mathbf{x}_i - \mathbf{q}) \times \exp[is_k(\mathbf{x}_i - \mathbf{q})/\hbar], \tag{3.5}$$

where f_k and s_k are real functions. $\Psi(k)$ is an eigenfunction of the total momentum with eigenvalue $\hbar\mathbf{k}$. $s_k(\mathbf{y})$ represents the velocity potential of the flow of atoms relative to the ion. It is to be determined, together with f_k, by functional variation of the expectation value of the energy. For slowly moving ions f_k can be taken as the function $f(\mathbf{x})$ discussed earlier. Then $s(\mathbf{x})$ obeys the continuity equation

$$\left(\frac{1}{M} + \frac{1}{\mu}\right)\nabla(p\nabla S) = \frac{1}{\mu}\left(\mathbf{k} + \int s\nabla p\, d^3x\right)\nabla p. \tag{3.6}$$

The problem is to solve for $s(\mathbf{x})$ with a density $p(r)$ determined by the polarization potential. By inserting the solution in the energy functional we find the effective mass from

$$\mathcal{E}(k) = \mathcal{E}(k = 0) + \hbar^2k^2/2m_{\text{eff}}. \tag{3.7}$$

The solution for the flow has the following features. It is quite different from the usual dipolar pattern for a rigid sphere moving through an incompressible fluid. Just ahead of the ion, the flow velocity is equal to, and in the direction of, the ion velocity, and falls off as one moves out. However, far in front of the ion there is a reversed dipolar flow. Because of the attractive polarization force between the ion and an atom, the atoms move toward the ion. At an intermediate distance from the moving ion there is a point of zero radial velocity along the direction of motion. The effective mass is given roughly by

$$\frac{m_{\text{eff}}}{\mu} \approx 1 + \frac{M}{M + \mu}\frac{b}{a}(4\pi b^3\rho_0). \tag{3.8}$$

It is thus larger than the total number of atoms contained in a volume $\frac{4}{3}\pi b^3$ at normal density. It follows that high effective masses are understandable in a simple way in the "manipulable condensate" approach.

IV. MOVING BOUNDARIES

Boundary Condition

There has been some confusion concerning the boundary conditions associated with the superfluid. However, if one adopts the London point of view that the condensate is described by a single wavefunction, there appears to be no room for ambiguity. As long as the wall can be treated as having no dynamically active degrees of freedom, it must be considered as an external time-dependent potential. Indeed, in the self-consistent field approximation, the system is described by a single-particle wavefunction $\psi(\mathbf{x}, t)$. As regards the boundary conditions, the situation is no different from that presented by the elementary quantum mechanics of a particle in a time-dependent potential. If there is no reference system in which the external potential is static, there are simply no stationary states. On the other hand, if there is such a reference frame, and if the walls can be idealized as infinitely high potential barriers, the boundary condition is $\psi = 0$ at the boundaries in the selected frame. With the hydrodynamic representation $\psi = R \exp[iS/\hbar]$, the condition is that the density R^2 is zero at the boundary. There are no conditions on the velocity potential, i.e. on the tangential or normal components of the velocity, as would be the case in ordinary hydrodynamics. That the $\psi = 0$ boundary condition fully determines the motion, follows by analogy with elementary quantum mechanics, since the nonlinear term $V\psi\,|\psi|^2$ plays no essential role in this type of question. In some cases the infinite potential assumption is inadequate and one may have to include the Van der Waals attraction between the atoms of the system and the walls.[21]

Rotating Circular Cylinder

As an example, we examine a Bose gas at absolute zero in a perfect circular cylinder (of radius b) rotating with angular velocity ω. There are then stationary states in the rotating frame given by the eigenstates of the Hamiltonian $H - \omega J_z$. For a many-body wavefunction Ψ_R in the rotating frame, we are presented with the problem

$$\delta\int \Psi_R^*\{H - \omega J_z\}\Psi_R\, d\tau = 0, \quad \int \Psi_R^*\Psi_R\, d\tau = 1. \tag{4.1}$$

We are to find the eigenfunctions and eigenvalues and to label them in order of increasing eigenvalues E_R. In the stationary frame, each such eigenfunction corresponds to a wavefunction

$$\begin{aligned}\Psi_s &= e^{i\omega t i_z}\Psi_R(r_1, \nu_1, z_1, \cdots)\exp[-iE_Rt/\hbar] \\ &= \Psi_R(r_1, \nu_1 - \omega t, z_1, \cdots)\exp[-iE_Rt/\hbar].\end{aligned} \tag{4.2}$$

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[21] C. G. Kuper, *Proc. Intern. Conf. Low Temp. Phys. 7th, Toronto, Ont.*, edited by Graham and Hallett (University of Toronto Press, Toronto, Canada, 1961), p. 516.

The expectation value of the energy in the stationary system is $E_R + \omega \bar{J}_z$ where $\bar{J}_z$ is the expectation value of the angular momentum. In the Hartree approximation the problem is to find the solutions of

$$E_R\psi_R = -\frac{\hbar^2}{2M}\nabla^2\psi_R + V\psi_R\,|\psi_R|^2 - \omega\left(-i\hbar\frac{\partial}{\partial\nu}\right)\psi_R$$

$$\int |\Psi_R|^2\,d^3x = N, \qquad \psi_R(r = b) = 0. \tag{4.3}$$

We remark that to obtain the stationary states does not directly answer the question of what will happen to such a system when the container is actually set rotating. We return to this consideration shortly.

One solution of Eq. (4.3) is $\psi_R = (N/\Omega)^{\frac{1}{2}} \exp[-iE_Rt/\hbar]$. This is true everywhere except in a healing layer near the boundary $r = b$. We will not try to write the exact solution that includes the boundary effect. The important point is that ψ_R is independent of ν and also of ω. The wavefunction in the stationary system is then the same as ψ_R. Since ψ_R is real, the velocity potential is zero and this can be interpreted as saying that the superfluid is at rest.

On the other hand, we can refer to the problem of the ideal Bose gas (without the self-consistent field term, i.e., $V = 0$) for guidance. This has been studied carefully by Blatt and Butler.[22] The solution corresponding to that of the previous paragraph has all the particles in a zero angular-momentum state. The radial function has no modes but the boundary condition at $r = b$ forces the large unphysical density variation characteristic of the ideal Bose gas. On the other hand we do get an important clue from the ideal gas. When ω reaches a value $4.45\ \hbar/Mb^2$ (a very small angular velocity), the lowest eigenvalue of $H - \omega J_z$ is a state in which each particle has unit angular momentum for which the density vanishes along the axis of the container. But with the self-consistent field, this corresponds to a single vortex about the axis of the container. This is indeed a solution of Eq. (4.3), except in the healing layer near the wall. It corresponds to a value of E_R,

$$E_R = (\hbar^2/2M)\rho \ln(b/a) + V\rho - \hbar\pi. \tag{4.4}$$

Thus if $\omega > (\hbar/2M)\ \rho \ln(b/a)$, the value of E_R is lower than for the state where the superfluid is at rest. One can look at the vortex state in the laboratory frame. It corresponds to a stationary state of angular momentum $N\hbar$ and energy $E_R + \hbar\omega$. The fluid is hardly moving near the container walls.

For an ideal Bose gas at absolute zero, the system makes a series of abrupt transitions as ω is increased. All the particles move to a state of higher angular momentum. On the other hand, it is not obvious what the lowest eigenstate is for the weakly interacting Bose gas. A single vortex in which each particle has μ units of angular momentum has an energy μ^2 times the energy of the simple vortex. It is unstable and could decay to form a number of vortices, which add up to the same angular momentum. For example, μ vortices have a much lower energy, even when one includes the extra cores. However, since one has the freedom to introduce well separated lines or surfaces of singularity almost at will, it is hard to be certain of the correct flow pattern. The calculation may be sensitive to the core-energy estimate. In the literature, proposals involving vortex sheets (which are hydrodynamically unstable) as well as parallel filaments have been considered.

For angular velocities of experimental importance, it emerges from all of these proposals that there is a large number of singular lines or surfaces. The Onsager–Feynman array of packed vortex filaments parallel to the axis of rotation appears to be the preferred arrangement, since it minimizes the amount of core volume, and simulates rigid-body rotation very closely on the average. The preference for an arrangement close to rigid-body rotation is clear since there is then no kinetic energy in the rotating reference frame. $H - \omega J_z$ is the total energy in the rotating frame. Rigid-body rotation is forbidden, since with $\mathbf{v} = \boldsymbol{\omega} \times \mathbf{r}$ there is a continuous distribution of vorticity curl $\mathbf{v} = 2\boldsymbol{\omega}$. For example, in the self-consistent field approximation the equation of motion does not have such a solution. Since $\mathbf{v} = \nabla S$, curl $\mathbf{v} = 0$ except on singular lines and surfaces. (We shall see later that the corrections to the Hartree theory actually permit volume vorticity, but only localized in the cores of vortices. This does not affect the present argument.) At reasonable angular velocities, a calculation based on the vortex filament idea leads to $2M\omega/h$ lines crossing a unit area normal to the axis of rotation. The energy in the stationary system for such an arrangement differs from the rigid-body value by a fraction of a per cent.

Mechanism of Entrainment of Superfluid

The fact that the lowest state involves some distribution of vorticity does not necessarily mean that when a cylinder is accelerated from rest, the fluid will reach this state. To convert superfluid from a state at rest to a state where a vortex is present requires moving an appreciable body of fluid. How-

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[22] J. Blatt and S. T. Butler, Phys. Rev. 100, 476 (1955).

ever, nonstationary disturbances in the condensate can exchange momentum as they impinge normally on a boundary even with the condition $\psi = 0$ (cf. Sec. V). Conversely, if the wall has protuberances, (or even if it is not exactly circular) it would be expected to excite disturbances in the superfluid when the container is in nonuniform rotation. For example the disturbances might be large-amplitude compression waves. The equilibrium state would be expected to be reached by a complicated intermediate process. The experimental situation in helium is not entirely clear at present. It has been possible to approach the Onsager–Feynman equilibrium by cooling from the λ point.[4] In direct experiments on accelerating the superfluid from rest,[4] it is much more difficult to produce the equilibrium circulation. More extensive experimental and theoretical analysis is required. However, we do not feel that difficulty in producing equilibrium contradicts the Onsager–Feynman definition of the nature of the equilibrium.

It should be noted that the classical field (or Hartree) analysis views all excitations as disturbances of the condensate. The normal fluid consists of those excitations that are thermally excited at a given temperature and come to equilibrium by mutual interactions. From this point of view, a large-amplitude compression wave is simply a disturbance of the condensate, although, of course, when it breaks up some of the energy ultimately becomes normal fluid.

V. TIME-DEPENDENT HARTREE APPROXIMATION

We have thus far confined the discussion to solutions of Eq. (2.4) of the form $\psi(\mathbf{x}, t) = f(\mathbf{x}) \exp[-iEt/\hbar]$ i.e., separable in time and space. This provides the security that, at the very least, they have the clear quantum mechanical interpretation of approximations to special stationary states of the exact many-body system. Of course we do not know how good these approximations are, (even for the weak smooth potential we have in mind). In the case of the excited states, such as a vortex line, we have as yet no idea as to the lifetime of the states. It has emerged, however, that Eq. (2.4) is an interesting hydrodynamical model. In fact, it seems to be more satisfactory than the equations of an ideal fluid, since the presence of a de Broglie length fully determines the structure of vortices.

It is natural to extend the discussion of Eq. (2.4) to include more general space–time solutions. In the quantized wave description, the Hamiltonian of the many-body system is

$$H = \frac{\hbar^2}{2M} \int \nabla \boldsymbol{\psi}^+ \nabla \boldsymbol{\psi}\, d^3x + \frac{1}{2} \iint \boldsymbol{\psi}^+(\mathbf{x}) \boldsymbol{\psi}^+(\mathbf{y}) \times V(\mathbf{x} - \mathbf{y}) \boldsymbol{\psi}(\mathbf{y}) \boldsymbol{\psi}(\mathbf{x})\, d^3x\, d^3y,$$

where the bold faced operators obey the commutation rules

$$[\boldsymbol{\psi}(\mathbf{x}), \boldsymbol{\psi}^+(\mathbf{y})] = \delta(\mathbf{x} - \mathbf{y}), \qquad [\boldsymbol{\psi}(\mathbf{x}), \boldsymbol{\psi}(\mathbf{y})] = 0,$$

and we are interested in eigenstates of the number operator $\mathbf{N} = \int \boldsymbol{\psi}^+ \boldsymbol{\psi}\, d^3x$. The Heisenberg equation of motion is

$$i\hbar \frac{\partial \boldsymbol{\psi}}{\partial t} = -\frac{\hbar^2}{2M} \nabla^2 \boldsymbol{\psi} + \boldsymbol{\psi} \int V(\mathbf{x} - \mathbf{y}) \boldsymbol{\psi}^+(\mathbf{y}) \boldsymbol{\psi}(\mathbf{y})\, d^3y.$$

The proposal[9] is to study the operator equation of motion as a classical wave theory, and then to establish the relevance of the results to the quantized wave description of the many-body system. The classical wave theory is closely related to the time-dependent Hartree approximation.

In a classical theory, after one has exact solutions, the next natural step is to study the small oscillations about the exact solution. If we write

$$\psi(\mathbf{x}, t) = \exp[-iEt/\hbar]\{f(\mathbf{x}) + \varphi(\mathbf{x}, t)\}, \tag{5.1}$$

the linearized equation of motion for $\varphi(x, t)$ is (using the feature that f is an exact solution),

$$i\hbar\dot{\varphi} = -\frac{\hbar^2}{2M} \nabla^2 \varphi + \varphi \int V(x - y)\, |f(y)|^2\, d^3y + f(x) \int V(x-y)\{f(y)\varphi^+(y) + f^*(y)\varphi(y)\}\, d^3y. \tag{5.2}$$

This is a linear integer-differential equation for the complex function $\varphi(x, t)$. One may look for the normal modes and proper values. An alternative form for the small oscillation theory can be obtained from the hydrodynamical form. With $S(\mathbf{x}, t) = -Et + S_0(x) + \tilde{S}(\mathbf{x}, t)$, we find in linear approximation

$$\frac{\partial \tilde{\rho}}{\partial t} = -\frac{1}{M} \nabla(\rho_0 \nabla \tilde{S} + \tilde{\rho} \nabla S_0)$$

$$-\frac{\partial \tilde{S}}{\partial t} = \frac{1}{M} \nabla S_0 \cdot \nabla \tilde{S} - \frac{\hbar^2}{2M}\left[\frac{1}{\rho_0^{\frac{1}{2}}} \nabla^2\left(\frac{\tilde{\rho}}{\rho_0^{\frac{1}{2}}}\right) + \frac{\tilde{\rho}}{\rho_0} \frac{\nabla^2 \rho_0^{\frac{1}{2}}}{\rho_0^{\frac{1}{2}}}\right]\frac{1}{2} + \int V(x - y)\tilde{\rho}(y)\, d^3y. \tag{5.3}$$

Disturbances in a Condensate with Periodic Boundary Conditions

For the special case of the uniform ground state with periodic boundary conditions $\rho_0 = (N/\Omega)^{\frac{1}{2}}$ and $S_0 = 0$, the equations reduce to

$$\begin{aligned} \frac{\partial\tilde{\rho}}{\partial t} &= -\frac{1}{M}\rho_0\nabla^2\tilde{S} \\ -\frac{\partial\tilde{S}}{\partial t} &= -\frac{\hbar^2}{4M}\frac{1}{\rho_0}\nabla^2\tilde{\rho} \\ &\qquad + \int V(x-y)\tilde{\rho}(y,t)\,d^3y. \end{aligned} \tag{5.4}$$

The solutions are of the form $\tilde{\rho} \propto e^{i(k.x-\omega t)}$

$$\hbar^2\omega^2 = \left(\frac{\hbar^2k^2}{2M}\right)^2 + \frac{\rho_0V_k}{M}\hbar^2k^2. \tag{5.5}$$

This is the famous Bogolyubov quasiparticle spectrum.[8] At long wavelengths $\omega \to k(\rho_0V_0/M)^{\frac{1}{2}}$, yield ing a sound dispersion relation. As $k \to \infty$, $\omega \to \hbar k^2/2M$, which is a free-particle dispersion relation. Here the Bogolyubov quasiparticles are interpreted as small-amplitude density waves of the superfluid condensate. This interpretation gives rise to the question, vital for the microscopic picture of the Tisza two-fluid model, of when motions belong to the superfluid and when they are to be assigned to the normal fluid.

Disturbances in the Presence of a Wall

In an unbounded medium one can form a wavepacket representing a general small-amplitude disturbance in the condensate. If long wavelengths alone are used, the packet propagates as a sound pulse with small dispersion. If short wavelengths are used the propagation is highly dispersive, as for free particles in quantum mechanics. In either case, if the underlying condensate were uniform up to a wall, the disturbance could be directed as a wall. It would be reflected and a net momentum exchange would occur, compatible with the condition that the amplitude of the disturbance is zero at the wall. Of course, in the presence of a wall, the condensate has the variable density $\rho = \rho_0 \tanh^2 (x/a)$. Long-wavelength disturbances are hardly affected by this variation. Disturbances made up of wavelengths short compared to a, can be thought of as having a variable frequency which tends to $\hbar k^2/2M$ as $\rho \to 0$ near the wall. They therefore reflect as free-particle wavepackets.

A detailed study of this process could be made by studying the spectrum of Eq. (5.2) with $f(x) = \rho_0^{\frac{1}{2}} \tanh (x/a)$. It has, however, not yet been carried out.

Large-Amplitude Plane Waves[9]

It is possible to find solutions of Eq. (2.4), of the form

$$\psi(\mathbf{x}, t) = \exp\,[-iEt/\hbar]\exp\,[i(M\mathbf{v}\cdot\mathbf{x}/\hbar)]\phi(\mathbf{x} - \boldsymbol{\lambda}t). \tag{5.6}$$

They represent a combination of a mass flow of the superfluid and a large-amplitude disturbance. The disturbance becomes static in a suitable reference frame. Such solutions are compatible with a restricted class of initial value problems, and it would be instructive to study the stability characteristics. However, it is more difficult to find solutions satisfying boundary conditions. It would be instructive to have solutions representing the excitation of large-amplitude compression waves of the condensate by an oscillating boundary.

Small Oscillations of a Vortex Line

We turn next to the small-oscillation spectrum of the system when a single vortex is present. Here, $\rho = \rho_0(r)$ is given in Eq. (2.13) and $S_0 = \hbar\nu$. The spectrum has two branches, the vortex waves, and the scattering solutions.

A. *Vortex Waves*

These are solutions in which $\tilde{\rho}$ and $\tilde{S}$ have the dependence $\tilde{\rho} = A(r, \vartheta)e^{i(kz-\omega t)}$, $\tilde{S} = B(r, \nu)e^{i(kz-\omega t)}$, $\tilde{S} = B(r, \nu)\,e^{i(kz-\omega t)}$, i.e. they are waves traveling along the vortex line. The physical origin lies in the fact that the energy of a vortex line is proportional to its length, so that a deformation produces a restoring force. These excitations are "bound" states in which the functions $A(r, \nu)$ and $B(r, \nu)$ decay to zero as one moves out from the line center. The characteristic decay length is $1/k$.

The oscillations of a vortex line in an incompressible fluid were discussed by W. Thomson.[23] The hydrodynamic equations used were

$$\begin{aligned} \operatorname{div}\mathbf{v} &= 0, \\ \partial\mathbf{v}/\partial t + (\mathbf{v}\cdot\nabla)\mathbf{v} &= -\nabla p, \end{aligned} \tag{5.7}$$

where p is the pressure. He found that undamped circularly polarized waves represented by

$$\begin{aligned} \tilde{v}_r &= V_r(r)\cos kz\sin(\omega t - \nu), \\ \tilde{v}_\nu &= V_\nu(r)\cos kz\cos(\omega t - \nu), \\ \tilde{v}_z &= V_z(r)\sin kz\sin(\omega t - \nu), \\ \tilde{p} &= \tilde{P}(r)\cos kz\cos(\omega t - \nu), \end{aligned} \tag{5.8}$$

are possible.

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[23] W. Thomson, *Collected Works* (Cambridge University Press, London, 1910), Vol. 4, p. 152.

The corresponding problem for the superfluid was studied by Pitaevski on the basis of Eq. (5.2). The waves have similar characteristics to those found by Thomson. Pitaevski finds for long wavelengths,

$$\omega \rightarrow (\hbar k^2/2M) \ln (1/ka). \tag{5.9}$$

The perturbation in velocity falls off more rapidly than the density perturbations.

The Onsager–Feynman hypothesis has found its most dramatic confirmations in experiments involving vortex waves.

B. *Scattering Solutions*

Far from the vortex line center, the superfluid is hardly moving. There exist disturbances which go over into the Bogolyubov excitations at large distances. By a suitable choice of boundary conditions one can find eigenfunctions of Eq. (5.2) which provide a stationary-state description of the scattering of an excitation by a vortex line. The theory is simple in the limit of phonons when the wavelength is large compared to the size of the vortex core. In that case, the density variation in the core of the underlying condensate can be neglected. The solution is then quite similar to the scattering of sound waves by a vortex line in a classical compressible fluid. This problem has been studied by Pitaevski.[24]

The continuum solutions are important in determining quantum corrections to the energy of a vortex line. If the system is enclosed in a large cylinder and one requires that the wavefunctions vanish on the container walls, a standing-wave description is appropriate. The quasi-continuous eigenfunctions experience energy shifts in the presence of the vortex line. The total zero-point energy shift then provides a correction to the Hartree energy of the vortex.[15] This correction is significant because it yields a modification of the classical energy-dependence on the superfluid density. The knowledge of the precise dependence of the energy is important in many problems, particularly in experiments on the pressure variation of flow phenomena. It has, however, not yet been studied in any detail, even for the weakly interacting Bose gas. The zero-point effects are also responsible for spreading the vorticity over the core volume, a basic conceptual point.

VI. LANDAU'S CRITERION FOR SUPERFLUIDITY

Landau's argument is essentially one involving degeneracy of quantum states or entropy at rests on Galilean invariance. We will amplify his argument. Suppose $\Psi(\mathbf{x}_1, \cdots \mathbf{x}_N)$ represents an exact solution of the many-body Schrödinger equation for the superfluid in a pipe. We assume the pipe to be represented by a static external potential. It is assumed to be uniform so that Ψ is an exact eigenfunction of the momentum. One can verify directly that if Ψ is an eigenfunction of energy E, then $\exp [i(M\mathbf{v}/\hbar)\cdot\sum \mathbf{x}_i]\Psi$ is also an eigenfunction of energy $E + N(Mv^2/2)$. It differs from Ψ by a mass flow of velocity $\mathbf{v}$. Now let Ψ represent, successively, the ground state Ψ_G with energy E_G and an exact eigenstate $\Psi(\mathbf{k})$ representing an excitation of wave vector $\mathbf{k}$ with energy $E_G + \epsilon(\mathbf{k})$. It is assumed for the sake of concreteness that a wave vector $\mathbf{k}$ can be used to label the excitations with sufficient accuracy. Then one can verify, again by direct substitution, that the energies of the corresponding states of the moving fluid are $E_G + N(Mv^2/2)$ and $E_G + N(Mv^2/2) + \epsilon(k) - \mathbf{k}\cdot\mathbf{v}$. As long as $\epsilon(\mathbf{k}) - \mathbf{k}\cdot\mathbf{v} > 0$ for all excitations, the lowest state of the moving fluid is separated from the state involving an excitation. But when v has the value $\epsilon(k)/k$, the state involving an excitation moving in the opposite direction from the fluid has equal energy, and the lowest state becomes degenerate. The crucial point is that we are looking for states of equal energy but with different total momenta. (The momenta are $NM\mathbf{v}$ and $NM\mathbf{v} + \hbar\mathbf{k}$ respectively). The extra momentum is supplied by an irregularity in the wall. As noted earlier, an exchange of momentum by a static potential such as a rigid irregularity is compatible with the vanishing of the wavefunction. Landau's argument is a characteristic one in statistical mechanics. The perturbation supplies the momentum and provides a matrix element to cause the transition, but is assumed so small that it does not disturb the labelling of states of the system.

Landau estimates the critical velocity by taking the value of k that gives the lowest v. This condition $(\partial/\partial k)(\epsilon - \mathbf{k}\cdot\mathbf{v}) = 0$ fixes k as the value at which the group velocity $d\epsilon/dk$ equals the phase velocity ϵ/k. Landau first applied the argument to the phonon–roton spectrum. This led to much too large a critical velocity (70 m/sec), to explain experimental data. However, it is clear that all the possible types of excitations of the system must be examined to find the ones excited at the lowest velocities.

It would be satisfying to have a detailed illustra-

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[24] L. P. Pitaevski, J. Exptl. Theoret. Phys. (U.S.S.R.) **8**, 888 (1959) [translation: Soviet Phys.—JETP **35**, 1271 (1958)].

tion of the mechanism of the breakdown of superfluidity. For example, one might examine, using the classical field theory, the case of fluid passing a weak potential barrier. This provides a one-dimensional case. At low velocities, the flow should be smooth on both sides and through the barrier. But at higher velocities, phonon–roton in stability should develop and the solutions should show a "backwash" of excitations created at the barrier. This calculation has not been carried out. However, it indicates the close similarity of the problem to that of the breakdown of laminar flow in classical fluid dynamics.

With the introduction of vortex lines and rings, hope has increased that a detailed understanding of critical phenomena can be found. Feynman called attention to the possibilities of vortex rings. The classical formulas for vortex rings of radius R,

$$\epsilon \approx 2\pi^2 R\rho \frac{\hbar^2}{M^2} \ln (R/a),$$

$$k \approx 2\pi^2 R^2 \rho \frac{\hbar}{M},$$

imply

$$(\epsilon/k) = (\hbar/MR) \ln (R/a).$$

For a pipe of radius d, the largest ring radius possible is also of order d. This gives a dependence of critical velocity on pipe radius which is essentially in agreement with experiment, but the absolute value is still too large.

It should be noted that the very existence of large vortex rings implies that the critical velocity should tend to zero in suitable large channels. This prediction presupposes that there is an appreciable matrix element to cause the transition. We have a similar problem to that of entrainment of superfluid in a rotating cylinder. It is not easy to change the state of a large volume of superfluid. The critical velocity should therefore depend on the pipe geometry and irregularities. Perhaps the specific model discussed here can aid in the analysis of the experimental data.

VII. EXCITATIONS OF THE CLASSICAL FLUID AND THE QUANTUM MANY-BODY PROBLEM

We have proceeded by taking the classical wave equation (2.4) seriously enough to study not only special solutions which can be identified as Hartree approximations to stationary states, but also more general space–time solutions. It is necessary to understand the relations of this classical analysis to the actual quantum many-body problem. We start by describing in intuitive terms, the picture that underlies the formal scheme based on the quantized wave representation.

One expects the small-oscillation spectrum for a given inhomogeneous condensate to correspond to a quasiparticle spectrum in the many-body theory. In the case of the uniform condensate, the oscillation spectrum was that of the Bogolyubov quasiparticle theory. However, there are characteristic relationships between any classical and quantum theory that certainly must appear. An oscillation spectrum in quantum theory implies zero-point motions and a zero-point energy. The classical assumption of infinitesimal oscillations is incompatible with the commutation relations. Thus, in the quantum theory we must find the imprint of the quasiparticle spectrum in the ground state wavefunction. In general the Hartree approximations must be refined to include this effect.

In the simple Bogolyubov theory the modified energy of the ground state is

$$E_G = N\rho_0 \int V(x)\, d^3x + \tfrac{1}{2} \sum_{k\neq 0} \left\{\hbar\omega_k - \left(\frac{\hbar^2 k^2}{2M} + \rho_0 V_k\right)\right\}.$$

It may be interpreted as a Hartree energy plus a (negative) shift in total zero-point energy. The term $\frac{1}{2}\rho_0 \sum V_k$ occurs in the unperturbed spectrum because there are diagonal elements in the Hamiltonian involving the interaction. In the same way, the energy of a vortex line relative to the state with no line is not just the difference of the simple Hartree energies. One must also include the difference of the total zero-point energies of the respective excitation spectra.

There are also important changes in the expectation values when they are recomputed with the enriched Hartree wavefunction. The momentum distribution, which is defined as the expectation value of $\sum_{i=1}^{N} \delta(p_i - k)$ (or of $n_k = a_k^+ a_k$ in the quantized wave description), retains the special delta function occupancy of the $k = 0$ mode. But this state is depleted by an amount that depends on the interaction. There is, in addition, a spread of the depleted particles over the states with $\mathbf{k} \neq 0$. The correlation function contains a short-range component as well as the long-range order arising from the existence of a finite fraction of the particles in a single-particle state. In the case of a vortex line, the density expectation value no longer goes to zero at the line center and the velocity deviates from the $1/r$ behavior in the core of the vortex. It is found that the vorticity is not zero in the core.[15] Thus the Hartree approximation of concentrated vorticity on a singular line is modified to yield a localized volume vorticity. The circulation is no longer quantized for a small circuit inside the core. Physically, it is the zero-point motions of the phonons that prevent strict localization of the position of the singular vortex line (node of the wavefunction) and hence of the vorticity. This is the same physical effect as the Lamb shift in quantum electrodynamics.[25]

The reason that one can make such a simple connection between the classical and quantum wave theories is that in both cases a linearization of the equation of motion is involved. Furthermore, the process of solution can be put in Hamiltonian form. Corresponding to a classical solution

$$\psi(x) = \exp\,[-iEt/\hbar]\{f(x) + \varphi(x, t)\},$$

one can introduce the time-dependent transform $\psi \rightarrow \psi \exp\,[-iEt/\hbar]$ to remove the time dependence. The Hamiltonian goes over to $H - EN$. The situation can be referred to the special solution $f(x)$ by the canonical transform $\psi(x) \rightarrow f(x) + \psi(x)$. These operations are identical in the classical and quantum wave theories. The transformed Hamiltonian

$$H'(\psi, \psi^+) = H(f(x) + \psi(x), f^* + \psi^+(x)) - E \int (\psi^+ + f^*)(\psi + f)\, d^3x$$

then breaks up into a series of five terms, ordered according to the number of ψ and ψ^+ functions occurring. Both the classical and quantum wave theories form the main attention on terms at most quadratic in the field variables and reduce this part of the Hamiltonian to diagonal form by a normal mode transformation.

In the classical theory one appeals to the possibility of oscillations of infinitesimal amplitude to neglect the anharmonic terms, provided the spectrum is stable. For small but finite amplitudes, the anharmonic terms represent interactions that scatter, create and destroy, and shift the frequency of normal modes. The finite-amplitude classical theory is in fact quite similar to the quantized wave theory where the effects of the anharmonic terms are even revealed in the ground state. The actual choice of the preferred state $f(x)$ and of the coefficients of the normal mode transformation is affected by time averages of the anharmonic terms. Perturbation theory can be used to analyze these terms in detail in both classical and quantum theories. Beyond the linear approximation, there is no clear understanding of the degree of correspondence between the classical and quantum theories. But we have no reason to believe that problems that are difficult for classical theory are easy for the quantum theory.

Our entire discussion has concerned a system of weakly repelling bosons at a temperature of absolute zero. A small number of quasiparticle excitations implies a negligible energy per particle for a large system. At a finite temperature, there is a nonvanishing energy per particle and a finite fraction of the total energy carried by quasiparticles. The equilibrium statistical properties of a dilute gas of hard spheres have been studied in detail by Lee and Yang.[26] They present no difficulties of principle, leaving apart the question of whether the approximations are adequate in the vicinity of the λ point.

It is harder to give a foundation to the two-fluid model. Lee and Yang[27] have given a particular clear and explicit formulation for the case of a gas of hard spheres. The two-fluid theory can be derived on the two assumptions that the condensate state is to be given special treatment, and that the excitations are in thermal equilibrium with each other. There has been a great deal of work by Landau and his collaborators concerning the kinetic theory of the approach to equilibrium in liquid helium. This work, while undoubtedly substantially correct, rests on a semiphenomenological foundation. We have no derivation from first principles.

The work of Lee and Yang is easily extended to include the more general condensates described in this paper. Since we have taken the point of view that all excitations are nonstationary disturbances of the condensate, we must face the question of when a disturbance "belongs" to the normal fluid. The problem is particularly interesting for small vortex rings and their oscillations, or for waves on a vortex line. We take the attitude that two conditions are necessary. First, at any given temperature, it is required that excitations are excited with appreciable probability thermally. This requires a favorable statistical weight and Boltzmann factor. Second, a two-fluid description is possible for processes involving characteristic lengths or times, large compared to the mean free path or collision time for the excitations. It is of course conceivable that there are situations where equilibrium is reached separately for the members of classes of excitations, but there is no equilibrium between different classes. In that case, a multifluid hydrodynamics may be applicable.

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[25] T. Welton, Phys. Rev. **74**, 1157 (1948).

[26] T. D. Lee and C. N. Yang, Phys. Rev. **112**, 1419 (1958).

[27] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1406 (1959).

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A Microscopic Approach to Superfluidity and Superconductivity†

PAUL C. MARTIN
Department of Physics, Harvard University, Cambridge, Massachusetts
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This lecture describes certain properties of interacting Bose gases and superconductors which have recently been considered at Harvard. It is a brief resumé of work by the lecturer, P. C. Hohenberg, A. Fetter, R. Lange, and C. De Dominicis, which will be reported in mathematical detail elsewhere. It concerns attempts to derive from fundamental principles, several aspects of the macroscopic two-fluid model of London, Landau, and Tisza, the Landau phonon spectrum for bosons, and the structured condensate envisaged by Onsager and Feynman. The lecture describes new results which have been obtained concerning: (1) methods for calculating properties of large, but not necessarily infinite, condensed systems at finite temperatures; (2) methods for performing calculations in boson systems consistent with current conservation and sum rules; (3) results obtained by these methods for the phonon spectrum; (4) more accurate results for the less physical single-particle spectrum at finite temperatures; (5) results obtained for the macroscopically structured condensate in rotating systems which agree with the macroscopically inferred results of Feynman and Onsager; (6) results which treat depletion of the condensate as a result of interaction consistently and verify that nonetheless, the superfluid density, as operationally determined, is not correspondingly depleted; (7) methods in which the entropy plays a central role, for casting the macroscopic theory in a form which lays stress on the renormalized excitations of renormalized interactions; (8) the almost identical features of the mathematics for condensed Fermi and Bose systems; (9) a restatement, in this microscopic transcription, of the Feynman–Onsager argument for flux and vorticity quantization.

IN a conference dedicated to Lars Onsager for his work on irreversible processes, perhaps a greater tribute to him is the variety of other topics we are discussing to which he has contributed in a fundamental way. The subject of this lecture, a systematic microscopic approach to systems exhibiting superfluidity, bears his imprint in at least four respects. Onsager introduced the notion of quantized vorticity in liquid helium, he and Penrose suggested what is the proper general definition of the condensate in an interacting Bose system, and he predicted the quantization of flux in superconductors in units of $hc/2e$. Moreover, in the approach to be described, the thermodynamics and irreversible behavior of superfluid systems are inextricably tied together. They are both obtained by calculating self-consistently time-dependent correlation functions which are essentially the same ones introduced by Onsager in the discussion of irreversible behavior thirty one years ago. Pierre Hohenberg, Robert Lange, Alexander Fetter, and Cyrano De Dominicis have collaborated in various aspects of the work reported here.

In this report our ideas and results will be stressed. The manner in which they lead to a practical successive approximation scheme will be reported in separate publications.

The macroscopic theory of superfluid systems, and in particular of superfluid helium, appears to be rather well understood. This theory has two important facets. The first is the characterization of the system, for many purposes, by two additional thermodynamic parameters which are generally taken to be the relative density and velocity of two interpenetrating fluids. This theory, proposed by Tisza and Landau, and discussed extensively by many authors, may be used to analyze most transport and steady-state phenomena in liquid helium, at all but the lowest temperatures and near the critical point. Of the two fluids, one, the superfluid is supposed to comprise the whole fluid at zero temperature, disappearing at the critical temperature.

The second feature of this macroscopic description is the possibility of structure in the superfluid. This feature has been independently investigated by Onsager and Feynman with similar conclusions. In particular, both of them have pointed out the possibility of vorticity, and indeed of the quantization of this vorticity. They discuss how this vorticity may be used to explain the critical velocities in liquid helium and the peculiarly normal behavior of the surface of a bucket of rotating liquid helium. The possibility of each of these facets in superconductors, persistence of supercurrents and quantization of flux, has been confirmed experimentally.

In the discussion of these phenomena from a microscopic point of view, the first important observation was that of London who noted that some

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of the qualitative features of liquid helium could be understood in terms of the free Bose gas. Indeed it is natural to associate the fraction of superfluid with the fraction of the Bose gas condensed in the lowest-energy single-particle mode.

The second essential advance in the microscopic theory was made by Bogolyubov in 1947. This advance consisted in recognizing that, when a mode was macroscopically occupied, it was more important, in treating the system approximately, to take into account nondiagonal features of this macroscopically occupied mode than to insist that an approximate density matrix consist of eigenfunctions of the number operator. Indeed, making the crudest approximation incorporating this feature, he showed that the behavior of a Bose gas with weak repulsive interactions was modified in an essential way. Whereas the energy ω required to remove a particle of unit mass (we shall also take $\hbar = 1$) and wavenumber k from a noninteracting Bose gas is $\frac{1}{2}k^2$, the energy necessary to remove a particle from a dilute weakly interacting system at zero temperature is:

$$\omega = \tfrac{1}{2}k(k^2 + 2\kappa^2)^{1/2} + \mu,$$

where μ the chemical potential, is approximately $\kappa^2 = \frac{1}{2}\rho v(0)$ and $v(0)/4\pi$ the scattering length. To the order of this calculation, the density and the condensate density are the same and therefore the energy necessary to remove a particle of wavenumber $\mathbf{k}$ (apart from μ) is phonon-like with a velocity equal, in this approximation, to the velocity expected of compressional sound waves in a system with its approximate density–pressure relationship. These excitations are therefore naturally identified with the phonons which Landau previously introduced as the normal fluid at low temperature.

Now it was pointed out by Onsager and Penrose that in real liquid helium, or in any interacting Bose system, the analogy between superfluid and Bose condensate was less direct. They observed that there was a unique reasonable definition for the fraction of condensate. In particular they argued that the reduced density matrix of the condensed Bose system must take the form

$$\rho(\mathbf{r}\mathbf{r}') = \langle\psi(\mathbf{r})\rangle\langle\psi^\dagger(\mathbf{r}')\rangle + \gamma(|\mathbf{r} - \mathbf{r}'|),$$

where $\gamma \to 0$ as $|\mathbf{r} - \mathbf{r}'| \to \infty$. The condensed mode could then have a stationary-state single-particle wavefunction $\langle\psi(\mathbf{r})\rangle$ associated with it, the fraction of condensate being determined by its normalization. In fact, the requirement of singlevaluedness on this measurable part of the density matrix is what leads to quantization of vorticity. Onsager and Penrose also observed that the condensed mode must be considerably depleted as a result of the interactions. Indeed they estimated that the density (ρ_0) of the condensed mode of liquid helium probably was only 8% of the total density ρ at 0°K. Since in real liquid helium the phenomenological parameter ρ_s is equal to ρ at low temperatures, a microscopic theory must distinguish between ρ_s and ρ_0.

By the same token, when depletion is significant, there is no compelling reason to expect the single-particle excitations computed by Bogolyubov to coincide with the density excitations or phonons discussed by Landau. The Bogolyubov computation is concerned with an approximate determination of the dominant excitation energy of the nonstationary state resulting from the creation or destruction of a particle of small wave number $\mathbf{k}$. (Only in the crudest approximation, is this state stationary.) Landau discussed, and neutron experiments measure, the change in energy when the density of particles is altered slightly with small wavenumber k. We may make this distinction formal in the usual language of the ground-state wavefunction at zero temperature by introducing typical ground states of large systems with n and $n + 1$ particles, denoted by Ψ_0^n and Ψ_0^{n+1}. We then can say that the n-particle state $\Psi_\mathbf{k}'$ obtained by applying the Heisenberg destruction operator $\psi_\mathbf{k}$ to Ψ_0^{n+1}, need not in its resolution into energy eigenstates, contain, for the most part, states which differ in energy from Ψ_0^n by the same amount as the state $\Psi_\mathbf{k}''$ obtained by applying the operator $\rho_\mathbf{k} = \sum_\mathbf{q} \psi_{\mathbf{k}-\mathbf{q}}{}^\dagger\psi_\mathbf{q}$ to Ψ_0^n. If depletion of a macroscopically occupied zero-wavenumber mode is negligible in Ψ_0^{n+1} *and* the dominant energy eigenstate in $\psi_0\ \Psi_0^{n+1}$ is Ψ_0^n, so that $\Psi_\mathbf{q}' = \psi_\mathbf{q},\ \Psi_0^{n+1} \cong n^{\frac{1}{2}}\ \Psi_0^n\ \delta_{\mathbf{q}0}$, the spectral resolutions of $\Psi_\mathbf{k}''$ and $\Psi_\mathbf{k}'$ will coincide. However, if Ψ_0^{n+1} contains Fourier components other than $\mathbf{q} = 0$, *or* if states of zero momentum other than the ground state are more frequently obtained by applying ψ_0 to Ψ_0^{n+1}, these spectra need not coincide.

This distinction is more conveniently and generally made in terms of correlation functions. That is to say, the positive-definite function

$$B(\mathbf{k}\omega) = 2 \coth \tfrac{1}{2}\beta\omega A(\mathbf{k}\omega)$$

$$= \int \exp\,[-i\mathbf{k}\cdot\mathbf{r} + i(\omega - \mu)t]\langle\{\psi^\dagger(\mathbf{r}t),\ \psi(0)\}\rangle\, d\mathbf{r}\, dt$$

need not, for every $\mathbf{k}$, be a function with the same dominating peak (as a function of ω) as the positive-definite function

$$S(\mathbf{k}\omega) = \int \exp(-i\mathbf{k}\cdot\mathbf{r} + i\omega t)\langle\{\rho(\mathbf{r}t), \rho(0)\}\rangle.$$

One might expect $B(\mathbf{k}\omega)$ to be nonzero in the neighborhood of the point $\bar{\omega} = ck$ at which the function $S(\mathbf{k}\omega)$ describing phonons is peaked, since there is no reason for $\rho_{\mathbf{k}}\Psi_0^n$ to be orthogonal to $\psi_{\mathbf{k}}\Psi_0^{n+1}$. On the other hand there is no *a priori* reason why the overlap of these states need be large. There is therefore no *a priori* reason to believe that the crudest approximation—one associating the best unique $\bar{\omega}$ with each k in the form $A(\mathbf{k}\omega) = 2\pi\lambda_{\mathbf{k}}\ \delta[\omega - \bar{\omega}(\mathbf{k})] + 2\pi(1 - \lambda_{\mathbf{k}})\ \delta[\omega + \bar{\omega}(\mathbf{k})]$ need yield for small k the same $\bar{\omega}$, the compressional sound velocity multiplied by k, at which we expect $S(\mathbf{k}\omega)$ to be peaked. Indeed, the Bogolyubov finite-temperature approximation does not give this velocity, although it leads to no gap in $A[\bar{\omega}(k) \to 0$ for small k.]

A density fluctuation satisfies particle conservation: when the density is increased in one part of the system it is decreased elsewhere. This property leads to what Feynman picturesquely calls backflow. With this backflow and momentum conservation, one can be sure that the density fluctuations will have no gap. They will usually have a soundwave-like dispersion relation quite apart from whether the single-particle excitations have this property.

While there is no such general argument for the function $A(\mathbf{k}\omega)$, there is a different, less general argument which Pines and Hugenholz proved in each order of perturbation theory. The theorem may be stated in the more general form: If in a condensed system, the macroscopically occupied mode is spatially uniform in any direction, then there will be no gap in the long-wavelength single-particle excitation spectrum in that direction unless the self-energy of the excitations cannot be expanded at long wavelengths and low frequencies. Their proof is the counterpart of the Van Hove—Hugenholz theorem which states that to all orders in Fermi systems, $\omega(k_F) = \mu$. In superconductors, that theorem is violated and the self-energy is singular. Their method of proof shows that whenever the spectrum is calculated from a sequence of nonsingular approximations which involve approximating the self energy in powers of the potential and the noninteracting single-particle propagator, there will be no gap in each stage of approximation. An example of the theorem is afforded by a system with a vortex line in the z direction in the condensate. Since the system is spatially uniform in the z direction, a perturbation calculation of the excitation spectrum leads to a spectrum which behaves as $\omega \approx ck_z^2 \ln(k_z/\kappa)$. We use this illustration to emphasize the fact that the theorem says nothing about how the spectral peak should move away from zero with increasing k, let alone what the velocity c should be if the peak behaves as $\bar{\omega} = ck$. As we have said, except at absolute zero, even in the lowest approximation for the spatially uniform case, the velocity of single-particle excitations differs from the velocity of sound. The existence of no gap in the exact answer is of course consistent with the expected lack of orthogonality between $\rho_{\mathbf{k}}\Psi_n^0$ and $\psi_{\mathbf{k}}\Psi_0^{n+1}$, i.e., with the likelihood that sometimes when a particle of momentum $\mathbf{k}$ is destroyed, the system will be left in a state in which there is one phonon with momentum $\mathbf{k}$.

However, this statement is quite different from the requirement that the dominant peak lie at this position. In particular, there is no reason to reject the simplest approximation in some other apparently less perturbative self-consistent scheme (in particular, one which involves perturbation theory in powers of real correlations) because it does not predict, in its lowest approximation, stable excitations for which $\bar{\omega} \to 0$ as $k \to 0$. In fact the prediction of a gap can be explained in two ways. The first is that the gap is real, the self-consistent scheme being an improvement over the scheme in which everything but the condensate is treated perturbatively. The second possibility—if the predicted gap is smaller than the accuracy of the calculation—is that in this respect, the scheme which gives rise to the best functions from a thermodynamic variational viewpoint is not as accurate as the more strictly perturbative scheme. It is of course easy to decide in principle. One must recalculate, with the self-consistent procedure, the best trial function containing all terms of the order of the predicted gap. If the gap does not disappear or at least become reduced in size to a term of higher order, it should be taken seriously. If the gap persists it must of course imply some kind of divergence in the more perturbative method, like the one occurring for a superconductor in the usual fermion perturbation theory.

The main purpose of this discussion is to indicate how to proceed systematically in the case when there are the distinctions between condensate and superfluid, and between phonons and single-particle excitations which we have explained. In particular, we have applied these techniques to treat the following boson problem. Both the absence of a gap in the observable density correlation function (indeed the presence of sound waves with the compressional velocity), and the fact that the spectrum satisfies the sum rule

$$\int_{-\infty}^{\infty} \tanh\left(\frac{\beta\omega}{2}\right) S(\mathbf{k}\omega)\omega \frac{d\omega}{2\pi} = \rho k^2,$$

where ρ is the *total* density, must be true even when the condensate is depleted. The single-particle excitation spectrum also must satisfy the sum rule

$$1 = \int \frac{d\omega}{2\pi} \tfrac{1}{2} \tanh \frac{\beta\omega}{2} B(\mathbf{k}\omega).$$

How does one generate, in a systematic manner, an approximation scheme consistent with these physical requirements when depletion is significant? We have found that the approximation techniques most convenient for solving this problem, and more generally for describing a two-fluid model, depart from the sequence of approximations which automatically lead to no single-particle excitation gap in their zeroth approximation. Nonetheless, in the first approximation which takes depletion into account, these approximations predict *phonons* which have the compressional sound velocity, and correlation functions which satisfy the sum rules.

As we have developed them, these techniques exhibit the extremely close parallel between the problems of superconductivity and superfluidity. Indeed, using this parallel, the distinction between condensate and superfluid, which has been resolved for the superconductor, ceases to be a problem. In the superconductor there is a pair wavefunction which is closely parallel to the single-particle wavefunction of the Bose system. The normalization of this wavefunction, the number of pairs, is very small in the weak coupling limit. It is a more useful microscopic quantity than the parameter ρ_s. Still, the latter parameter which approaches ρ at low temperatures is connected, in a specified way, with the former parameter involving the energy gap. Moreover, ρ_s may itself be identified from long wavelength transport properties of the system.

A superconductor is a two-component system with electrons and phonons. The momentum of the electrons themselves is not conserved. The mode of the entire system, which is similar to the helium phonon mode in the sense that it lies at low frequencies for low wavenumbers, is the lattice phonon mode. The dynamic structure function for the electrons, satisfies the same sum rule as $S(\mathbf{k}\omega)$, but, because the electron momentum is not conserved, it has a gap and its dominant peak for long wavelengths lies at the plasma frequency.

If, however, we had a one-component superconductor, (a Fermi gas with short range attractive interactions), the density correlations of the electrons would have to lie at low energies because of conservation of particles and momentum. Because of a Pines–Hugenholz theorem, fluctuations in the condensate would also possess no gap in this case. Not only are these statements satisfied, but the absence of a gap comes about in the simplest reasonable approximation in a manner which strongly couples the condensate fluctuations with density fluctuations in a system with two fewer or two more particles. These modes, which dominate the specific heat at sufficiently low temperatures do not, however, give rise to the principal peak in the single-particle spectral function $B(\mathbf{k}, \omega)$.

In the superconductor it is the pair wavefunction, and in the Bose gas the condensate wavefunction which is the appropriate quantity for discussing phenomena connected with vortices, flux quantization, impurities and the like. The latter function satisfies the Schrödinger-like equation which has been used by Gross and Pitaevskii to put the Onsager–Feynman vortices on a satisfactory basis at least for Bose systems with weak repulsive forces. The former has been used by Gorkov to make contact with and improve upon the Landau–Ginsburg theory. Here again we are immediately led to the notion of flux quantization by requiring single-valuedness of an effective wavefunction.

With the exception of the calculation of the Bose pair-correlation function previously referred to, a statement about the single-particle excitations at finite temperature, and some results on vortex excitations, none of the calculations we have performed on weakly interacting Bose systems is new. However, the method is an extremely useful one in that it yields a convenient flexible mathematical form for treating superfluids and superconductors at arbitrary temperatures, and in arbitrary spatially nonuniform configurations. For boson systems the method reduces for the one-particle propagator to the one employed by Belyaev in the spatially uniform zero-temperature boson problem. For fermions it reduces to the system extensively employed by Gorkov with a restriction on spins.

The idea we apply is best understood in terms of a more familiar example. The measurable properties in a simple model of a ferromagnet are expectation values of products of spin operators. If the calculation of these expectation values is attempted by some kind of coupled differential equation scheme, it is necessary to specify a spatial boundary condition on some of these expectation values since otherwise there will be many solutions corresponding to different orientations of the ferromagnet. Any kind of perturbation scheme implicitly involves the assumption that the inversion of all the coupled equations is unique. That is to say, it assumes that the limiting processes of averaging the coupled operator equations over states, and iterating in powers of the potential to solve them, can be interchanged. This is not true when the differential equations have many solutions, as they may when there are long-range correlations. When this is the case, and the averaging process is done before the iterative process, the iterative process does not converge. The terms which lead to a lack of convergence are sequences of terms which correspond to approximate expressions for certain functions. In particular, they correspond to approximations for fluctuations in quantities for which there would have been different solutions if the equations had been solved before averaging. Specifically, the quantities having large fluctuations are expectation values of products of spin operators at different space–time points. To derive a convergent approximation scheme with these large fluctuations, it is necessary to give these quantities a specific set of allowed values. These values, however, are among the unknowns. On the other hand, we do not wish to calculate them before averaging since the whole point of employing correlation function techniques is to save one from solving the problem before performing the thermal averaging.

The problem is circumvented in the following manner: We calculate the cumulant functions

$$\langle\sigma(\mathbf{r}t) - \langle\sigma(\mathbf{r}t)\rangle, \sigma(\mathbf{r}'t') - \langle\sigma(\mathbf{r}'t')\rangle, \cdots\rangle$$

for a distribution of states specified by a local magnetization (which varies macroscopically), as well as by a definite energy. That is to say, we calculate the correlations in fluctuations of $\sigma(\mathbf{r})$ as a functional of the local $\sigma(\mathbf{r})$. We suppose for simplicity that the correlations of fluctuations die down rapidly enough so that it would not be wrong to invert their averaging and the iterative solution procedures for them. From these equations we obtain approximations for the correlations of fluctuations as a functional of the value of $\langle\sigma(\mathbf{r})\rangle$. We then take the first equation of the hierarchy and use it to solve self consistently for $\langle\sigma(\mathbf{r})\rangle$. This equation will have many solutions. The thermally averaged correlation functions are then obtained, if desired, by averaging over values of $\langle\sigma(\mathbf{r})\rangle$.

A convenient method for generating these equations for $\langle\sigma\rangle$ and the correlations of its fluctuations is to introduce an infinitesimal external variable field which will energetically favor a particular $\langle\sigma(\mathbf{r})\rangle$. In the presence of the field, we can perform the thermal averages and go through the interactive procedures for computing correlations of fluctuations, in the same manner as with a nonmagnetic substance. It is not, however, the magnetic field which interests us, but rather the value of $\langle\sigma(\mathbf{r})\rangle$. It is therefore convenient to transfer our attention, at an early stage, from equations in which $\mathbf{H}(\mathbf{r})$ appears, to equations in which only $\langle\sigma(\mathbf{r})\rangle$ and its cumulants appear. In this manner, we can generate directly the set of equations with a multiplicity of solutions, but where each solution corresponding to a different density matrix gives rise to the same thermodynamic properties. These solutions are not equivalent, there being, in the absence of $\mathbf{H}$, one associated with each direction of the spin. The response to external disturbances of any of the density matrices (which of course still corresponds to extremely many states of the system) need not be the same. If not, we must specify the particular density matrix on which the experiment is performed. (For example, in the more relevant situation of flux quantization, the number of units of flux passing through the superconducting ring must be specified.)

We generate the equations in this form by performing a Legendre transformation from the thermodynamic potential as a functional of the magnetic field, to the free energy as a functional of the magnetization. The statement that the magnetic field vanishes becomes a statement that the free energy is minimal as a functional of the magnetization and this equation serves to determine the magnetization. To this equation is coupled the equations which determine the fluctuations of correlations, the latter being capable of iterative solution. These lead to a scheme of successive approximations, the magnetization having to be recalculated self-consistently at each stage. The thermally averaged correlation functions can, of course, be obtained by performing a final averaging, but as we have indicated, this final averaging is not appropriate for describing experiments of a nonthermodynamic nature. These ideas are immediately generalized to the case where pair or higher correlations of fluctuations must be specified, as for example, in a classical turbulent system. They must be applied to specify the specific equilibrium configuration characteristic of any system which has undergone a phase transition.

The method is applicable to any ring of operators whose expectation values characterize the different possibilities for measurements in a system. For quantum mechanical systems, the simplest way to construct such a ring is to use the quantum field and its adjoint. Condensation, the analog of ferromagnetism, occurs when the field—or in the case of superconductors, products of field variables—have long-range correlations.

We can understand this physically in terms of the Onsager–Penrose argument regarding the appropriate one-particle density matrix. In this matrix the first term $\langle\psi(\mathbf{r})\rangle\langle\psi^\dagger(\mathbf{r}')\rangle$ is of order N, and $\langle\psi(\mathbf{r})\rangle$ is of order $N^{\frac{1}{2}}$. If we were to average over all the different possible equilibrium values of $\langle\psi(\mathbf{r})\rangle$, the average value of $\langle\psi(\mathbf{r})\rangle$ would probably be zero because of the arbitrary phase of $\langle\psi(\mathbf{r})\rangle$. The value of $\langle\psi^\dagger(\mathbf{r})\psi(\mathbf{r}')\rangle$ in the larger reducible ensemble would be large but it would not cause immediate trouble. However, the average of higher correlations would behave as higher powers of N and the radius of convergence of any iterative process for finding the effect of the potential would be zero. The simplest illustration of this trouble is afforded by the noninteracting boson system for which, in the reducible grand-canonical ensemble, we have rigorously

$$\begin{aligned}\langle\psi_0^\dagger(\mathbf{r})\psi_0^\dagger(\mathbf{r})\psi_0(\mathbf{r})\psi_0(\mathbf{r})\rangle &= \langle\rho_0^2(\mathbf{r})\rangle \\ &= 2\langle\rho_0(\mathbf{r})\rangle^2.\end{aligned}$$

This property of the correlation functions results from the fact that it is really true that grand-canonical averages satisfy $\langle N^2\rangle = 2\langle N\rangle^2$ for a noninteracting system. The effect of an infinitesimal interaction is to remove these fluctuations and in perturbation theory, the formal removal of the factor of two in an expansion for the potential energy can be said to come about in the lowest approximation because

$$\langle N^2\rangle = \langle N\rangle^2 + \langle N\rangle^2[1 - c\langle N\rangle + c^2\langle N\rangle^2 \cdots].$$

Clearly, this is an absurd way to perform an iterative calculation, and hardly a method which can be trusted even if a formal resummation is carried out, since it is the unknown real condensate and not the unperturbed condensate which must be removed, and there may be many permissible values of the real condensate. In fact, there is no reason to believe that the different $\langle\psi(\mathbf{r})\rangle$ corresponding to equilibrium need be spatially uniform. (The Feynman picture with closed vortex lines may be likened to a domain picture in ferromagnetism.) Finally, there is little reason to take the average values of correlation functions in the larger ensemble to mean anything, just as the spin correlation function averaged over all systems contributing to the thermodynamics does not describe the transport property of any one system. The physical information regarding adequately specified systems is contained in the correlation functions in irreducible representations, each of which corresponds to a separate thermodynamic phase, characterized here by a possible value of $\langle\psi(\mathbf{r})\rangle$.

We determine possible values which the field $\langle\psi\rangle$ may have in a phase self-consistently from successively more accurate iterative evaluations of its cumulants. It is convenient at least to calculate the first cumulant self-consistently, and the remaining fluctuations of correlations iteratively to obtain forms which satisfy the previously discussed sum rules.

Since the fundamental field is Ψ (considered as a matrix with components ψ and $\psi^\dagger$), the quantity corresponding to the magnetic field is an external force which creates and destroys particles. We introduce this field, as we do the magnetic field and then remove it by a Legendre transformation. There remain equations to be solved iteratively for correlations of fluctuations in the quantum field in conjunction with equations to determine self-consistently the condensate and its first cumulant, the single-particle excitation spectrum. These equations are the expression of generalized matrix mass-operator perturbation theory for fermions, and the same kind of perturbation theory with an additional equation for the single-particle wavefunction in the case of bosons.

The method by which this procedure can be extended is covered in the report of Dr. De Dominicis. The procedure described up to this point puts calculations with superfluid systems on the same footing as calculations with normal systems where the effects of the interaction on the self-consistently determined time-dependent one-particle phase space distribution function are determined in successively higher approximations. At this stage the mass or energy of excitation has been renormalized. It is also possible to eliminate the potential in favor of higher correlation functions, (the analog of charge or interaction renormalization in elementary particle physics.) This is accomplished for superfluids in two stages. First a three-point potential is introduced which characterizes interactions in which the number of excitations is changed, and a Legendre transformation performed to eliminate this potential in favor of the three-point vertex. Next, a Legendre transformation is performed to eliminate the two-particle interaction potential in terms of its conjugate variable, the fourth cumulant of the field. In this manner, four self-consistent equations for the field and its first four cumulants are obtained, each of which contains an expansion in powers of the renormalized vertices, or three- and four-point cumulants of all higher cumulants. The potential, mass, temperature, and chemical potential occur only linearly as the inhomogeneous terms in these equations. These equations comprise an alternative exact description of the superfluid in terms of the physical excitations and correlations. They lead to the correct description of the extended two-fluid model together with a renormalized iterative calculational procedure. Moreover, these equations are the stationarity conditions for a functional of the distribution functions only (no temperature or chemical potential, interaction potential, or kinetic energy occur in them), subject to prescribed conditions on the total number of particles and energy. The value of this functional at its extreme is what one might suspect—the entropy.

We have examined these equations for bosons in the lowest approximation and have shown that they lead to the results of Gross and Pitaevskii and to the result of Feynman on the number of vortices in a bucket of helium. They also lead to the results of Balyaev for the single-particle spectrum in the spatially uniform case. Finally, they lead to no gap at least to order $[v(0)]^3$ in the single-particle excitation spectrum at any temperature below the condensation point.

To make these ideas precise, at least to those familiar with the field theoretic approach to many-particle problems, the first two stages of this procedure for boson systems are summarized using a notation which is not the most convenient, but the most similar to that employed for normal systems. We introduce the generating functional

$$\begin{aligned}\exp W[\chi, U]&\\ = \operatorname{Tr} \exp &\left[-i \int_0^{-i\beta} \{H(E) + H^\chi(t') + H^U(t')\}\, dt'\right]_+\\ \equiv \operatorname{Tr} \exp &(-\beta H)(S)_+\end{aligned}$$

where H is the ordinary Hamiltonian and

$$H^\chi = \int d\mathbf{r}\, \chi_i(1')\Psi_i^\dagger(1'),$$

$$H^U = \int d\mathbf{r}\, \tfrac{1}{2}\Psi_i^\dagger(1) U_{ij}(11')\Psi_j(1').$$

The quantity $(S)_+$ is the ordered exponential $(\ )_+$ of H^χ and H^U in terms of operators Ψ_i which evolve in time according to H. The operator Ψ is a two component quantity whose components are $\Psi_1 = \psi$ $\Psi_2 = \psi^\dagger$. We define thermal averaging with respect to the Hamiltonian $H + H^\chi + H^U$ according to

$$\langle A\rangle = \exp(-W) \operatorname{Tr} \exp(-\beta H)(SA)_+,$$

and Green's functions

$$\begin{aligned} G_m(1) &= i[\delta/\delta\chi_m^\dagger(1)]W = \langle\Psi_m(1)\rangle;\\ G_{lm}(11') &= \langle[\Psi_l(1)\Psi_m^\dagger(1')]_+\\ &= G_{lm}(11') + G_l(1)G_m^\dagger(1');\\ \tilde{G}_{lm}(11') &= -[\delta/\delta\chi_l^\dagger(1)][\delta/\delta\chi_m(1')]W,\end{aligned}$$

where

$$\chi_l^\dagger(1) = \tau_{lm}^1\chi_m(1),$$

and τ^1 is the matrix $\binom{01}{10}$.

Also we note the relation

$$i\,\frac{\delta}{\delta U_{ij}(22)}\, W = \tfrac{1}{2}G_{ij}(22),$$

which implies the equality

$$\tfrac{1}{2}[\delta G_{ij}(22)/\delta G_k(1)] = \delta G_k(1)/\delta U_{ij}(22).$$

We introduce the usual Schrödinger operator

$$iG_0^{-1}(11') = [i\tau_{ij}^3\,\partial_t + (\tfrac{1}{2}\nabla^2 + \mu)\delta_{ij}]\delta(11') - U_{ij}(11'),$$

where μ is the chemical potential, and τ_3 the matrix $\binom{10}{01}$.

We next observe that if we define

$$Q[\langle\Psi\rangle, U] = W[\chi, U] - i\int_0^{-i\beta} dr\, dt\, \chi_i(1)G_i^\dagger(1),$$

we have

$$\chi_i(1) = i(\delta Q[\langle\Psi\rangle, U]/\delta G_i^\dagger(1)).$$

Thus the condition that $\chi = 0$, and hence that $W = Q$, is achieved by demanding the stationarity of Q as a functional of $\langle\Psi\rangle$. For arbitrary χ we have the equation of motion

$$iG_0^{-1}(11')G(1') - v_{12}[\tfrac{1}{2}G(22) + i\delta/\delta U(22)]G(1) = \chi(1),$$

where we have surpressed matrix indices and introduced a summation convention for repeated arguments of the functions. The condition of stationarity eliminates χ from the problem. The possible values of $\langle\Psi\rangle$ consistent with $\chi = 0$ are many-fold, and each may be realized.

The parallel equation for the first cumulant of the field is

$$\begin{aligned} iG_0^{-1}(1\bar{1})\tilde{G}(\bar{1}1') = {}& i\delta(11')\\ &+ v_{12}[\tfrac{1}{2}G(22) + i\delta/\delta U(22)]\tilde{G}(11')\\ &+ v_{12}G(1)i\delta/\delta U(22)G^\dagger(1').\end{aligned}$$

The boundary conditions on these equations are determined from the fluctuation–dissipation theorem, and simply incorporated by using Fourier series in time. We proceed in the canonical manner introducing the mass operator $\Sigma(11') = G_0^{-1}(11') - \tilde{G}^{-1}(11')$ and the vertex functions

$$\begin{aligned} \Gamma(12;3) &= i[\delta\Sigma(12)/\delta U(33)], \\ \Delta(12;3) &= \delta\Sigma(12)/\delta G(3), \\ \Delta^T(12;3) &= \delta\Sigma(12)/\delta G^\dagger(3), \\ V_2(12;34) &= \delta^2\Sigma(12)/\delta G(3)\,\delta G^\dagger(4), \end{aligned}$$

and the effective source function

$$\chi(1) + J(1) \equiv iG_0^{-1}(12)G(2).$$

If we were to expand Σ in powers of G_0, we could guarantee that at each stage the Pines–Hugenholz theorem would be satisfied. Instead, we expand Σ in powers of $\tilde{G}$ using the equations above. This gives us

$$\begin{aligned} i\Sigma(11') = {} & \tfrac{1}{2}v_{12}[\tilde{G}(22) + G(2)G^\dagger(2)]\,\delta(11') \\ & + v_{11'}G(1)G^\dagger(1') - v_{12}\tilde{G}(13)\Gamma(31';2) \\ & - \tfrac{1}{2}v_{12}G(1)\tilde{G}(23)\Delta(34;1')\tilde{G}(42), \end{aligned}$$

$$\begin{aligned} v_{12}\tilde{G}(13)\Gamma(31';2) = {} & v_{12}\,\frac{\delta}{\delta G(1')}\,[\tilde{G}(12)G(2)] \\ & + \tfrac{1}{2}v_{12}\,\frac{\delta}{\delta G(1')}\,[\tilde{G}(14)\tilde{G}(23)]\Delta^\dagger(35;4)\tilde{G}(52) \\ = {} & v_{11'}\tilde{G}(11') + v_{12}\tilde{G}(13)\Delta(34;1')\tilde{G}(32)G(2) \\ & + \tfrac{1}{2}v_{12}\,\frac{\delta}{\delta G(1')}\,[\tilde{G}(14)\tilde{G}(23)\tilde{G}(52)]\Delta^\dagger(35;4) \\ & + \tfrac{1}{2}v_{12}\tilde{G}(14)\tilde{G}(23)\tilde{G}(52)\,V_2(35;41'), \end{aligned}$$

and

$$\begin{aligned} J(1) = {} & \tfrac{1}{2}v_{12}[\tilde{G}(22) + G(2)G^\dagger(2)]G(1) + v_{12}\tilde{G}(12)G(2) \\ & + \tfrac{1}{2}v_{12}\tilde{G}(14)\tilde{G}(23)\Delta^\dagger(35;4)\tilde{G}(52). \end{aligned}$$

These equations may be iterated in conjunction with the equations for the condensate and the single-particle excitations. The lowest approximation is seen to be the equation of Gross and Pitaevskii. The requirement that $G(1)$ be time-independent serves to fix the chemical potential. The number of particles then determines the normalization condition on $G(1)$, the condensate. The first approximation to the equation for $G(11')$ yields, in the spatially uniform case, the Bogolyubov spectrum. The second approximation in the spatially uniform case yields the equations of Girardeau and Arnowitt. The depletion in this approximation is for a short-range repulsive force

$$n - n_0 \approx [n_0 v(0)]^{3/2}(3\pi^2)^{-1}.$$

The function $S(\mathbf{k}\omega)$ is obtained from integral equations coupling the three- and four-point correlation functions. These matrix equations may be shown to satisfy the conservation laws and therefore to predict no gap using a technique of Baym and Kadanoff. They are similar to, but more complicated than, the equations from which Anderson and Bogolyubov determined the collective mode of the superconductor. The quadratures in their solution may be evaluated in the long-wavelength limit. At zero temperature they yield the expected results for the frequency of *phonons*

$$\omega = \sqrt{2}\kappa k\{1 + (7/6\pi^2)[n_0 v(0)]^{\frac{3}{2}}\},$$

and for their lifetime

$$\mathrm{Im}\,\omega \approx 3k^5/640\pi n_0.$$

For arbitrary k and temperature, the mode is not sharply defined, but the approximate spectral function satisfies the sum rule.

The gap predicted in the one-particle excitation spectrum in the Girardeau–Arnowitt approximation is smaller than the order to which that calculation is valid. When all terms of the same order are retained, the mode in that spectrum occurs at a lower frequency at all temperatures, closing the gap. In the nonspatially uniform case, the small oscillation frequencies of a vortex line and their approximate lifetimes are obtained from the first approximation which treats not only $G(1)$ but $G(11')$. This calculation has been performed and estimates of the damping have been carried out. When the force is attractive, the self-consistent solutions are more complicated, and we have not yet found one with which we are completely satisfied.

It seems appropriate to point out in conclusion what was perhaps obvious from the beginning—namely, that the perturbation-theory approaches to the many-boson problem which have been considered by many authors in the past few years, are in fact extremely primitive. They must be extended in the various ways we have discussed above, before they are rich enough for the discussion of liquid helium. When, and only when these extensions are made, does the problem take on an appearance in which the picturesque qualitative ideas of Onsager and Feynman can be quantitatively investigated. For example, we are investigating the form of the attraction between oppositely directed vortices to see whether vortex rings might be energetically farorable and whether they have anything to do with rotons. It will be interesting to see to what extent it will be feasible to calculate and verify some of Onsager's and Feynman's more detailed ideas about rotons, turbulence, and the phase transition.

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On the van der Waals Theory of the Vapor–Liquid Equilibrium. I. Discussion of a One-Dimensional Model

M. Kac, G. E. Uhlenbeck, and P. C. Hemmer
The Rockefeller Institute, New York, New York

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For a one-dimensional fluid model where the pair interaction potential between the molecules consists of a hard core and an exponential attraction, Kac has shown that the partition function can be determined exactly in the thermodynamic limit. In Sec. II this calculation is reviewed and further discussed. In Sec. III, we show that in the so-called van der Waals limit when the range of the attractive force goes to infinity while its strength becomes proportionally weaker, a phase transition appears which is described exactly by the van der Waals equation plus the Maxwell equal-area rule. In Sec. IV the approach to the van der Waals limit is discussed by an appropriate perturbation method applied to the basic integral equation. The perturbation parameter is the ratio of the size of the hard core to the range of the attractive force. It is seen that the phase transition persists in any order of the perturbation. The two-phase equilibrium is characterized by the fact that in this range of density, the maximum eigenvalue of the integral equation is doubly degenerate and that the corresponding two eigenfunctions do not overlap. In Sec. V we comment on the relevance of our results for the three-dimensional problem.

I. INTRODUCTION

In this series of papers we intend to present a new discussion of the old theory of van der Waals[1] of the continuity of the gaseous and liquid states of matter. It is well known that the great merit of this theory lies in the fact that it gave the first qualitative kinetic interpretation of condensation phenomena and of the existence of a critical point. On the other hand, it has proved very difficult to make the theory more rigorous and as a result the modern theory[2] of the equation of state of a nonideal gas, has followed more the idea of Kamerlingh Onnes to represent all properties of the gas as power series in the density—the so-called virial expansion. In this way one can take successively into account the interaction of the molecules in pairs, triples, quadruples, etc., and one can derive precise expressions for the successive deviations from the ideal gas laws in terms of the intermolecular potential. Many attempts,[3] thus far unsuccessful, have been made to construct a rigorous theory of condensation phenomena from such expansions. In fact we believe that such a construction is very difficult, if not impossible,[4] and it therefore seems worthwhile to try to reformulate in a more rigorous way, the basic ideas of van der Waals.

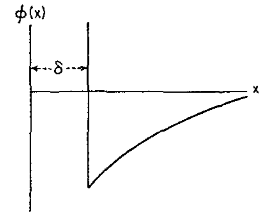

FIG. 1. Interaction potential $\varphi(x)$.

We have attempted to do this starting always from a one-dimensional gas model, first proposed by M. Kac,[5] for which all calculations can be carried out exactly. The model consists of N particles moving on a line of length L and interacting in pairs through a potential $\varphi(x)$ which consists of a hard core of length δ and an exponential attraction (see Fig. 1.) For this model it is possible to give an exact discussion of the partition function in the *thermodynamic limit* $L \to \infty$, $N \to \infty$, $l = L/N$ finite. As shown already by Kac, the problem in this limit can be reduced to the discussion of a linear integral equation with a positive definite, Hilbert–Schmidt kernel of which the maximum eigenvalue determines the

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[1] J. D. van der Waals, Dissertation Leiden, 1873. This was expanded in the book: *Die Kontinuität des gasförmigen und flüssigen Zustandes* (Johann A. Barth, Leipzig, Germany, 1899), 2 volumes. Compare also the monograph by J. P. Kuenen, Die Zustandsgleichung (Vieweg, Braunschweig, 1907).

[2] Due mainly to J. E. Mayer. A summary is given in the book by J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Chaps. 13 and 14. For a recent account see the monograph by G. E. Uhlenbeck and G. W. Ford in *Studies in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), Vol. 1, Part B.

[3] These also go back to J. E. Mayer; (see reference 2, Chap. 14). For a more recent discussion, see K. Ikeda, Progr. of Theoret. Phys. (Kyoto) **19**, 653 (1958), and **26**, 173 (1961). Much of the motivation came from the analogy with the Bose–Einstein condensation, which was pointed out by B. Kahn and G. E. Uhlenbeck [Physica **5**, 399 (1938)]. However, we now believe that this analogy is superficial and that there is no real connection between the Bose–Einstein condensation and ordinary condensation phenomena.

[4] The difficulties become especially clear in the formulation of the condensation problem according to C. N. Yang and T. D. Lee, Phys. Rev. **87**, 404 (1952). Compare also the discussion by G. E. Uhlenbeck and G. W. Ford in Chapter 3 of the book *Lectures in Statistical Mechanics* (Proceedings of the Summer Seminar, Boulder, Colorado, 1960, published by the American Mathematical Society, Providence, Rhode Island, 1963.)

[5] M. Kac, Phys. Fluids **2**, 8 (1959).

thermodynamic potential (Gibbs free energy) of the system. These results will be recapitulated in Sec. II.

For finite γ, that is for a finite range of the attractive force, the system does *not* show a phase transition in agreement with all previously known results[6] for one-dimensional systems. However, if one sets $\alpha = \alpha_0\gamma$, and then lets $\gamma \to 0$, (i.e., for a weak but very long-range force) so that the integral

$$\int_0^\infty dx\, \varphi_{\text{attr.}}(x)$$

is finite (we will call this the *van der Waals limit*), a phase transition appears which is described exactly by the van der Waals equation

$$p = kT/(l - \delta) - \alpha_0/l^2, \tag{1}$$

together with the well known Maxwell rule.[7] This will be shown in detail in Sec. III.

In Sec. IV, all the eigenfunctions and eigenvalues of the Kac integral equation are found in this limit by a perturbation procedure with $\gamma\delta$ as the expansion parameter. The phase transition appears as a double degeneracy of the maximum eigenvalue, and the phase transition *persists* when the perturbation calculation is carried further to any finite power of $\gamma\delta$. One should also note that this entire development breaks down near the critical point. For the critical region, a separate discussion is required which will be given in Part III of this series of papers.

In the last section, we will comment on the relevance of our results for the three-dimensional problem, and on the relation to the usual derivation of the van der Waals equation.

II. THE KAC INTEGRAL EQUATION

The partition function for our one-dimensional gas is given by

$$\begin{aligned} Z(L, T, N) &= \frac{1}{\Lambda^N}\cdot\frac{1}{N!}\int_0^L \cdots \int_0^L dt_1 \cdots dt_N \\ &\quad \times \exp\left[-\frac{1}{kT}\sum_{i<j}\varphi(|t_i - t_j|)\right] \\ &= \frac{1}{\Lambda^N}\cdot\frac{1}{N!}\int_0^L \cdots \int_0^L dt_1 \cdots dt_N \\ &\quad \times \exp\,[\nu \sum_{i<j} e^{-\gamma|t_i - t_j|}] \prod_{i<j} S(|t_i - t_j|), \end{aligned} \tag{2}$$

with $\Lambda^2 = h^2/2\pi mkT$, $\nu = \alpha/kT$, and where the stepfunction $S(x)$ is defined by

$$S(x) = \begin{cases} 0 & \text{for } |x| < \delta \\ 1 & \text{for } |x| > \delta. \end{cases}$$

Since the integrand is symmetric in $t_1, t_2 \cdots t_N$, and because the hard cores impose a linear order of the molecules in L, one can write (2) in the form

$$\begin{aligned} Z(L, T, N) &= \frac{e^{-\frac{1}{2}N\nu}}{\Lambda^N} \int_{0<t_1<t_2\cdots<t_N<L} \cdots \int dt_1 \cdots dt_N \\ &\quad \times \exp\left[\frac{\nu}{2}\sum_{i=1}^N \sum_{j=1}^N e^{-\gamma|t_i - t_j|}\right]\cdot\prod_{j=1}^{N-1} S(|t_{j+1} - t_j|). \end{aligned} \tag{3}$$

Also the attractive part of the integrand can be ordered by making use of the identity

$$\begin{aligned} \exp&\left[\frac{\nu}{2}\sum_{i,j=1}^N \exp\,(-\gamma\,|t_i - t_j|)\right] \\ &= \int_{-\infty}^{+\infty} \cdots \int dx_1 \cdots dx_N \\ &\quad \times \exp\,[\nu^{\frac{1}{2}}(x_1 + x_2 + \cdots + x_N)] \\ &\quad \cdot W(x_1) \prod_{j=1}^N P(x_j \mid x_{j+1}, t_{j+1} - t_j), \end{aligned} \tag{4}$$

where

$$W(x) = \frac{1}{(2\pi)^{\frac{1}{2}}} \exp\,[-\tfrac{1}{2}x^2],$$

$$\begin{aligned} P(x \mid y, t) &= [\{2\pi(1 - e^{-2\gamma t})\}^{\frac{1}{2}}]^{-1} \\ &\quad \times \exp\,[-(y - xe^{-\gamma t})^2/2(1 - e^{-2\gamma t})]. \end{aligned} \tag{5}$$

The motivation and the proof of the identity (4) follows from the observation that $\exp\,(-\gamma\,|t_i - t_j|)$ is the covariance of a one-dimensional, Gaussian Markoff process (the so-called *O–U* process), but of course one can also prove (4) directly. By substituting (4) into (3) and by making a Laplace transformation in L, the integrals over the t_i can be separated in pairs since clearly

$$\int_0^\infty e^{-sL} Z(L, T, N)\, dL$$

is of the form

$$\int_0^\infty dL e^{-sL} \int_0^L dt_1 \int_{t_1}^L dt_2 \times \int_{t_2}^L dt_3 \cdots \int_{t_{N-1}}^L dt_N \prod_{j=1}^{N-1} F_j(t_{j+1} - t_j)$$

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[6] That there is no phase transition for a one-dimensional system with only nearest-neighbor interaction, was shown first by F. Gursey, Proc. Cambridge Phil. Soc. **46**, 182 (1950). This was generalized (with the same result) to the case where each molecule interacts with a finite number of neighbors by L. Van Hove, Physica **16**, 137 (1950). Compare also the discussion given by A. Munster in his book *Statistische Thermodynamik* (Springer-Verlag, Berlin, Germany, 1956), Secs. 7.7 and 8.8, where one also finds further references.

[7] Also called the equal-area rule. See Maxwell, *Collected Works*, Dover reprint, Vol. II, p. 425.

$$= \int_0^\infty dt_1 \int_{t_1}^\infty dt_2 \cdots \int_{t_{N-1}}^\infty dt_N \times \int_{t_N}^\infty dL e^{-sL} \prod_{j=1}^{N-1} F_j(t_{j+1} - t_j). \tag{6}$$

Setting

$$t_1 = \tau_1,$$
$$t_2 = \tau_1 + \tau_2, \cdots, t_N = \tau_1 + \tau_2 + \cdots + \tau_N,$$
$$L = \tau_1 + \tau_2 + \cdots + \tau_N + \tau_{N+1},$$

one easily shows that (6) becomes

$$\frac{1}{s^2} \prod_{j=1}^{N-1} \int_0^\infty d\tau\, e^{-s\tau} F_j(\tau),$$

so that by putting in the appropriate form for the $F_j(z)$, one obtains (suppressing the temperature T from now on)

$$\int_0^\infty dL e^{-sL} Z(L, N) = \frac{1}{\Lambda^N} \frac{e^{-N\nu/2}}{s^2} \int_{-\infty}^{+\infty} \cdots \int dx_1 \cdots dx_N \times \exp\,[\nu^{\frac{1}{2}}(x_1 + \cdots + x_N)] W(x_1) \prod_{j=1}^{N-1} p_s(x_j \mid x_{j+1}) \tag{7}$$

with

$$p_s(x \mid y) = \int_\delta^\infty d\tau\, e^{-s\tau} P(x \mid y, \tau). \tag{8}$$

The ordering of the x_i in successive pairs suggests the introduction of the kernel

$$K_s(x, y) = \frac{W(x) p_s(x \mid y)}{[W(x) W(y)]^{\frac{1}{2}}} \exp\,[(\nu^{\frac{1}{2}}/2)(x + y)] \tag{9}$$

and the corresponding Kac integral equation

$$\int_{-\infty}^{+\infty} dy\, K_s(x, y) \psi(y) = \lambda \psi(x). \tag{10}$$

It is easy to see that $K_s(x, y)$ is symmetric and in addition one can show (for the proof, see Kac[5]):

(a) $K_s(x, y)$ is positive definite, which means that

$$\iint K_s(x, y) \psi(x) \psi(y)\, dx\, dy$$

is always positive, whenever $\psi(x)$ is not identically 0;

(b) $K_s(x, y)$ is a Hilbert–Schmidt kernel, which means that

$$\iint K_s^2(x, y)\, dx\, dy < \infty.$$

From these facts, one can conclude that Eq. (10) has a *discrete* set of *positive* eigenvalues $\lambda_i(s)$ starting from a maximum eigenvalue $\lambda_0(s)$ and converging to zero as $i \to \infty$, that the corresponding eigenfunctions $\psi_i(x, s)$ form a complete orthonormal set, and that the kernel $K_s(x, y)$ can be expanded in the convergent series

$$K_s(x, y) = \sum_i \lambda_i(s) \psi_i(x, s) \psi_i(y, s). \tag{11}$$

Writing Eq. (7) in the form

$$\int_0^\infty dL e^{-sL} Z(L, N) = \frac{e^{-\frac{1}{2}N\nu}}{\Lambda^N s^2} \int_{-\infty}^{+\infty} \cdots \int dx_1 \cdots dx_N \exp\left[\frac{\nu^{\frac{1}{2}}}{2}(x_1 + x_N)\right] \times [W(x_1) W(x_N)]^{\frac{1}{2}} \prod_{j=1}^{N} K_s(x_j, x_{j+1}),$$

and using Eq. (11), one can integrate over x_2, $x_3 \cdots x_{N-1}$ and obtain

$$\int_0^\infty dL e^{-sL} Z(L, N) = \frac{e^{-\frac{1}{2}N\nu}}{\Lambda^N s^2} \sum_{j=0}^\infty \lambda_j^{N-1}(s) A_j^2 \tag{12}$$

with

$$A_j = \int_{-\infty}^{+\infty} dx\, \psi_j(x, s) W^{\frac{1}{2}}(x) e^{\frac{1}{2}\nu^{\frac{1}{2}} x}. \tag{13}$$

If one now forms the grand partition function

$$G(L, z) = \sum_{N=1}^\infty Z(L, N)(\Lambda z)^N, \tag{14}$$

it follows from Eq. (12), that

$$\int_0^\infty dL e^{-sL} G(L, z) = \frac{z e^{-\frac{1}{2}\nu}}{s^2} \sum_j \frac{A_j^2}{1 - \lambda_j z e^{-\frac{1}{2}\nu}}, \tag{15}$$

provided $z < e^{\frac{1}{2}\nu}/\lambda_0(s)$. It is clear therefore that the abscissa of convergence of the Laplace transform of $G(L, z)$ is that value of s, for which

$$z = e^{\frac{1}{2}\nu}/\lambda_0(s). \tag{16}$$

Since on the other hand this abscissa is also

$$\lim_{L \to \infty} \frac{1}{L} \ln G(L, z), \tag{17}$$

which has the thermodynamic meaning of p/kT, it follows that the relation between z and the pressure of the gas is given by

$$\lambda_0(p/kT) = e^{\frac{1}{2}\nu}/z. \tag{18}$$

Furthermore, since the thermodynamic meaning of z is the fugacity, which is related to the chemical potential (Gibbs free energy per particle) $\mu(p, T)$ by

$$\mu = kT \ln (\Lambda z), \tag{19}$$

the equation of state follows from

$$l = (\partial\mu/\partial p)_T = -\lambda_0'(s)/\lambda_0(s), \quad s = p/kT, \tag{20}$$

where the prime denotes differentiation after s.

The following statements can be proved concerning the maximum eigenvalue $\lambda_0(s)$ and the eigenvalue spectrum $\lambda_i(s)$ (see Appendix 1):

(a) *All* eigenvalues are monotonically decreasing functions of s and approach zero for $s \to \infty$.

(b) The maximum eigenvalue $\lambda_0(s)$ goes to infinity for $s \to 0$. For no value of s can it be degenerate, and it is an analytic function of s for all real $s > 0$. Finally there is the inequality

$$\lambda_0'(s)^2 - \lambda_0(s)\lambda_0''(s) < 0, \tag{21}$$

which implies that $\lambda_0''(s)$ is always positive.

(c) All other eigenvalues are finite for $s = 0$.

It seems very likely that the curves $\lambda_i(s)$, $i > 0$ will also not cross each other, in which case the spectrum as a function of s may look as shown in Fig. 2.

One can conclude that for any value of z there is an *unique* value s fulfilling Eq. (16), and from Eqs. (20) and (21) it then follows that l is a monotonically decreasing and analytic function of $s = p/kT$ for all positive values of s. There is therefore *no* phase transition. Note that the theory gives directly [see Eqs. (18) and (19)], the Gibbs free energy as a function of the pressure, and that therefore one obtains the specific volume l as a function of the pressure instead of the pressure as a function of l as in the Mayer theory. The connection with the virial expansion of the equation of state is therefore quite complicated. One can show that the maximum eigenvalue $\lambda_0(s)$ can be expanded in the form

$$\lambda_0(s) = e^{\frac{1}{2}\nu}(s^{-1} + a_0 + a_1 s + a_2 s^2 + \cdots). \tag{22}$$

The coefficients a_i can be calculated successively and they are related to the Mayer cluster integrals b_l. One finds

$$a_0 = b_2; \qquad a_1 = b_3 - b_2^2; \tag{23}$$

and so on. For the proof we refer again to Appendix I. From Eqs. (22) and (23) one can then verify that the equation of state (20) is, for small pressures, simply the inversion of the usual virial expansion

$$pl/kT = 1 + B/l + C/l^2 + \cdots,$$

with $B = -b_2$, $C = -2b_3 + 4b_2^2$, etc. We have been unable to find a simple "graphological" characterization of the coefficients a_i.

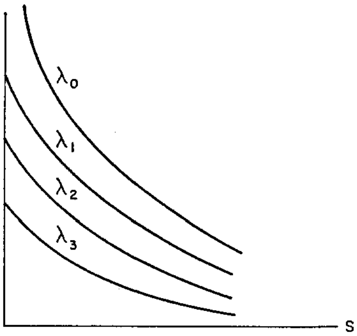

FIG. 2. Eigenvalue sprectrum as a function of s.

III. THE VAN DER WAALS LIMIT

We will now study what happens to the maximum eigenvalue $\lambda_0(s)$, if one puts $\alpha = \alpha_0\gamma$ and then goes to the limit $\gamma \to 0$. To do this, we investigate the moments $\sum_i \lambda_i^n(s)$ of the distribution of the eigenvalues $\lambda_i(s)$. One has

$$\begin{aligned}\sum_i \lambda_i^n &= \int_{-\infty}^{+\infty}\cdots\int dx_1 \cdots dx_n \\ &\quad\times K_s(x_1, x_2)K_s(x_2, x_3) \cdots K_s(x_n, x_1) \\ &= \int_{-\infty}^{+\infty}\cdots\int dx_1 \cdots dx_n \\ &\quad\times \exp\,[-(\nu_0\gamma)^{\frac{1}{2}}(x_1 + x_2 \cdots + x_n)] \\ &\quad\times \int_{\delta}^{\infty}\cdots\int d\tau_1 \cdots d\tau_n \\ &\quad\times \exp\,[-s(\tau_1 + \cdots + \tau_n)] \prod_{i=1}^{n} P(x_i \,|\, x_{i+1}, \tau_i),\end{aligned}$$

where $\nu_0 = \alpha_0/kT$ and $x_{n+1} \equiv x_1$. The integrals over the x_i can be carried out and one can then investigate the limit $\gamma \to 0$. Some of the details are given in Appendix II. The result is the following theorem. For $\gamma \to 0$,

$$\lim_{\gamma\to 0} \gamma \sum_i \lambda_i^n = \frac{1}{2\pi}\iint_{-\infty}^{+\infty} d\xi\, d\eta \times \left(\exp\,[\eta(2\nu_0)^{\frac{1}{2}}] \int_{\delta}^{\infty} d\tau \exp\,[-s\tau - \tfrac{1}{2}(\xi^2 + \eta^2)\tau]\right)^n. \tag{24}$$

One now can reason heuristically as follows. Call

$$f(\xi, \eta) = \exp\,[\eta(2\nu_0)^{\frac{1}{2}}] \int_{\delta}^{\infty} d\tau \times \exp\,[-s\tau - \tfrac{1}{2}(\xi^2 + \eta^2)\tau]; \tag{25}$$

then since (24) holds for all n, one can expect that for any reasonable function $g(x)$,

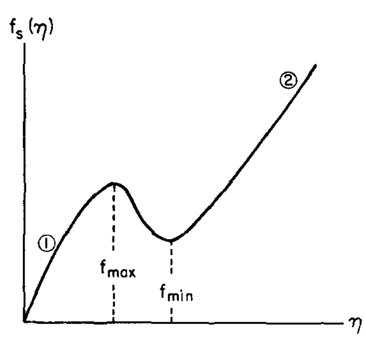

FIG. 3. The function $f_s(\eta)$ in the two-phase region.

$$\lim_{\gamma\to 0} \gamma \sum_i g(\lambda_i) = \frac{1}{2\pi} \iint_{-\infty}^{+\infty} d\xi\, d\eta\; g[f(\xi, \eta)]. \tag{26}$$

Take now for $g(x)$ the step function

$$g(x) = \begin{cases} 1 & \text{for } \alpha < x < \beta \\ 0 & \text{otherwise}, \end{cases}$$

and let $N_\gamma(\alpha, \beta)$ be the number of eigenvalues between α and β; then one concludes from Eq. (26) that

$$\lim_{\gamma\to 0} \gamma N_\gamma(\alpha, \beta) = \frac{1}{2\pi}$$
$$\times \text{ [Area in } (\xi, \eta) \text{ plane for which } \alpha < f(\xi, \eta) < \beta]. \tag{27}$$

Suppose that $f(\xi, \eta)$ has an *absolute* maximum $\omega(s)$, then it is clear that for $\gamma \to 0$, ω must be a limit point for the series of eigenvalues, because in any interval between $\omega - \epsilon$ and ω there must be in the limit $\gamma \to 0$, an infinite number of eigenvalues because the area $(\omega - \epsilon) < f(\xi, \eta) < \omega$ is finite. It seems therefore reasonable to expect that for $\gamma \to 0$, $\omega(s)$ is the maximum eigenvalue, or in other words that

$$\lim_{\gamma\to 0} \lambda_0(s, \gamma) = \omega(s) = \max_{(\xi,\eta)} f(\xi, \eta) = \max_{(\eta)} F(\eta), \tag{28}$$

with

$$F(\eta) \equiv f(0, \eta)$$
$$= \exp\left[-\delta(s + \tfrac{1}{2}\eta^2) - \ln(s + \tfrac{1}{2}\eta^2) + \eta(2\nu_0)^{\frac{1}{2}}\right],$$

since the maximum of $f(\xi, \eta)$ will always occur for $\xi = 0$.

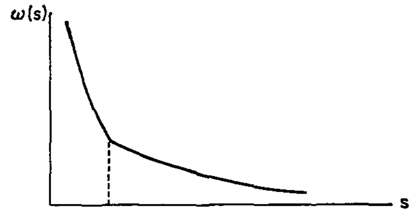

FIG. 4. The maximum eigenvalue, in the van der Waals limit, for a temperature below the critical.

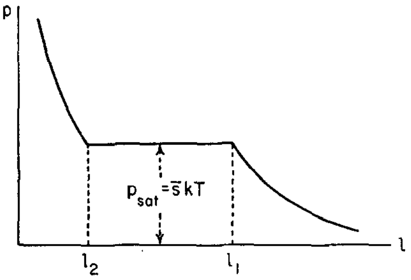

FIG. 5. Isotherm corresponding to Fig. 4.

Note that our argument from Eq. (27) does not really prove Eq. (28), since (27) does not exclude that a few discrete eigenvalues remain above $\omega(s)$ for $\gamma \to 0$. However, Eq. (28) is correct and the argument can be made completely rigorous. This is not done, because in the next section, the detailed investigation of the approach to the limit $\gamma \to 0$ implies a rigorous proof of Eq. (28).

To discuss Eq. (28) further, first note that the maximum will occur for that value $\eta(s)$ for which

$$f_s(\eta) \equiv \eta[\delta + 1/(s + \tfrac{1}{2}\eta^2)] = (2\nu_0)^{\frac{1}{2}}. \tag{29}$$

Since $df_s/d\eta = 0$ implies

$$s + \tfrac{1}{2}\eta^2 = (1/2\delta)[1 \pm (1 - 8s\delta)^{\frac{1}{2}}], \tag{30}$$

one must distinguish two cases.

(a) $8s\delta > 1$; $f_s(\eta)$ is then a monotonically increasing function of η, so that (29) has always one solution $\eta(s)$ corresponding to an unique maximum for $F(\eta)$. The equation of state follows from

$$l = -\omega'(s)/\omega(s) = +\delta$$
$$+ [1/(s + \tfrac{1}{2}\eta^2(s))] = +(2\nu_0)^{\frac{1}{2}}/\eta(s), \tag{31}$$

using (29). Putting $s = p/kT$ and $\eta(s) = (2\nu_0)^{\frac{1}{2}}/l$ in Eq. (29), one obtains the van der Waals equation

$$p = kT/(l - \delta) - \alpha_0/l^2.$$

(b) $8s\delta < 1$; $f_s(\eta)$ has then a maximum and a minimum (see Fig. 3), and one easily verifies that for $s = 1/8\delta$, $f_{\min} = f_{\max} = (\tfrac{3}{2})(3\delta)^{\frac{1}{2}}$, and that for decreasing s, $f_{\min}$ and $f_{\max}$ increase monotonically; $f_{\min}$ remains finite, while $f_{\max}$ goes to infinity for $s \to 0$.

If now $(2\nu_0)^{\frac{1}{2}} < f_{\min}$, then again there is only one solution of Eq. (29) corresponding to an unique maximum of $F(\eta)$. This is also the case if $(2\nu_0)^{\frac{1}{2}} > f_{\max}$. However if $f_{\min} < (2\nu_0)^{\frac{1}{2}} < f_{\max}$, then Eq. (29) has *three* roots, the outer two corresponding to local maxima of $F(\eta)$ and the inner one to a local minimum. One must now decide which of the two maxima is the absolute maximum. Clearly if one varies ν_0 at fixed s, or if one varies s (keeping $8s\delta < 1$) at fixed ν_0, there must be a value $\bar{s}(\nu_0)$ for which the two maxima are equal. It is at this value that $\omega(s)$ changes its analytic behavior abruptly, since $\eta(s)$ will suddenly jump from the branch ① to the branch ② of the $f_s(\eta)$ curve (see Fig. 3). In fact it is easy to show that for $s = \bar{s}$, $\omega(s)$ has a discontinuity in slope, and since $l = -\omega'(s)/\omega(s)$ this corresponds to an isotherm with a horizontal piece (see Figs. 4 and 5). Furthermore, since (31) remains valid, *both* the liquid and the vapor part are *still* described by the van der Waals equation. Finally, the equality of the maxima of $F(\eta)$ for $s = \bar{s}$ or of the two values of $\omega(s)$ means the equality of the Gibbs free energy of the two phases for $s = \bar{s}$, which in turn is equivalent to the Maxwell rule.

The critical point is determined by $8s_c\delta = 1$ and $(2\nu_c)^{\frac{1}{2}} = f_{\min}(s_c) = f_{\max}(s_c) = (\frac{3}{2})(3\delta)^{\frac{1}{2}}$, and this leads to the well-known formula

$$v_c = 3\delta; \quad p_c = \alpha_0/27\delta^2; \quad kT_c = 8\alpha_0/27\delta. \tag{32}$$

IV. THE EIGENFUNCTIONS AND EIGENVALUES FOR SMALL γ

Clearly the reason that, for small γ, the eigenvalues $\lambda_n(s, \gamma)$ of the Kac equation crowd together near the value $\omega(s)$, must be related to the fact that for $\gamma \to 0$, $P(x \mid y, t)$ approaches the Dirac δ function $\delta(x - y)$. However if one assumes that for $\gamma \to 0$, the eigenfunctions $\psi_n(x, s, \gamma)$ would remain centered around $x = 0$, as in the usual eigenvalue problems, then it follows from Eq. (10) that for $\gamma \to 0$, the eigenvalues would cluster around $e^{-s\delta}/s$ which is the maximum eigenvalue for the gas of hard rods. This contradiction can only be removed if, for $\gamma \to 0$, the eigenfunctions are centered farther and farther away from the origin. This in fact is the clue for constructing a consistent successive-approximation method for the eigenfunctions and eigenvalues if γ is small.

In the basic integral equation (10), substitute

$$x = x' + \eta(2/\gamma)^{\frac{1}{2}}, \qquad y = y' + \eta(2/\gamma)^{\frac{1}{2}}, \tag{33}$$

where $\eta \equiv \eta(s)$ is the value of η for which the function $F(\eta, s)$ defined by (28) has an absolute maximum. Think *first* of the *one-phase region*, so that $\eta(s)$ is unique. Let

$$h(x') \equiv \psi[x' + \eta(2/\gamma)^{\frac{1}{2}}]; \tag{34}$$

then Eq. (10) can be written in the form

$$\exp\,[\eta(2\nu_0)^{\frac{1}{2}}] \int_{-\infty}^{+\infty} dy' \int_{\delta}^{\infty} d\tau \left[\frac{W(x')}{W(y')}\right]^{\frac{1}{2}} P(x' \mid y', \tau)$$
$$\times \exp\left[-s\tau - \frac{\eta^2}{\gamma}\tanh\left(\frac{\gamma\tau}{2}\right) + (x' + y')\,\frac{(\nu_0\gamma)^{\frac{1}{2}}}{2} - \frac{\eta}{2}\left(\frac{2}{\gamma}\right)^{\frac{1}{2}}\tanh\left(\frac{\gamma\tau}{2}\right)(x' + y')\right] h(y') = \lambda h(x'). \tag{35}$$

Clearly now for $\gamma \to 0$, $P(x' \mid y', \tau) \to \delta(x' - y')$ if $h(x')$ is centered around $x' = 0$, the eigenvalues will approach

$$\exp\,[\eta(2\nu_0)^{\frac{1}{2}}] \int_{\delta}^{\infty} d\tau \exp\left[-s\tau - \frac{\eta^2\tau}{2}\right] = \omega(s),$$

as expected. One may say that by the substitution (33) one has "tamed" the integral equation for a perturbation expansion of the form

$$\begin{aligned}\lambda &= \omega(s)\{1 + \mu^{(1)}\gamma + \mu^{(2)}\gamma^2 + \cdots\},\\ h(x') &= h^{(0)}(x') + \gamma^{\frac{1}{2}}h^{(1)}(x') + \gamma h^{(2)}(x') + \cdots .\end{aligned} \tag{36}$$

Since the algebra is involved, we simply indicate how this is done. In the left-hand side of Eq. (35), set

$$y' = x'e^{-\gamma\tau} + \zeta(1 - e^{-2\gamma\tau})^{\frac{1}{2}},$$

and develop the whole integrand in powers of $\gamma^{\frac{1}{2}}$. The integrals over ζ are Gaussian integrals and the integrals over τ can all be expressed in terms of $\omega(s)$ and its derivatives. Up to order $\gamma^{\frac{3}{2}}$, and except for a common factor $\omega(s)$, the left-hand side of (35) becomes

$$\begin{aligned}&h(x') + \gamma l[h''(x') + h(x)(\tfrac{1}{2} - \tfrac{1}{4}x'^2 + \tfrac{1}{2}x'^2\nu_0(l - \delta)^2/l^3)]\\ &\quad + [\gamma^{\frac{3}{2}}\nu_0^{\frac{1}{2}}(l - \delta)^2/l][\tfrac{1}{4}x'^3h(x')(1 - 4\nu_0(l - \delta)/l^2)\\ &\quad - \tfrac{1}{2}x'h(x') - h'(x') - x'h''(x')],\end{aligned}$$

where (31) has been used to express $\eta(s)$ in terms of l. If one now introduces the expansions (36) on both sides of Eq. (35) and equates equal powers of $\gamma^{\frac{1}{2}}$, one obtains, in zeroth approximation,

$$\frac{d^2H^{(0)}}{dz^2} + \left[\frac{1}{B}\left(\frac{l}{2} - \mu^{(1)}\right) - \frac{z^2}{4}\right]H^{(0)}(z) = 0, \tag{37}$$

where we have set

$$\begin{gathered}B^2 = l^2 - 2\nu_0(l - \delta)^2/l, \qquad x' = z(l/B)^{\frac{1}{2}},\\ h^{(0)}(x') = H^{(0)}(z).\end{gathered} \tag{38}$$

This is the equation for the Weber functions and hence one concludes that

$$\begin{aligned}\mu_n^{(1)} &= \tfrac{1}{2}[l - (2n + 1)B],\\ H_n^{(0)}(z) &= N_nD_n(z),\end{aligned} \tag{39}$$

where N_n is the normalization factor $(B/2\pi l)^{\frac{1}{2}}(n!)^{-\frac{1}{2}}$. Note that the quantity B is related to the compressibility of the gas, since, from the van der Waals equation,

$$B^2 = [-l^2(l - \delta)^2/kT](\partial p/\partial l)_T. \tag{40}$$

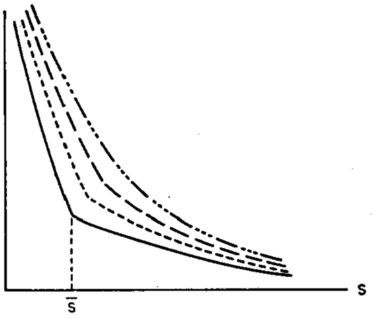

FIG. 6. ——— $\omega(s)$; —···— $\lambda(s,\gamma)$ (exact); -------- $\lambda(s,\gamma)$ to order $\gamma\delta$; — — — $\lambda(s,\gamma)$ to order $(\gamma\delta)^2$.

In the one-phase region $\partial p/\partial l$ is always negative, and therefore B can be taken positive. The maximum eigenvalue corresponds therefore to $n = 0$, and is given up to first order by

$$\lambda_0(s,\gamma) = \omega(s)[1 + \tfrac{1}{2}\gamma(l - B)]. \tag{41}$$

This proves the statement in Sec. III, that the maximum eigenvalue is $\omega(s)$ in the van der Waals limit.

In first approximation one obtains

$$\begin{aligned}\frac{d^2H_n^{(1)}}{dz^2} + (n + \tfrac{1}{2} - \tfrac{1}{4}z^2)H_n^{(1)} = {}& \frac{\nu_0^{\frac{1}{2}}(l-\delta)^2}{l^{\frac{3}{2}}B^{\frac{1}{2}}}\frac{dH_n^{(0)}}{dz} \\ & + \frac{\nu_0^{\frac{1}{2}}(l-\delta)^2}{l^{\frac{3}{2}}B^{\frac{3}{2}}}\left(\frac{l}{2B} - n - \tfrac{1}{2}\right)zH_n^{(0)} \\ & - \frac{\nu_0^{\frac{3}{2}}(l-\delta)^3(l-3\delta)}{6l^{5/2}B^{5/2}}\,z^3H_n^{(0)}.\end{aligned} \tag{42}$$

It can be easily verified that the right-hand side is orthogonal to $H_n^{(0)}$, so that (42) has an unique solution. For the explicit form of the solution and also for the second approximation, which will be needed in Part II of this series of papers, we refer to Appendix III.

Let us now consider the *two-phase region.*

It is clear that in this case the argument must be revised, since the $\eta(s)$ in the shift (33) is no longer unique. In fact, since $F(\eta, s)$ has now two equal maxima, there are *two* values of $\eta(s)$ corresponding to the volumes l_1 and l_2 of the saturated vapor and liquid phase (see Fig. 5). For each of these two values one can make the shift (33), and repeat the the argument. Clearly in both cases one will get the *same* zeroth-order eigenvalue $\omega(s)$, but one will get *another* eigenfunction, since the quantity l/B will be different at l_1 and l_2. One must say therefore that for $l_2 < l < l_1$, i.e. in the two-phase region, the maximum eigenvalue in the van der Waals limit is *doubly degenerate,* and in lowest order, the eigenfunction will have the form [since $D_0(z) = \exp(-\frac{1}{4}z^2)$],

$$\begin{aligned}\psi_0(x,s) = {}& \alpha_1\left(\frac{B_1}{2\pi l_1}\right)^{\frac{1}{4}}\exp\left[-\frac{B_1}{4l_1}\left(x - \eta_1\left[\frac{2}{\gamma}\right]^{\frac{1}{2}}\right)^2\right] \\ & + \alpha_2\left(\frac{B_2}{2\pi l_2}\right)^{\frac{1}{4}}\exp\left[-\frac{B_2}{4l_2}\left(x - \eta_2\left[\frac{2}{\gamma}\right]^{\frac{1}{2}}\right)^2\right],\end{aligned} \tag{43}$$

where $\eta_1(\bar{s}) = (2\nu_0)^{\frac{1}{2}}/l_1$ and $\eta_2(\bar{s}) = (2\nu_0)^{\frac{1}{2}}/l_2$.

The question now arises as to the appropriate linear combination corresponding to a specific length $l = \xi_1 l_1 + \xi_2 l_2$, (where ξ_1, ξ_2 are the mole fractions of the vapor and liquid phase), so that $\xi_1 + \xi_2 = 1$. We show that the answer is given by

$$\xi_1 = \alpha_1^2 \qquad \xi_2 = \alpha_2^2. \tag{44}$$

To prove this, note first that for small γ, *the two Gaussian functions in* (43) *do not overlap.* Hence from the normalization of $\psi(x, \bar{s})$, one obtains $\alpha_1^2 + \alpha_2^2 = 1$. Furthermore, for any finite γ, it follows from the Kac equation that

$$\begin{aligned}\lambda_0(s,\gamma) &= \iint dx\,dy\,K_s(x,y) \\ &\qquad \times \psi_0(x,s,\gamma)\psi_0(y,s,\gamma), \\ \lambda_0'(s,\gamma) &= -\lambda_0(s,\gamma)l = \iint dx\,dy\,\frac{\partial K_s}{\partial s} \\ &\qquad \times \psi_0(x,s,\gamma)\psi_0(y,s,\gamma)\end{aligned} \tag{45}$$

[since the differentiation of the eigenfunctions after s gives zero because the normalization of $\psi_0(x, s, \gamma)$ implies

$$\int \psi_0(x,s,\gamma)\frac{\partial}{\partial s}\psi_0(x,s,\gamma)\,dx = 0].$$

Now take $s = \bar{s}$, and let $\gamma \to 0$. Since for each of the two functions in Eq. (43) one has an equation like (45) with the same s and the same $\lambda_0(s) = \omega(s)$, but with l successively l_1 and l_2, and since one can again neglect the overlap of the two functions, it follows from Eq. (45) that for $\gamma \to 0$,

$$l = \alpha_1^2 l_1 + \alpha_2^2 l_2,$$

which proves Eq. (44).

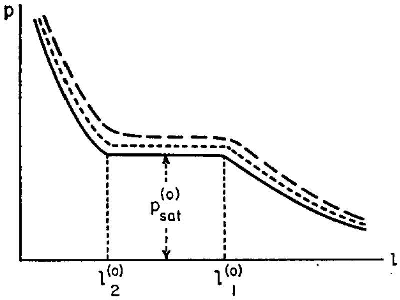

FIG. 7. ——— The van der Waals isotherm ($\gamma = 0$); — — — The exact isotherm; ······· The isotherm to order $\gamma\delta$.

We conclude this section with the following two remarks.

(a) It is clear that the entire development breaks down near the critical point because at that point, $B \to 0$ and $l_1 \cong l_2$. The overlap of the two eigenfunctions in the two-phase region can therefore no longer be neglected. In the critical region, one has to "tame" the integral equation in a different way, which will be explained in the third part of this series.

(b) It follows from Eq. (41) that up to first order in γ, $\lambda_0(s, \gamma)$ *still* shows a discontinuity in slope, and one can be convinced that the discontinuity *remains* if the perturbation calculation is continued up to *any* finite order in γ. For finite γ, $\lambda_0(s, \gamma)$ is an analytic function of s for $s > 0$. This means that for small γ, the successive-approximation method which we have developed, approximates the analytic function $\lambda_0(s, \gamma)$ by a series of functions which have a discontinuity in slope in the region of s, where the slope of $\lambda_0(s, \gamma)$ varies very quickly (see Fig. 6). This implies that *the phase transition persists* up to any finite order in γ, although the equation of state is then of course different from the van der Waals equation. In fact it is not difficult to show from Eq. (41), that, up to first order in γ, the equation of state in the one-phase region is given by

$$p = \frac{kT}{l-\delta} - \frac{\alpha_0}{l^2} + \frac{\gamma}{2}\left\{kT - \frac{l}{B}\left[kT - \frac{\alpha_0(l^2-\delta^2)}{l^3}\right]\right\}.$$

The saturated vapor pressure and the densities of the saturated vapor and liquid also change accordingly. One finds

$$p_{\text{sat}} = p_{\text{sat}}^{(0)} + \gamma\frac{kT}{2}\left(\frac{B_1 - B_2}{l_1 - l_2} - 1\right)$$

$$l_i = l_i^{(0)} + \frac{\gamma}{2}(l_i - \delta)^2\left(\frac{l_i}{B}\right)^2 \times\left[\frac{B_1 - B_2}{l_1 - l_2} - \frac{l_i}{B_i}\left(1 - \frac{\alpha_0(l_i^2 - \delta^2)}{kTl_i^3}\right)\right]$$

with $i = 1, 2$.

V. CONCLUDING REMARKS

To judge the relevance of our results for the three-dimensional case, let us first recall the usual derivation[8] of the van der Waals equation from the partition function. One can argue as follows: If the range of the attractive force is very large so that there are many molecules in the action sphere of each molecule, then the potential energy of the attractive forces should for almost all configurations of the molecules, be equal to the average value

$$\Phi_{\text{attr}} = -CN^2/2V, \tag{46}$$

where

$$C = -\int d\mathbf{r}\, \varphi_{\text{attr}}(r).$$

Equation (46) follows because on the average, the potential energy of *one* molecule will be proportional to the number density N/V and is in fact equal to $-CN/V$. The factor two in (46) is of course needed because each molecule interacts with all other molecules. For long-range attractive forces it seems reasonable therefore to approximate the partition function by

$$Z(V,T,N) = \frac{1}{\Lambda^{3N}}\frac{1}{N!}\exp\left[CN^2/2kTV\right] \times \int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \prod_{i<j} S(|\mathbf{r}_i - \mathbf{r}_j|), \tag{47}$$

where $S(x)$ is the same step function as used in Sec. II. Now if V is very large compared to the total proper volume Nv_0, $v_0 = \frac{4}{3}\pi r_0^3$ of the molecules, then clearly the integral approaches V^N, while if V is of the same order as Nv_0 the integral will become strongly zero about as $(V - Nv_0)^N$. Approximation of the integral by the "interpolation" formula $(V - b)^N$ with $b \cong Nv_0$, then leads immediately to the van der Waals equation

$$(p + a/V^2)(V - b) = RT, \tag{48}$$

with $a = \frac{1}{2}CN^2$.

This derivation has been criticized mainly for two reasons:

1. A correct evaluation of the partition function in the thermodynamic limit should *always* give a *stable* isotherm for which $\partial p/\partial v \leq 0$. This has been proved rigorously by Van Hove[9] for an intermolecular force of finite range and with a hard core. Since there is an unstable part in the van der Waals equation below the critical temperature, the equation is in conflict with this theorem.

2. The approximation $(V - b)^N$ for the repulsive

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[8] This derivation goes back to L. S. Ornstein, Dissertation Leiden 1908. Van der Waals himself, and then later also Lorentz [*Collected Papers* (Martinus Nyhoff, The Hague, Netherlands, 1935), Vol. 6, p. 40], started from the virial theorem of Clausius. We will come back to this in Part II in this series of papers.

[9] L. Van Hove, Physica 15, 951 (1949). Recently Dr. N. G. van Kampen has pointed out a gap in Van Hove's argument. Apparently the theorem can be proved even under less restrictive conditions by a different method. See a recent paper by D. Ruelle, which will appear in the Helv. Phys. Acta. (to be published).

part of the partition function must be very rough. Even if b is fixed so that the correct second virial coefficient (which makes $b = 4Nv_0$) is obtained, the higher virial coefficients which can be computed exactly, do *not* agree with the van der Waals' values.

Let us now return to our one-dimensional system. Note that by the same reasoning as used above, one would obtain

$$Z(L, T, N) = \frac{1}{\Lambda^N}\frac{1}{N!}\exp\left[\frac{\alpha_0 N^2}{kTL}\right] \times \int_L \cdots \int_L dt_1 \cdots dt_N \prod_{i<j} S(|t_i - t_j|), \quad (49)$$

since C becomes $2\alpha_0$, with the factor two because of the two sides of the attractive force $-\alpha_0\gamma \exp[-\gamma|t|]$. The *great difference* between Eqs. (47) and (49) is that the integral in Eq. (49) can be carried out *exactly* because of the linear order which the hard cores impose. The result is $(L - N\delta)^N$. For a gas of hard rods of length δ, the equation of state as noted by Tonks[10] has precisely the van der Waals form

$$p = kT/(l - \delta). \quad (50)$$

The second objection against the van der Waals equation disappears in one dimension, and it is therefore *no* wonder that for our model in the van der Waals limit, Eq. (48) with $b = N\delta$, $a = \alpha_0 N^2$ is obtained exactly. The only question which remains is the conflict of the form (49) for Z with the Van Hove theorem. From the point of view of the development in Secs. II and III, it is clear that this conflict is due to the fact that in the derivation given above, the thermodynamic and the van der Waals limits have been coupled together, while they should be taken separately and in the proper order. Since we go *first* to the thermodynamic limit for a finite range of the attractive force, and *then* allow the range to go to infinity, we do not conflict with the Van Hove theorem, and we always obtain the stable isotherm[11]). It seems to us therefore, that the first objection against the van der Waals equation is *not* as serious as we have been led to believe.

To summarize this discussion, we conclude with the following statements.

(a) It seems a good idea, following the example of van der Waals, to try to separate the effects of the repulsive and the attractive forces on the equation of state, and to develop all thermodynamic functions in the ratio

$$\rho = \frac{\text{range of repulsive force}}{\text{range of attractive force}}. \quad (51)$$

One expects that for $\rho \ll 1$ one will get a van der Waals-*like* equation of state which would lead to the condensation phenomena and the existence of a critical point. The thermodynamic equilibrium conditions will follow automatically by going first to the thermodynamic limit.

(b) *Only* in *one* dimension does one obtain in the limit $\rho \to 0$, *exactly* the van der Waals equation of state for hard-core repulsion. This should be independent of the precise form of the attractive force. We have been able to confirm this by generalizing the Kac model to the case where the attractive force is of the form

$$\varphi_{\text{attr}}(x) = -\sum_{i=1}^{m} \alpha_i\gamma \exp[-\gamma\sigma_i x]. \quad (52)$$

The calculation of the partition function can be reduced as in Sec. II to an integral equation in m variables and the behavior of the maximum eigenvalue in the limit $\gamma \to 0$ may be considered in the same way as in Sec. III: the *same* equation (28) is obtained, except that $2\nu_0$ is replaced by

$$\frac{1}{kT}\sum_{i=1}^{m}\frac{2\alpha_i}{\sigma_i} = -\frac{2}{kT}\int_0^\infty \varphi_{\text{attr}}(x)\,dx. \quad (53)$$

Thus, again the van der Waals equation is obtained and the van der Waals a is again proportional to the area of the attractive potential.

(c) In *three* dimensions, the equation of state of a gas of hard spheres is certainly *not* $p = kT(v - b)$, although qualitatively the behavior may be similar. Even for very long-range attractive forces one can only hope to get a van der Waals-*like* equation of state. In a sense, the problem of the gas of hard spheres becomes the central problem. Whether such a gas would show a phase transition for densities near close packing (the so-called Kirkwood transition), is a famous open question. We believe that there are strong indications for the existence of such a transition and that this transition might be an idealization (or caricature!) of the fluid-solid transition. Clearly, in one dimension [see Eq. (50)], such a transition does *not* exist, and we believe therefore that even with long-range forces, to enforce cooperation, *one phase transition at most* can occur in one dimension.

Finally, we would like to mention two questions

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[10] L. Tonks, Phys. Rev. **50**, 955 (1936).

[11] For our model, the Van Hove theorem is expressed by the inequality (21) for the maximum eigenvalue $\lambda_0(s, \gamma)$, which holds for any value of γ. The isotherm is monotonically decreasing for any γ, and therefore also in the limit $\gamma = 0$, $\partial p/\partial l \leq 0$.

which we have so far been unable to answer in a satisfactory way.

1. What is the relation of our theory with the Yang–Lee theory of condensation? From the existence of a hard core, it follows that the grand partition function $G(L, z)$ must be a polynomial of degree $M = L/\delta$ in z with positive coefficients. Setting

$$G(L, z) = \exp [L\chi(L, z)],$$

one can write

$$\chi(L, z) = \frac{1}{L} \sum_{i=1}^{M} \ln \left(1 - \frac{z}{z_i}\right),$$

where the z_i are the zero's of $G(L, z)$, none of which can be on the positive real axis. One can interpret $\chi(L, z)$ as the complex logarithmic potential of M point charges of strength $1/L$ situated at the points z_i. In the limit $L \rightarrow \infty$, the strength of the charges becomes smaller and smaller while the number M increases. Suppose now that in the limit $L \rightarrow \infty$, a number of the charges concentrate in a single layer *which crosses the positive real axis*, say at $z = z_0$. The limit function

$$\bar{\chi}(z) = \lim_{L\rightarrow\infty} \chi(L, z),$$

which surely exists, will then for positive and real z, consist of two analytic pieces, one for $z < z_0$ and the other for $z > z_0$. At z_0 these two pieces will be continuous but the first derivative will have a discontinuity. Since $\bar{\chi}(z) = p/kT$ one would therefore obtain a curve as in Fig. 4 (with abscissa and ordinates interchanged), and condensation would occur. It is clear that something like this must happen for our model in the van der Waals limit. It must be that for finite γ, the single layer will *not* cross the positive real axis but leave a gap, say, of order γ. For finite γ, $\bar{\chi}(z)$ will then be analytic for all real and positive z, but in the van der Waals limit when the gap closes, condensation occurs. However, we have been unable to substantiate this picture, because it is difficult to discuss the behavior of the eigenvalues of the Kac equation for complex values of s.

2. What is the relation of our theory with the Ursell–Mayer theory? We have already mentioned the problem of the "graphological" interpretation of the coefficients a_i in the expansion of $\lambda_0(s)$ [see Eq. (22)], but there are also other questions. For instance it should be possible to introduce Mayer f functions both for the repulsive and for the attractive parts of the intermolecular potential, which would lead to graphs with two types of lines. The question is then, which simplifications occur if the attractive force is long range, and whether one can learn from the one-dimensional model how to characterize better the van der Waals-like equation in three dimensions.

APPENDIX 1

For the proof of statement (a) see Kac (reference 5, p. 11). There one also finds the proof that

$$\lambda_0(s) \geq e^{\frac{1}{2}\nu} \int_\delta^\infty d\tau \exp [-s\tau + \nu e^{-\gamma\tau}], \qquad (A.1)$$

and since for $s = 0$ the integral diverges, $\lambda_0(s) \rightarrow \infty$ for $s \rightarrow 0$. Furthermore, since the right hand side of (A.1) can be shown to correspond to the "nearest-neighbor" approximation, one should expect that for small s (i.e. small pressure), $\lambda_0(s)$ becomes equal to it, which implies that for $s \rightarrow 0$, $\lambda_0(s) \sim e^{\frac{1}{2}\nu}/s$, and this will be confirmed later when we derive the expansion (22).

The statement that $\lambda_0(s)$ cannot be degenerate for any value of s, follows from the fact that the kernel $K_s(x, y)$ is positive for all x, y and for $s > 0$. Since

$$\lambda_0(s) \geq \frac{\iint dx\, dy\, \varphi(x) K_s(x, y) \varphi(y)}{\int dx\, \varphi^2(x)} \qquad (A.2)$$

for any function $\varphi(x)$, and since the maximum is reached when $\varphi(x) = \psi_0(x)$, $K_s(x, y) > 0$ implies that $\psi_0(x)$ must have the same sign for all x, and we may assume therefore $\psi_0(x) \geq 0$. Furthermore, $\psi_0(x)$ cannot be zero, unless for some particular value of x, say x_0, $K_s(x_0, y) \equiv 0$ in y, which is excluded by $K_s > 0$. Now suppose that for some value of s, $\lambda_0(s)$ was degenerate and corresponded to the two eigenfunctions $\psi_0^{(1)}(x)$ and $\psi_0^{(2)}(x)$. Taking $\psi_0^{(1)}(x) > 0$, one then can construct a linear combination $\varphi(x)$ of $\psi_0^{(1)}$ and $\psi_0^{(2)}$ which is *orthogonal* to $\psi_0^{(1)}$, and which fulfills the equation

$$\lambda_0(s) = \frac{\iint dx\, dy\, \varphi(x) K_s(x, y) \varphi(y)}{\int dx\, \varphi^2(x)}. \qquad (A.3)$$

Since $\psi_0^{(1)}(x)$ cannot be zero, $\varphi(x)$, being orthogonal to $\psi_0^{(1)}$, must be both positive and negative over some intervals, and this yields a contradiction. The absence of a degeneracy of $\lambda_0(s)$ implies that $\lambda_0(s)$ is an analytic function of s for all real $s > 0$. This is because it is known that the eigenvalues $\lambda_i(s)$ are the zero's in λ of the Fredholm determinant

$D(x, \lambda)$, which is an entire function of λ, and is analytic for all real $s > 0$. Therefore the $\lambda_i(s)$ must be analytic functions of s except at those values of s where two or more eigenvalues cross.

Finally the inequality (21) is proved as follows: With normalized eigenfunctions, one finds from

$$\lambda_0(s) = \iint dx\, dy\; \psi_0(x, s) K_s(x, y) \psi_0(y, s),$$

that the quadratic form

$$\begin{aligned} Q(z) &\equiv \lambda_0(s)z^2 + 2\lambda_0'(s)z + \lambda_0''(s) \\ &= \iint_{-\infty}^{+\infty} dx\, dy\; \psi_0(x, s)\psi_0(y, s) \\ &\qquad \times \left[z^2 K_s(x, y) + 2z \frac{\partial K_s}{\partial s} + \frac{\partial^2 K_s}{\partial s^2} \right] \\ &\qquad + \iint_{-\infty}^{+\infty} dx\, dy \frac{\partial K_s}{\partial s} \left[\psi_0(x, s) \frac{\partial \psi_0(y, s)}{\partial s} \right. \\ &\qquad \left. + \psi_0(y, s) \frac{\partial \psi_0(x, s)}{\partial s} \right]. \end{aligned} \tag{A.4}$$

From Eq. (9) for $K_s(x, y)$, it can be seen that the variable s enters only through $p_s(x, y)$, and from Eq. (8) it follows that the first term in Eq. (4) is positive for all z. Also the second term in Eq. (4) is positive, since by using

$$K_s(x, y) = \sum_0^\infty \lambda_n(s)\psi_n(x, s)\psi_n(y, s),$$

and the fact that for any s the $\psi_n(x, s)$ form an orthonormal set, it can be transformed into

$$2\lambda_0(s) \int_{-\infty}^{+\infty} dx \left[\frac{\partial \psi_0(x, s)}{\partial s} \right]^2 - 2 \sum_{n=1}^{\infty} \lambda_n(s) \left[\int_{-\infty}^{+\infty} dx \frac{\partial \psi_0(x, s)}{\partial s} \psi_n(x, s) \right]^2,$$

and since $\lambda_n(s) < \lambda_0(s)$ for $n \geq 1$, this is bigger than

$$2\lambda_0(s) \left[\int_{-\infty}^{+\infty} dx \left(\frac{\partial \psi_0}{\partial s} \right)^2 - \sum_0^\infty \left(\int_{-\infty}^{+\infty} dx\, \psi_n \frac{\partial \psi_0}{\partial s} \right)^2 \right],$$

which is zero because of Parseval's relation applied to the function $\partial\psi_0/\partial s$. Hence $Q(z) > 0$ for all z, which implies Eq. (21).

Statement (*c*), Sec. II follows from the relation

$$\sum_0^\infty \lambda_i = \int_{-\infty}^{+\infty} dx\, K_s(x, x) = \int_\delta^\infty \frac{d\tau}{1 - e^{-\gamma\tau}} \exp \left[-s\tau + \frac{\nu}{2} \frac{1 + e^{-\gamma\tau}}{1 - e^{-\gamma\tau}} \right],$$

which shows that for $s \to 0$, the sum of all the eigenvalues goes to infinity as $e^{\frac{1}{2}\nu}/s$, and since this is also the behavior of $\lambda_0(s)$, all other eigenvalues must be finite for $s = 0$.

To find the expansion (22) for $\lambda_0(s)$, one must make a perturbation calculation around $s = 0$ for the eigenvalue problem

$$\int_{-\infty}^{+\infty} dy\; K_s(x, y)\psi_0(y, s) = \lambda_0(s)\psi_0(x, s). \tag{A.5}$$

First we expand $K_s(x, y)$ in powers of s. To do this we write $K_s(x, y)$ in the form

$$\begin{aligned} K_s(x, y) = \exp\left[\tfrac{1}{2}\nu^{\frac{1}{2}}(x + y)\right] \Bigg\{ & \frac{e^{-s\delta}}{s} [W(x)W(y)]^{\frac{1}{2}} \\ & + \sum_{n=0}^{\infty} \frac{(-s)^n}{n!} \int_\delta^\infty d\tau\; \tau^n \left(\left[\frac{W(x)}{W(y)} \right]^{\frac{1}{2}} P(x \mid y, \tau) \right. \\ & \left. - [W(x)W(y)]^{\frac{1}{2}} \right) \Bigg\}. \end{aligned} \tag{A.6}$$

Now put

$$\begin{aligned} \lambda_0(s) &= (e^{\frac{1}{2}\nu}/s)(a_{-1} + a_0 s + a_1 s^2 + \cdots), \\ \psi_0(x, s) &= \psi^{(0)}(x) + s\psi^{(1)}(x) + \cdots, \end{aligned} \tag{A.7}$$

and let $\psi^{(0)}(x)$ be normalized to one. Introducing (6) and (7) into (5) and equating the terms proportional to $1/s$, one obtains

$$\int_{-\infty}^{+\infty} dy\; [W(x)W(y)]^{\frac{1}{2}} \times \exp\left[\tfrac{1}{2}\nu^{\frac{1}{2}}(x + y)\right]\psi^{(0)}(y) = a_{-1}\psi^{(0)}(x)e^{\frac{1}{2}\nu}. \tag{A.8}$$

One easily verifies that this has the solution

$$a_{-1} = 1; \quad \psi^{(0)}(x) = (W(x))^{\frac{1}{2}} \exp\left[-\tfrac{1}{4}\nu + \tfrac{1}{2}\nu^{\frac{1}{2}}x\right]. \tag{A.9}$$

Notice that if we try to determine in the same way the values of the other eigenvalues $\lambda_n(s)$ at $s = 0$, we would find in this approximation that $a_{-1}^{(n)} = 0$, so that all $\lambda_n(0)$ for $n > 0$ are degenerate, and to find the actual values, we would have to solve an infinite secular determinant. *Only* $\lambda_0(s)$ becomes infinite for $s \to 0$, and only for $\lambda_0(s)$ can we carry the perturbation calculation further.

Equating in Eq. (5) the terms independent of s, one finds

$$\begin{aligned} \int_{-\infty}^{+\infty} dy \exp\left[\tfrac{1}{2}\nu^{\frac{1}{2}}(x + y)\right] \Bigg\{ & \Bigg(-\delta[W(x)W(y)]^{\frac{1}{2}} \\ & + \int_\delta^\infty d\tau \left[\frac{W(x)}{W(y)} \right]^{\frac{1}{2}} \\ & \times [P(x \mid y, \tau) - W(y)] \Bigg) \psi^{(0)}(y) \\ & + [W(x)W(y)]^{\frac{1}{2}}\psi^{(1)}(y) \Bigg\} \\ = e^{\frac{1}{2}\nu}[\psi^{(1)}(x) + a_0\psi^{(0)}(x)]. & \end{aligned} \tag{A.10}$$

Multiply with $\psi^{(0)}(x)$ and integrate over x. Using Eq. (9), the fact that $\psi^{(1)}(x)$ is orthogonal to $\psi^{(0)}(x)$, and the formula

$$\iint_{-\infty}^{+\infty} dx\, dy \exp\,[\nu^{\frac{1}{2}}(x+y)]W(x)P(x \mid y, \tau) = \exp\,[\nu(1+e^{-\gamma\tau})],$$

which is a special case of Eq. (4), one obtains

$$a_0 = -\delta + \int_{\delta}^{\infty} d\tau\,\{\exp\,(\nu e^{-\gamma\tau} - 1)\}. \tag{A.11}$$

The right-hand side can be written as

$$\lim_{L\to\infty} \frac{1}{2L} \iint_L dt_1\, dt_2 \left\{\exp\left[\frac{1}{kT}\varphi(|t_1 - t_2|)\right] - 1\right\},$$

which is the definition of Mayer's b_2. One also easily verifies from Eq. (10), that

$$\psi^{(1)}(x) = -(a_0+\delta)\psi^{(0)}(x) + e^{-\frac{1}{2}\nu} \int_{-\infty}^{+\infty} dy\, \psi^{(0)}(y) \exp\left[\frac{\nu^{\frac{1}{2}}}{2}(x+y)\right] \times \int_{\delta}^{\infty} d\tau \left[\frac{W(x)}{W(y)}\right]^{\frac{1}{2}} [P(x \mid y, \tau) - W(y)].$$

We can go on in this way, but the calculation soon becomes very lengthy. We have verified that in next approximation, one obtains $a_1 = b_3 - b_2^2$, where Mayer's b_3 is defined by

$$b_3 = \lim_{L\to\infty} \frac{1}{6L} \iiint_L dt_1\, dt_2\, dt_3 \times [f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23}]$$

with

$$f_{ij} = \exp\left[\frac{1}{kT}\varphi(|t_i - t_j|)\right] - 1.$$

The general expression for the a_i in terms of the Mayer b_l is lacking. To obtain the correct equation of state up to the fourth virial coefficient, a_2 should be equal to $b_4 - 3b_2b_3 + 2b_2^3$, but we have not verified this.

APPENDIX II

To indicate the proof of Eq. (24), it will be sufficient to consider the case $n = 3$. One has

$$\sum_i \lambda_i^3 = \iiint_{\delta}^{\infty} d\tau_1\, d\tau_2\, d\tau_3\, e^{-s(\tau_1+\tau_2+\tau_3)} \times \iiint_{-\infty}^{+\infty} dx_1\, dx_2\, dx_3 \exp\,[-(\nu_0\gamma)^{\frac{1}{2}}(x_1+x_2+x_3)] \times P(x_1 \mid x_2, \tau_1)P(x_2 \mid x_3, \tau_2)P(x_3 \mid x_1, \tau_3),$$

where $P(x \mid y, \tau)$ is given by Eq. (5). Introduce the new variables

$$\xi_1 = (x_2 - x_1e^{-\gamma\tau_1})(1-e^{-2\gamma\tau_1})^{-\frac{1}{2}}$$
$$\xi_2 = (x_3 - x_2e^{-\gamma\tau_2})(1-e^{-2\gamma\tau_2})^{-\frac{1}{2}}$$
$$\xi_3 = (x_1 - x_3e^{-\gamma\tau_3})(1-e^{-2\gamma\tau_3})^{-\frac{1}{2}},$$

with the Jacobian

$$\frac{\partial(\xi_1, \xi_2, \xi_3)}{\partial(x_1, x_2, x_3)} = \{1 - e^{-\gamma(\tau_1+\tau_2+\tau_3)}\} \times \prod_{i=1}^{3} (1 - \exp\,[-2\gamma\tau_i])^{-\frac{1}{2}}.$$

The integral over the x_i then becomes

$$\{(2\pi)^{\frac{3}{2}}[1-e^{-\gamma(\tau_1+\tau_2+\tau_3)}]\}^{-1} \times \iiint_{-\infty}^{+\infty} d\xi_1\, d\xi_2\, d\xi_3 \exp\,[-\tfrac{1}{2}(\xi_1^2+\xi_2^2+\xi_3^2) \times \exp\left[\frac{(\nu_0\gamma)^{\frac{1}{2}}}{e^{-\gamma(\tau_1+\tau_2+\tau_3)}-1} \sum_{i=1}^{3} A_i\xi_i\right],$$

with

$$A_i = (1-e^{-2\gamma\tau_i})^{\frac{1}{2}}[e^{-\gamma(\tau_{i+1}+\tau_{i+2})} + e^{-\gamma\tau_{i+1}} + 1],$$

and $\tau_4 \equiv \tau_1$, $\tau_5 \equiv \tau_2$.

In this form it is convenient to go to the limit $\gamma \to 0$. Since the A_i approach $3(2\gamma\tau_i)^{\frac{1}{2}}$, the integrand of the ξ_i integral becomes independent of γ, and one obtains

$$\lim_{\gamma\to 0} \gamma \sum_i \lambda_i^3 = \iiint_{\delta}^{\infty} d\tau_1 d\tau_2\, d\tau_3\, e^{-s(\tau_1+\tau_2+\tau_3)} \times [(2\pi)^{\frac{3}{2}}(\tau_1+\tau_2+\tau_3)]^{-1} \iiint_{-\infty}^{+\infty} d\xi_1\, d\xi_2\, d\xi_3 \times \prod_{i=1}^{3} \exp\left[-\tfrac{1}{2}\xi_i^2 - \frac{3(2\nu_0\tau_i)^{\frac{1}{2}}\xi_i}{\tau_1+\tau_2+\tau_3}\right]. \tag{a}$$

To uncouple the τ_i integrals, introduce the auxiliary variable

$$\eta = \frac{1}{\tau_1+\tau_2+\tau_3} \sum_{i=1}^{3} \xi_i\tau_i^{\frac{1}{2}},$$

and multiply (a) with

$$1 = \int_{-\infty}^{+\infty} d\eta\, \delta\left(\eta - \frac{1}{\tau_1+\tau_2+\tau_3}\sum_{i=1}^{3}\xi_i\tau_i^{\frac{1}{2}}\right) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} dv \times \exp\left[iv\left(\eta - \frac{1}{\tau_1+\tau_2+\tau_3}\sum_{i=1}^{3}\xi_i\tau_i^{\frac{1}{2}}\right)\right],$$

using the Fourier representation of the δ function. Set $v = w(\tau_1 + \tau_2 + \tau_3)$, and integrate first over the ξ_i. We then obtain

$$\lim_{\gamma \to 0} \gamma \sum_i \lambda_i^3 = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} dw \\ \times \left\{ \int_\delta^\infty d\tau \exp\left[-\eta(2\nu_0)^{\frac{1}{2}} + i\tau\eta w - \frac{\tau}{2} w^2 \right] \right\}^3 .$$

Finally, setting $w = \xi + i\eta$, one obtains Eq. (24) for $n = 3$. The proof for arbitrary n follows the same procedure.

APPENDIX III

The solution of Eq. (42) can be written in the form

$$H_n^{(1)}(z) = N_n[P_n D_{n+3}(z) + Q_n D_{n+1}(z) \\ + R_n D_{n-1}(z) + S_n D_{n-3}(z)],$$

where

$$P_n \equiv P = \frac{\nu_0^{\frac{3}{2}}(l - \delta)^3(l - 3\delta)}{18 l^{5/2} B^{5/2}} ,$$

$$Q_n = 9(n + 1)P + (n + 1)V - W,$$

$$R_n = -9n^2 P - n^2 V + nW,$$

$$S_n = -n(n - 1)(n - 2)P,$$

with

$$V = \nu_0^{\frac{1}{2}}(l - \delta)^2 / l^{\frac{3}{2}} B^{\frac{1}{2}}, \qquad W = \nu_0^{\frac{1}{2}}(l - \delta)^2 / 2 l^{\frac{1}{2}} B^{\frac{3}{2}}.$$

To obtain the equation for the next approximation, the left-hand side of Eq. (35) must be expanded to terms of order γ^2. Using the expansions (36), and equating terms of order γ^2, one obtains

$$\frac{d^2 H_n^{(2)}}{dz^2} + \left(n + \tfrac{1}{2} - \frac{z^2}{4}\right) H_n^{(2)} = \frac{\mu_n^{(2)}}{B} H_n^{(0)} \\ + \frac{\nu_0^{\frac{1}{2}}(l - \delta)^2 l^{\frac{1}{2}}}{4B^{5/2}} \left(\frac{4\nu_0}{3l^2} - 1\right) z^3 H_n^{(1)} \\ + \frac{\nu_0^{\frac{1}{2}}(l - \delta)^2}{l^{\frac{3}{2}} B^{\frac{1}{2}}} z \frac{d^2 H_n^{(1)}}{dz^2} + \frac{\nu_0^{\frac{1}{2}}(l - \delta)^2}{l^{\frac{3}{2}} B^{\frac{3}{2}}} \\ \times \left\{ \tfrac{1}{2} z H_n^{(1)} + \frac{B}{l} \frac{dH_n^{(1)}}{dz} \right\} \\ + H_n^{(0)}(z) \left[\frac{\nu_0^2 (l - \delta)^4 (l^2 - 2l\delta - \delta^2)}{8 l^4 B^3} z^4 \right. \\ + \frac{\nu_0 (l + \delta)(l - \delta)^3}{2 l^3 B} \left(n + \tfrac{1}{2} - \frac{l}{2B}\right) z^2 \\ - \frac{\nu_0}{12 l^2 B} (15 l^3 - 36 l^2 \delta + 30 l \delta^2 - 8\delta^3) \\ + \frac{1}{2B} (2l^2 - 2l\delta + \delta^2) \\ \left. \times \left\{ \tfrac{1}{4} + (n + \tfrac{1}{2}) \frac{B}{l} - (n^2 + n + \tfrac{3}{4}) \frac{B^2}{l^2} \right\} \right] \\ - \frac{\nu_0 (l - \delta)^3 (l + \delta)}{l^3 B} z \frac{dH_n^{(0)}}{dz} ,$$

from which $\mu_n^{(2)}$ and then $H_n^{(2)}$ can be determined in the usual way.

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On the van der Waals Theory of the Vapor–Liquid Equilibrium. II. Discussion of the Distribution Functions

G. E. UHLENBECK, P. C. HEMMER, AND M. KAC
The Rockefeller Institute, New York, New York

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For the same one-dimensional fluid model discussed in Part I, we have derived general expressions for the two- and three-particle distribution functions. It is seen that these distribution functions depend on all the eigenvalues and eigenfunctions of the basic Kac integral equation, and the dependence is so transparent that the generalization to s particles is obvious. The fluctuation and virial theorems are discussed and shown to be consequences of our general formula. In the van der Waals limit, the behavior of the two-point distribution function is discussed, both for distances of the order of the hard core and for distances of the order of the range of the attractive force. The long-range behavior is, in first approximation, equivalent to the one-dimensional version of the Ornstein–Zernike theory, but only in the one-phase region and not too near the critical point. In the two-phase region, all distribution functions are linear combinations of the two corresponding distribution functions of the saturated vapor and liquid, with coefficients proportional to the mole fractions of vapor and liquid. This is shown for our model; we also give arguments for our belief that these relations are general, and express the geometrical separation of the two phases. The relation to the Ornstein–Zernike theory is discussed in more detail, especially in connection with a recent formulation of this theory by Lebowitz and Percus. We conclude with some comments on the relevance of our results for the three-dimensional problem.

I. INTRODUCTION

THE first attempt to go beyond the question of the equation of state of a nonideal gas to the deeper problem of the correlation in position of the molecules in a gas or liquid, was made by Ornstein and Zernike in their well known theory of the critical opalescence.[1] Zernike, Prins and others[2] later used the same ideas to interpret the results of the x-ray scattering in liquids in terms of the so-called two-point correlation function. This correlation function is found to be essentially the Fourier transform of the angular distribution of the scattered rays, and it is therefore directly observable. This cannot be said of the so-called n-point correlation functions ($n = 3, 4, \cdots$) but these functions *can* be defined precisely for a system in equilibrium, and with increasing n, they describe the structure of the system in more and more detail.

The general theory of these correlation or distribution functions was developed in the forties mainly by Kirkwood, Yvon, de Boer, Mayer,[3] and their collaborators. These authors developed the general expansion theorems for these distribution functions in powers of the fugacity or in powers of the density,[4] which generalize and include the corresponding expansions for the equation of state. They also proposed various approximation schemes, of which Kirkwood's superposition approximation is the best known. This leads to new attempts to discuss the problem of phase transitions, which are of great interest.[5]

So far as we know, no one has tried to relate these general developments with the basic ideas of van der Waals in a systematic way, and it seems to us

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[1] L. S. Orsntein and F. Zernike, Proc. Acad. Sci. Amsterdam **17**, 793 (1914); Physik. Z. **19**, 134 (1918); **27**, 761 (1926). See also F. Zernike, Dissertation, Groningen, Netherlands 1916, reprinted in Arch. Neerl. Zool., Serie 13A, 4, 74 (1917). For more recent accounts compare Landau and Lifshitz, *Statistical Physics* (Pergamon Press, London, 1958), p. 366; M. Klein and L. Tisza, Phys. Rev. **76**, 1861 (1949); M. Fierz, Pauli Memorial Volume (Interscience Publishing Co., New York, 1960), p. 175; and especially P. Debye, *Non-Crystalline Solids* (John Wiley & Sons, New York, 1960), pp. 1–20; J. Chem. Phys. **31**, 680 (1959).

[2] F. Zernike and J. A. Prins, Z. Physik. **41**, 184 (1927); P. Debye and H. Menke, Physik. Z. **33**, 593 (1932).

[3] Since the literature is quite extensive, we refer to the reports by J. Yvon, *Fluctuations en densité* (Hermann & Cie., Paris, 1937); by J. de Boer, Rep. Progr. Phys. **12**, 305 (1949); by A. Munster in his book, *Statistische Thermodynamik* (Springer-Verlag, Berlin, Germany, 1956), Chap. 8; and by J. Mayer, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958) Vol. XXII, p. 152.

[4] For a complete discussion of these expansions see J. E. Mayer and E. W. Montroll, J. Chem. Phys. **9**, 2 (1941). Compare also the account given by G. E. Uhlenbeck and G. W. Ford in *Studies in Statistical Mechanics*, (North-Holland Publishing Company, Amsterdam) Vol. I, Part B.

[5] We are thinking especially of the attempts by Kirkwood and his co-workers to derive the liquid–solid phase transition and to show that such a transition even exists for a system of hard spheres. See J. G. Kirkwood and E. Monroe, J. Chem. Phys. **9**, 514 (1941); J. G. Kirkwood, E. K. Mann and B. J. Alder, J. Chem. Phys. **18**, 1040 (1950).

of interest, therefore, to derive the expression for the distribution functions for the one-dimensional gas model described in Part I of this series and to see what these functions become in the van der Waals limit. In Sec. II, the derivation of the two- and three-point distribution function is given, from which the general expression for the n-point function can easily be inferred. It is found that the distribution functions depend on *all* eigenvalues and eigenfunctions of the basic Kac integral equation (Part I, Eq. 10), and one may say that this gives a physical interpretation of the eigenvalues and eigenfunctions, although we do not know as yet whether these eigenvalues and eigenfunctions are uniquely determined by the set of distribution functions. Another general expression for the distribution functions, also derived in Sec. II, is in terms of the resolvent of the Kac equation and the eigenfunction $\psi_0(x)$ corresponding to the maximum eigenvalue $\lambda_0(s)$. This expression is especially important for the discussion of the distribution functions in the two-phase region.

In Sec. III we derive the well-known virial and fluctuation theorems. General proofs of these basic theorems are of course available, but it seems worth while to prove them directly from the Kac equation. Since these theorems connect the two-point distribution function with the equation of state, they give valuable checks for any successive-approximation method. Furthermore, they provide a link with the original derivation of the van der Waals equation.

In Secs. IV and V, the van der Waals limit and the successive approximations in powers of $\gamma\delta$ of the two-point distribution function are discussed for the *one-phase region*. It is seen that one must distinguish the case when the distance between the two molecules is of order δ from the case when this distance is of the order of the range of the attractive force $1/\gamma$. The short-range behavior is, as expected, in zeroth approximation, the same as for a gas of hard rods, since in the van der Waals limit the attractive force is very weak. In first approximation, the attractive force influences somewhat the short-range behavior, but the more interesting effect is on the long-range behavior. We find in this approximation, an exponential dependence on the distance, but with a range which is modified by the compressibility of the gas. This behavior is related to the form predicted by the one-dimensional version of the Ornstein–Zernike theory, and this relation is general (i.e., independent of the form of the long range attractive force) when we approach the critical region. However *in* the critical region our development breaks down, and deviations from the Ornstein–Zernike theory should be expected to occur. We will come back to this in Part III of this series, where the behavior of the two-point distribution function in the critical region will be discussed in detail.

In Sec. VI, the distribution functions in the van der Waals limit are discussed for the *two-phase region*. We show that *all* distribution functions in this region are linear combinations of the two corresponding distribution functions of the saturated vapor and liquid with coefficients proportional to the mole fractions of vapor and liquid. In our opinion, this shows for the first time that the geometric separation of the two phases follows automatically from the theory. In fact it seems that this property of the distribution functions is a deeper formulation of the condensation problem than the property of the constant vapor pressure (horizontal portion of the isotherm), which it implies. This has already been indicated in a basic paper by Mayer[6] in 1947, and perhaps our results can be looked upon as a strict proof, for a special case, of the general considerations given in that paper, although the precise connection is still dark to us.

In Sec. VII we discuss in detail, the connection of our results with the Ornstein–Zernike theory and especially in respect to a recent, very interesting formulation of this theory given by Lebowitz and Percus.[7] We conclude with some comments on the relevance of our results for the three-dimensional problem.

II. GENERAL EXPRESSIONS FOR THE DISTRIBUTION FUNCTIONS

First let us recall the general definitions for the distribution functions. For the *canonical ensemble*, the s-particle distribution function is defined by

$$n_s(\mathbf{r}_1 \cdots \mathbf{r}_s, N, V) = \frac{N!}{(N-s)!} \times \int_V \cdots \int_V d\mathbf{r}_{s+1} \cdots d\mathbf{r}_N D_N(\mathbf{r}_1 \cdots \mathbf{r}_N), \qquad (1)$$

where

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[6] J. E. Mayer, J. Chem. Phys. 15, 187 (1947). Compare also his paper J. Chem. Phys. 16, 665 (1948) and the account in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1958) Vol. XII, p. 165.

[7] J. L. Lebowitz and J. K. Percus, "Asymptotic behavior of the radial distribution function" (Preprint) (to be published).

$$D_N = \frac{1}{\Lambda^{3N}N!}\frac{1}{Z(V,N)} \times \exp\left[-\frac{1}{kT}\sum_{i<j}\varphi(|\mathbf{r}_i - \mathbf{r}_j|)\right]. \qquad (2)$$

The corresponding formula for the *grand-canonical ensemble* are

$$\rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s, V, z) = \sum_{N\geq s} n_s(\mathbf{r}_1 \cdots \mathbf{r}_s, V, N)P_N, \qquad (3)$$

where

$$P_N = (\Lambda z)^N Z(V, N)/G(V, z). \qquad (4)$$

In the following we will always have in mind a *single-fluid phase*. In this case one knows that in the thermodynamic limit the distribution functions approach the definite values

$$\lim_{N,V\to\infty} n_s(\mathbf{r}_1 \cdots \mathbf{r}_s, N, V) = \bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v),$$
$$\lim_{V\to\infty} \rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s, V, z) = \bar{\rho}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; z). \qquad (5)$$

and these functions differ *only* in the dependence on v, and z, respectively, which however are uniquely related to each other by the second Mayer relation

$$1/v = z\chi'(z). \qquad (6)$$

Furthermore one knows that in this case the $\bar{n}_s$ and $\bar{\rho}_s$ are *spatially homogeneous*. Adding a constant vector to $\mathbf{r}_1 \cdots \mathbf{r}_s$ will not change the functions $\bar{n}_s$ and $\bar{\rho}_s$. Therefore $\bar{n}_2(\mathbf{r}_1, \mathbf{r}_2, v)$ depends only on $|\mathbf{r}_1 - \mathbf{r}_2|$, $\bar{n}_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, v)$ depends only on the lengths of the sides of the triangle $(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, etc. Finally it is known that in this case, the functions $\bar{n}_s$ and $\bar{\rho}_s$ have the *product property*. This means that if the s particles are divided in groups containing α_1, $\alpha_2 \cdots$ particles, then for configurations in which these groups are very far apart from each other

$$\bar{n}_s = \bar{n}_{\alpha_1}\cdot\bar{n}_{\alpha_2}\cdots, \qquad (7)$$

and similarly for $\bar{\rho}_s$. Note that the meaning of "far" depends on the value of v or z. The product property implies that if all particles are far apart from each other, then $\bar{n}_s \to (1/v)^s$ and $\bar{\rho}_s \to \bar{\rho}_1^s$. Note that this product property is the only direct relation between the $\bar{n}_s$ or $\bar{\rho}_s$ and the lower distribution functions. One cannot find the lower distribution functions only by integrating over the positions of some of the particles. There are integral relations between the distribution functions, the so-called fluctuation theorems, but these relations are more complicated. We return to them in the next section.

For small density or small z, the distribution functions approach the Boltzmann factor

$$\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v) \to \frac{1}{v^s} \times \exp\left[-\frac{1}{kT}\sum_{i<j}^{s}\varphi(|\mathbf{r}_i - \mathbf{r}_j|)\right], \qquad (8)$$

and as we have already mentioned, the complete virial and fugacity expansions have been worked out (see reference 4).

After these preliminaries, let us return to our one-dimensional model. We prove that all the distribution functions can be expressed in terms of the eigenvalues $\lambda_n(s)$ and eigenfunctions $\psi_n(x, s)$ of the Kac integral equation (Part I, Eq. 10), and especially we will show that

$$l\int_0^\infty dx\, e^{-\sigma x}\bar{n}_2(x; l) = \sum_{n=0}\langle 0, s \mid n, s+\sigma\rangle \times \frac{\lambda_n(s+\sigma)}{\lambda_0(s) - \lambda_n(s+\sigma)}\langle n, s+\sigma \mid 0, s\rangle, \qquad (9a)$$

$$l\iint_0^\infty dx\, dy\, e^{-\sigma x-\sigma' y}\bar{n}_3(x, y; l)$$
$$= \sum_{n=0}^{\infty}\sum_{n'=0}^{\infty}\langle 0, s \mid n, s+\sigma\rangle \times \frac{\lambda_n(s+\sigma)}{\lambda_0(s) - \lambda_n(s+\sigma)}\langle n, s+\sigma \mid n', s+\sigma'\rangle \times \frac{\lambda_{n'}(s+\sigma')}{\lambda_0(s) - \lambda_{n'}(s+\sigma')}\langle n', s+\sigma' \mid 0, s\rangle. \qquad (9b)$$

Here, $s = p/kT$ and the symbol $\langle k, m \mid k', m'\rangle = \langle k', m' \mid k, m\rangle$, stands for the matrix element

$$\langle k, m \mid k', m'\rangle = \int_{-\infty}^{+\infty} dx\, \psi_k(x, m)\psi_{k'}(x, m'). \qquad (10)$$

The distribution functions are expressed in relative coordinates, so that

$$\bar{n}_2(x; l) = \bar{n}_2(t_2 - t_1; l) \qquad t_2 \geq t_1, \qquad (11)$$
$$\bar{n}_3(x, y; l) = \bar{n}_3(t_2 - t_1, t_3 - t_2; l) \quad t_3 \geq t_2 \geq t_1,$$

where t_1, t_2, t_3 are the coordinates of the particles. We have not derived in detail, the expression for the Laplace transform of the s-particle distribution function, but the structure of the Eqs. (9a) and (9b) is so transparent, that the generalization to the higher distribution functions seems obvious.

Proof of Eq. (9a)

As an artifice, we introduce an additional exponential attraction between all pairs of molecules and start from the new partition function

$$\tilde{Z}(L, N) = \frac{1}{\Lambda^N N!} \int_0^L \cdots \int_0^L dt_1 \cdots dt_N \prod_{i<j} S(|t_i - t_j|) \times \exp\left[\nu \sum_{i<j} e^{-\gamma|t_i-t_j|} + \epsilon \sum_{i<j} e^{-\sigma|t_i-t_j|}\right], \tag{12}$$

using the same notation as Part I, Eq. (2). It is then easy to show, that

$$\left(\frac{\partial \ln \tilde{Z}}{\partial \epsilon}\right)_{\epsilon=0} = \tfrac{1}{2} \iint_0^L dt_1\, dt_2\, e^{-\sigma|t_1-t_2|} n_2(t_1, t_2; N, L),$$

from which follows the analogous expression

$$\left(\frac{\partial \ln \tilde{G}}{\partial \epsilon}\right)_{\epsilon=0} = \tfrac{1}{2} \iint_0^L dt_1\, dt_2\, e^{-\sigma|t_1-t_2|} \rho_2(t_1, t_2; L, z) \tag{13}$$

in terms of the grand-canonical quantities. Since in the thermodynamic limit, $\ln \tilde{G} \to L\tilde{\bar{\chi}}(z, \epsilon)$, one obtains from (13) in this limit,

$$\left(\frac{\partial \tilde{\bar{\chi}}(z, \epsilon)}{\partial \epsilon}\right)_{\epsilon=0} = \int_0^\infty dx\, e^{-\sigma x} \bar{\rho}_2(x; z), \tag{14}$$

where $x = t_2 - t_1$.

Exactly in the same way as in Part I, Sec. II, one can associate with the partition function (12) the integral equation

$$\iint_{-\infty}^{+\infty} dy\, dy'\, \tilde{K}_s(x, x'; y, y')\Psi(y, y') = \Lambda\Psi(x, x'), \tag{15}$$

with

$$\tilde{K}_s(x, x'; y, y') = \left[\frac{W(x)W(x')}{W(y)W(y')}\right]^{\frac{1}{2}} \times \exp\left[\tfrac{1}{2}\nu^{\frac{1}{2}}(x + y) + \tfrac{1}{2}\epsilon^{\frac{1}{2}}(x' + y')\right] \times \int_\delta^\infty d\tau\, e^{-s\tau} P_\gamma(x \mid y, \tau) P_\sigma(x' \mid y', \tau). \tag{16}$$

We omit the proof, since it will be obvious to the reader. The notation is again the same as in Part I except that in the P functions, the different ranges of the exponential attractions are indicated. The function $\tilde{\bar{\chi}}(z, \epsilon)$ is related to the maximum eigenvalue $\Lambda_0(s, \epsilon)$ of Eq. (15) by the equation [similar to Part I, Eq. (18)]

$$\Lambda_0(s, \epsilon) = (1/z) \exp\left[\tfrac{1}{2}(\nu + \epsilon)\right], \tag{17}$$

where $s = \bar{p}/kT = \tilde{\bar{\chi}}(z, \epsilon)$. To calculate the left-hand side of Eq. (14), one must make therefore a perturbation calculation for Λ_0 up to first order in ϵ.

It is easy to see that for $\epsilon = 0$, Eq. (15) is separable and that then the eigenfunctions are given by

$$\Psi^{(0)}_{n,n'}(x, x', s) = \psi_n(x, s + n'\sigma) N_{n'} D_{n'}(x'), \tag{18}$$

corresponding to the eigenvalues

$$\Lambda^{(0)}_{nn'}(s) = \lambda_n(s + n'\sigma), \tag{19}$$

where $\psi_n(x, s)$, $\lambda_n(s)$ are the eigenfunctions and eigenvalues of the Kac equation, Part I, (10), $D_n(x)$ are the Weber functions, and N_n are the normalization constants $(2\pi)^{-\frac{1}{4}}(n!)^{-\frac{1}{2}}$. Setting

$$\Lambda(s, \epsilon) = \Lambda^{(0)}(s) + \epsilon\Lambda^{(1)}(s) + \cdots,$$

$$\Psi(x, x', s, \epsilon) = \Psi^{(0)}(x, x', s) + \epsilon^{\frac{1}{2}}\Psi^{(1)}(x, x', s) + \cdots,$$

one finds by a straightforward perturbation calculation for the maximum eigenvalue and the corresponding eigenfunction

$$\Psi^{(1)}_{00}(x, x', s) = \tfrac{1}{2} \sum_{n=0}^{\infty} \frac{\lambda_0(s) + \lambda_n(s + \sigma)}{\lambda_0(s) - \lambda_n(s + \sigma)} \times \langle 0, s \mid n, s + \sigma\rangle \Psi^{(0)}_{n1}(x, x', s),$$

$$\Lambda^{(1)}_{00}(s) = \lambda_0(s) \times \left[\tfrac{1}{2} + \sum_{n=0}^{\infty} \frac{\lambda_n(s + \sigma)}{\lambda_0(s) - \lambda_n(s + \sigma)} \langle 0, s \mid n, s + \sigma\rangle^2\right], \tag{20}$$

where the completeness relation

$$\sum_n \langle 0, s \mid n, s + \sigma\rangle^2 = 1 \tag{21}$$

has been used.

Now return to Eq. (17). We have found the maximum eigenvalue of (15):

$$\Lambda_0(s, \epsilon) = \lambda_0(s) + \epsilon\Lambda^{(1)}_{00}(s) + \cdots.$$

Introduce here:

$$s = \tilde{\bar{\chi}}(z, \epsilon) = \bar{\chi}(z) + \epsilon\chi_1(z) + \cdots,$$

where $\bar{\chi}(z) = p/kT$ follows from Part I, Eq. (18). One then obtains from (17), by equating the terms proportional to ϵ,

$$\bar{\chi}_1(z) = \left(\frac{\partial \tilde{\bar{\chi}}(z, \epsilon)}{\partial \epsilon}\right)_{\epsilon=0} = \frac{1}{l}\left[\frac{\Lambda^{(1)}_{00}(\bar{\chi})}{\lambda_0(\bar{\chi})} - \frac{1}{2}\right], \tag{22}$$

using Eq. (20) from Part I. Substituting in (14) one obtains Eq. (9a), from (20), since in the thermodynamic limit $\bar{\rho}_2(x, z) = \bar{n}_2(x, l)$ with $1/l = z\bar{\chi}'(z)$.

Proof of Eq. (9b)

To generalize the trick used for the two-point distribution function, one is inclined to introduce three additional exponential potentials corresponding to the three distances between the three particles. However to ensure the triangular relation between the three distances it then becomes necessary to associate with each molecule, an additional "internal coordinate" μ_i, which can be ± 1, and to average over-all sets of values of the μ_i. We start therefore from the new partition function

$$\tilde{Z}(L, N, \epsilon_1, \epsilon_2, \epsilon_3) = \frac{1}{2^N \Lambda^N N!}$$
$$\times \sum_{\{\mu_i\}} \int_0^L \cdots \int_0^L dt_1 \cdots dt_N \prod_{i<j} S(|t_i - t_j|)$$
$$\times \exp\left[\nu \sum_{i<j} e^{-\gamma|t_i - t_j|} + \sum_{\alpha=1}^{3} \epsilon_\alpha \sum_{i<j} \mu_i \mu_j e^{-\sigma_\alpha |t_i - t_j|}\right]. \tag{23}$$

By differentiating after the ϵ_α and then setting them equal to zero, and by summing over the μ_i, it is found, using also the fact that $\rho_3(t_1, t_2, t_3; L, z)$ is symmetric in t_1, t_2, t_3:

$$\left(\frac{\partial^3 \ln \tilde{G}}{\partial\epsilon_1\, \partial\epsilon_2\, \partial\epsilon_3}\right)_{\epsilon_\alpha = 0}$$
$$= \iiint\limits_{0 \le t_1 \le t_2 \le t_3 \le L} dt_1\, dt_2\, dt_3\, \rho_3(t_1, t_2, t_3; L, z)$$
$$\times \sum_{P_i} \exp\left[-\sigma_{P_1}|t_1 - t_2| - \sigma_{P_2}|t_2 - t_3| - \sigma_{P_3}|t_3 - t_1|\right],$$

where the sum goes over the six permutations of the indices 1, 2 and 3. This result is similar to Eq. (13). By going to the thermodynamic limit, setting $\ln \tilde{G} = L\tilde{\bar{\chi}}(z, \epsilon_1, \epsilon_2, \epsilon_3)$ and $t_2 - t_1 = x$, $t_3 - t_2 = y$, one obtains

$$\left(\frac{\partial^3 \tilde{\bar{\chi}}}{\partial\epsilon_1\, \partial\epsilon_2\, \partial\epsilon_3}\right)_{\epsilon_\alpha = 0} = \iint\limits_0^\infty dx\, dy\, \bar{\rho}_3(x, y; z)$$
$$\times \sum_{P_i} \exp\left[-\sigma_{P_1} x - \sigma_{P_2} y - \sigma_{P_3}(x + y)\right], \tag{24}$$

which is similar to Eq. (14).

One now associates again with the partition function (23), the corresponding integral equation, which is

$$\iiiint\limits_{-\infty}^{+\infty} dy\, dy_1\, dy_2\, dy_3\, K_0(\mathbf{x}, \mathbf{y})$$
$$\times \left[\cosh\left(\sum_{\alpha=1}^{3} x_\alpha \epsilon_\alpha^{\frac{1}{2}}\right) \cosh\left(\sum_{\alpha=1}^{3} y_\alpha \epsilon_\alpha^{\frac{1}{2}}\right)\right]$$
$$\times \Psi(\mathbf{y}) = \Lambda \Psi(\mathbf{x}), \tag{25}$$

with $\mathbf{x} = (x, x_1, x_2, x_3)$, $\mathbf{y} = (y, y_1, y_2, y_3)$ and

$$K_0(\mathbf{x}, \mathbf{y}) = \left[\frac{W(x)W(x_1)W(x_2)W(x_3)}{W(y)W(y_1)W(y_2)W(y_3)}\right]^{\frac{1}{2}}$$
$$\times \exp\left[\tfrac{1}{2}\nu^{\frac{1}{2}}(x + y)\right]$$
$$\times \int_\delta^\infty d\tau\, e^{-s\tau} P_\gamma(x \mid y, \tau) \prod_{\alpha=1}^{3} P_{\sigma_\alpha}(x_\alpha \mid y_\alpha, \tau), \tag{26}$$

which is similar to Eqs. (15) and (16). The appearance of the cosh functions instead of exponential functions is due to the summation over the μ_i. The maximum eigenvalue $\Lambda_0(s, \epsilon_1, \epsilon_2, \epsilon_3)$ of Eq. (25) is again related to the function $\tilde{\bar{\chi}}(z, \epsilon_1, \epsilon_2, \epsilon_3)$ by

$$\Lambda_0(s, \epsilon_1, \epsilon_2, \epsilon_3) = (1/z) \exp\left[\tfrac{1}{2}(\nu + \epsilon_1 + \epsilon_2 + \epsilon_3)\right], \tag{27}$$

with $s = \tilde{p}/kT = \tilde{\bar{\chi}}(z, \epsilon_1, \epsilon_2, \epsilon_3)$, and to determine the left-hand side of Eq. (24) one must perform a perturbation calculation for Λ_0 up to first order in ϵ_1, ϵ_2 and ϵ_3. This is now much more involved, and we refer to Appendix A for some of the details and the completion of the proof.

By introducing the *resolvent* $R_s(x, y; \rho)$ of the Kac integral equation, [Part I, Eq. (10)], the expressions (9a) and (9b) for the distribution functions can be transformed into

$$l \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2(x; l) = \frac{1}{\lambda_0(s)} \iint\limits_{-\infty}^{+\infty} dx\, dy\, \psi_0(x, s)$$
$$\times R_{s+\sigma}\left(x, y; \frac{1}{\lambda_0(s)}\right) \psi_0(y, s) \tag{28a}$$

$$l \iint\limits_0^\infty dx\, dy\, e^{-\sigma x - \sigma' y} \bar{n}_3(x, y; l)$$
$$= \frac{1}{\lambda_0^2(s)} \iiint\limits_{-\infty}^{+\infty} dx_1\, dx_2\, dx_3$$
$$\times \psi_0(x_1, s) R_{s+\sigma}\left(x_1, x_2; \frac{1}{\lambda_0(s)}\right)$$
$$\times R_{s+\sigma'}\left(x_2, x_3; \frac{1}{\lambda_0(s)}\right) \psi_0(x_3, s). \tag{28b}$$

The proof is simple. The resolvent is defined in terms of the iterated kernels by

$$R_s(x, y; \rho) = K_s(x, y) + \rho K_s^{(1)}(x, y)$$
$$+ \rho^2 K_s^{(2)}(x, y) + \cdots, \tag{29}$$

where

$$K_s^{(l)}(x, y) = \int_{-\infty}^{+\infty} dz\, K_s^{(l-1)}(x, z) K_s(z, y),$$

with $K_s^{(0)}(x, y) \equiv K_s(x, y)$. Since in terms of the eigenfunctions,

$$K_s^{(l)}(x, y) = \sum_{n=0}^{\infty} \lambda_n^{l+1}(s) \psi_n(x, s) \psi_n(y, s), \tag{30}$$

then Eq. (28a) and (28b) follow from (9a) and (9b) by expanding the fractions in the latter equations in powers of $\lambda_n(s+\sigma)/\lambda_0(s)$, and performing the summations over n.

We conclude this section with some simple checks of the general formulas (9a) and (9b).

(a) For $\nu = 0$, i.e. for a gas of hard rods, the ψ_n are independent of s, so that $\langle 0, s \mid n, s+\sigma\rangle = \delta_{n0}$, and $\lambda_0(s) = e^{-s\delta}/s$. Therefore Eq. (9a) gives

$$l \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2^{\text{h.c.}}(x; l) = \frac{1}{[1+\sigma(l-\delta)]e^{\delta\sigma} - 1}, \quad (31)$$

using $s = p/kT = 1/(l-\delta)$. This is equivalent to a well-known result first derived by Zernike and Prins.[8]

(b) For $\nu = 0$, one obtains from Eq. (9b)

$$\begin{aligned} l \iint_0^\infty dx\, dy\, e^{-\sigma x - \sigma' y} \bar{n}_3^{\text{h.c.}}(x, y; l) &= l \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2^{\text{h.c.}}(x; l) \\ &\quad \cdot l \int_0^\infty dy\, e^{-\sigma' y} \bar{n}_2^{\text{h.c.}}(y; l), \qquad (31a) \end{aligned}$$

which is expected, since it is known[9] that Kirkwood's superposition principle is valid for one-dimensional systems with nearest-neighbor interaction.

(c) For large x, $\bar{n}_2(x; l) \to 1/l^2$, since

$$\begin{aligned} \lim_{x\to\infty} \bar{n}_2(x, l) &= \lim_{\sigma\to 0} \sigma \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2(x, l) \\ &= -\frac{1}{l} \frac{\lambda_0(s)}{\lambda_0'(s)} = \frac{1}{l^2}, \end{aligned}$$

using the fact that $\langle 0, s \mid n, s\rangle = \delta_{n0}$. In a similar way one proves that for large y

$$\lim_{y\to\infty} \int_0^\infty dx\, e^{-\sigma x} \bar{n}_3(x, y; l) = \frac{1}{l} \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2(x, l).$$

We have thus verified the product property for $\bar{n}_2$ and $\bar{n}_3$. It can also be shown that for large l, $\bar{n}_2$ and $\bar{n}_3$ approach the corresponding Boltzmann factor [see Eq. (8)], but we will leave the proof to the reader.

III. THE FLUCTUATION AND VIRIAL THEOREMS

From the product property of the distribution functions $\bar{n}_s$ and $\bar{\rho}_s$, it follows that the corresponding *cluster functions*, defined by

$$\begin{aligned} \chi_1(\mathbf{r}_1; z) &= \bar{\rho}_1(\mathbf{r}_1; z) \\ \chi_2(\mathbf{r}_1, \mathbf{r}_2; z) &= \bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2; z) - \bar{\rho}_1(\mathbf{r}_1; z)\bar{\rho}_1(\mathbf{r}_2; z) \\ \chi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; z) &= \bar{\rho}_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; z) - \bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2; z)\bar{\rho}_1(\mathbf{r}_3; z) \\ &\quad - \bar{\rho}_2(\mathbf{r}_2, \mathbf{r}_3; z)\bar{\rho}_1(\mathbf{r}_1; z) \\ &\quad - \bar{\rho}_2(\mathbf{r}_3, \mathbf{r}_1; z)\bar{\rho}_1(\mathbf{r}_2; z) \\ &\quad + 2\bar{\rho}_1(\mathbf{r}_1; z)\bar{\rho}_1(\mathbf{r}_2; z)\bar{\rho}_1(\mathbf{r}_3; z), \qquad (32) \end{aligned}$$

etc.,[10] have the *cluster property*, which means that for any configuration where the s particles are divided in two or more noninteracting groups the $\chi_s(\mathbf{r}_1 \cdots \mathbf{r}_s; z)$ vanishes. As a consequence the integrals

$$\lim_{V\to\infty} \frac{1}{V} \int_V \cdots \int_V \chi_s(\mathbf{r}_1 \cdots \mathbf{r}_s; z)\, d\mathbf{r}_1 \cdots d\mathbf{r}_s \qquad (33)$$

must have a thermodynamic meaning, and the results are the so-called fluctuation theorems. From the definitions of the $\bar{\rho}_s$ one easily finds[11]

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[8] The result of Zernike and Prins [Z. Physik. **41**, 184 (1927)] can be written

$$\begin{aligned} n_2^{\text{h.c.}}(x; l) &= \frac{1}{l} \sum_{k=1}^\infty S(x - k\delta) \frac{(x-k\delta)^{k-1}}{(l-\delta)^k (k-1)!} \\ &\qquad \times \exp\left[-\frac{x-k\delta}{l-\delta}\right], \end{aligned}$$

where $S(y)$ is again the stepfunction. By taking the Laplace transform one obtains (31).

[9] Z. W. Salsburg, R. W. Zwanzig, and J. G. Kirkwood, J. Chem. Phys. **21**, 1098 (1953). Compare also the discussion of one-dimensional systems by A. Munster (*Statistische Thermodynamik*, Sec. 8.8).

[10] The general rule is as follows: Divide the s particles in a number of groups and form the product of the functions $\bar{\rho}_l$ which depend on the particles in each group. Then χ_s will be the sum of products for all possible ways of division of the s particles with the coefficient $(-1)^{k-1}(k-1)!$, where k is the number of groups into which the s particles were divided. Similar formulas hold for the functions $\bar{n}_s$; one obtains the same functions χ_s except that z must be expressed in v.

[11] There is the following difficulty: Eqs. (34 a & b) are derived, starting from the normalization condition

$$\int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_s\, \rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s; V, z) = \left\langle \frac{N!}{(N-s)!} \right\rangle_{\text{av}}$$

which follows from the definition of ρ_s. The average of $N!/(N-s)!$ over the grand canonical ensemble can be expressed in terms of $\bar{N}$ and its derivatives after the chemical potential μ and this then leads to the Eqs. (34 a & b). Now if one uses the *same* argument for the canonical distribution function $n_s(\mathbf{r}_1 \cdots \mathbf{r}_s; N, V)$, which is normalized according to

$$\int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_s\, n_s(\mathbf{r}_1 \cdots \mathbf{r}_s; N, V) = \frac{N!}{(N-s)!},$$

then one obtains a different answer because it is the averaging over N which brings in the derivatives of the specific volume after the pressure. On the other hand, for a single-fluid phase, the limit functions $\bar{n}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; v)$ and $\bar{\rho}_s(\mathbf{r}_1 \cdots \mathbf{r}_s; z)$ are identical and therefore also the cluster functions formed from them should be the same if one expresses v in z or vice versa.

This paradox has often been discussed in the literature [see for instance J. C. Mayer, Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1958) Vol. XII, p. 156)]. The mathematical reason for the apparent discrepancy must lie in the interchange of the two limiting processes which are required to derive Eqs. (34 a & b). Apparently this interchange is *not* allowed for the canonical distribution functions, although the exact reason is not clear to us.

$$\lim_{V\to\infty}\frac{1}{V}\iint_V d\mathbf{r}_1\,d\mathbf{r}_2\,\chi_2=\frac{kT}{v}\frac{\partial}{\partial p}\left(\frac{1}{v}\right)-\frac{1}{v}\,,\tag{34a}$$

$$\lim_{V\to\infty}\frac{1}{V}\iiint_V d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3\,\chi_3=\frac{k^2T^2}{v}\frac{\partial}{\partial p}\left[\frac{1}{v}\frac{\partial}{\partial p}\left(\frac{1}{v}\right)\right]$$

$$-\frac{3kT}{v}\frac{\partial}{\partial p}\left(\frac{1}{v}\right)+\frac{2}{v}\,,\tag{34b}$$

etc.

These results can also be derived directly from the expressions (9a), and (9b) for the distribution functions. For instance from (9a), it follows that

$$\int_0^\infty dx\,e^{-\sigma x}\left[\bar{n}_2(x,l)-\frac{1}{l^2}\right]=-\frac{1}{\sigma l^2}-\frac{1}{l}$$

$$+\frac{1}{l}\sum_{n=0}^{\infty}\frac{\lambda_0(s)}{\lambda_0(s)-\lambda_n(s+\sigma)}\langle 0,s\mid n,s+\sigma\rangle^2,\tag{35}$$

using the completeness relation (21). Now for $\sigma\to 0$, $\langle 0,s\mid n,s+\sigma\rangle\to 0$ for $n\neq 0$, and $\langle 0,s\mid 0,s+\sigma\rangle\to 1+O(\sigma^2)$, which follows from the normalization condition. Therefore for $\sigma\to 0$ the right-hand side of (35) becomes

$$-\frac{1}{\sigma l^2}-\frac{1}{l}+\frac{\lambda_0(s)(1+O(\sigma^2))}{-\sigma\lambda_0'(s)-\frac{1}{2}\sigma^2\lambda_0''(s)-\cdots}$$

$$=-\frac{1}{l}-\frac{1}{2l^2}\frac{\lambda_0''(s)}{\lambda_0'(s)}=-\frac{1}{2l}-\frac{kT}{2l^3}\frac{\partial l}{\partial p}\,,$$

using $l=-\lambda_0'/\lambda_0$, $s=p/kT$. Therefore

$$\lim_{L\to\infty}\frac{1}{L}\iint_L dt_1\,dt_2\,\chi_2$$

$$=2\int_0^\infty dx\left[\bar{n}_2(x;l)-\frac{1}{l^2}\right]=-\frac{1}{l}-\frac{kT}{l^3}\frac{\partial l}{\partial p}\,,\tag{36}$$

which is Eq. (34a). In a similar way one can verify Eq. (34b).

A second group of "thermodynamical" relations for the distribution functions follow from the fact that the Helmholtz free energy $\Psi=-kT\ln Z(V,T,N)$. This has as a consequence that the internal energy is given by

$$E=\Psi-T\frac{\partial\Psi}{\partial T}=\frac{3NkT}{2}$$

$$+\frac{1}{2}\iint_V d\mathbf{r}_1\,d\mathbf{r}_2\,\varphi(|\mathbf{r}_1-\mathbf{r}_2|)n_2(\mathbf{r}_1,\mathbf{r}_2;V,N),\tag{37}$$

and the pressure by[12]

$$p=-\frac{\partial\Psi}{\partial V}=\frac{NkT}{V}$$

$$-\frac{1}{6V}\iint_V d\mathbf{r}_1\,d\mathbf{r}_2\left(r_{12}\frac{d\varphi}{dr_{12}}\right)n_2(\mathbf{r}_1,\mathbf{r}_2;V,N),\tag{38}$$

which becomes, in the thermodynamic limit,

$$p=\frac{kT}{v}-\frac{1}{6}\int d\mathbf{r}\,r\,\frac{d\varphi}{dr}\,\bar{n}_2(r;v).\tag{39}$$

This is called the virial theorem, since it can also be derived directly from the virial theorem of Clausius. If the intermolecular potential $\varphi(r)$ contains a hard-sphere repulsion, then at $r=d=$ diameter of the sphere, $d\varphi/dr$ is not defined and (39) must be replaced by

$$p=\frac{kT}{v}+bkT\bar{n}_2(d^+;v)$$

$$-\tfrac{2}{3}\pi\int_d^\infty dr\,r^3\,\frac{d\varphi_{\text{attr}}}{dr}\,\bar{n}_2(r;v)\,,\tag{40}$$

where $b=\frac{2}{3}\pi\,d^3$ and $\bar{n}_2(d^+;v)=\lim_{r\to d}n_2(r;v)$. Note that the one-dimensional version of Eq. (40) is

$$p=\frac{kT}{l}+\delta kTn_2(\delta^+;l)$$

$$-\int_\delta^\infty dx\,x\,\frac{d\varphi_{\text{attr}}}{dx}\,\bar{n}_2(x;l)\,,\tag{40a}$$

where δ is again the length of the hard rod.

By further differentiation after T and V, one obtains from (37) and (38), thermodynamic relations involving the higher distribution functions. For instance, from (37) one gets for the specific heat per particle at constant volume, the general expression

$$c_v=\frac{3k}{2}+\frac{v}{2kT^2}\int d\mathbf{r}\,\varphi(r)\Big\{\varphi(r)\bar{n}_2(r;v)$$

$$+\int d\mathbf{r}_3\,[\varphi(r_{13})+\varphi(r_{23})]\bar{n}_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;v)$$

$$+\tfrac{1}{2}\iint d\mathbf{r}_3\,d\mathbf{r}_4\,[\bar{n}_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4;v)$$

$$-\bar{n}_2(\mathbf{r}_1,\mathbf{r}_2;v)\bar{n}_2(\mathbf{r}_3,\mathbf{r}_4;v)]\Big\}.$$

The question arises as to the verification of these relations directly from the expressions (9) or (28) for the distribution functions, and here one encounters the following apparent difficulty. Since $\varphi_{\text{attr.}}=-\alpha e^{-\gamma x}$, the integrals in (37) and (40a) involving $\bar{n}_2(x;l)$, are similar to the Laplace transform of $\bar{n}_2(x;l)$, if σ is made equal to γ. However, according to (9a), the Laplace transform of $\bar{n}_2(x;l)$

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[12] Following H. S. Green [Proc. Roy. Soc. (London) **189**, 103 (1947)], the simplest way of deriving Eq. (38) is by assuming a cubical vessel of volume $V=L^3$. By setting $\mathbf{r}_i^*=\mathbf{r}_i/L$, the limits of integral in Ψ then become independent of L and one can carry out the differentiation after V or L under the integral signs.

depends on *all* the eigenvalues and eigenfunctions of the Kac equation, while according to (37) [which for our model becomes ($\epsilon = E/N$)],

$$\epsilon = \frac{kT}{2} - \alpha l \int_\delta^\infty dx\, e^{-\gamma x} \bar{n}_2(x; l); \tag{41}$$

the Laplace transform for $\sigma = \gamma$ has thermodynamic meaning and therefore can depend only on the maximum eigenvalue λ_0. The reason for the remarkable simplification occurring when $\sigma = \gamma$ becomes clear if we go back to the derivation of Eq. (9a). Clearly, if $\sigma = \gamma$, the device of adding the exponential attraction $\epsilon e^{-\sigma x}$ amounts to increasing the strength of the real attractive potential from ν to $\nu + \epsilon$. Equations (14) and (17) are still valid, but the associated integral equation is now almost exactly like the Kac equation, except that ν is replaced by $\nu + \epsilon$. The kernel, developed in powers of ϵ is therefore

$$K_s(x, y, \epsilon) = K_s(x, y)[1 + (\epsilon/4\nu^{\frac{1}{2}})(x + y) + \cdots],$$

and performing the perturbation calculation one now finds

$$\Lambda_0(s, \epsilon) = \lambda_0(s) + \epsilon\lambda_0^{(1)}(s) + \cdots,$$

with

$$\lambda_0^{(1)}(s) = \frac{\lambda_0(s)}{2\nu^{\frac{1}{2}}} \int_{-\infty}^{+\infty} dx\, x\psi_0^2(x).$$

From the analog of (22) one therefore obtains instead of (9a), the equation

$$l \int_0^\infty dx\, e^{-\gamma x} \bar{n}_2(x; l) = \frac{1}{2\nu^{\frac{1}{2}}} \int_{-\infty}^{+\infty} dx\, x\psi_0^2(x) - \tfrac{1}{2}. \tag{42}$$

It is easy to verify that this equation is equivalent to (41). In fact, since in terms of the chemical potential,

$$\epsilon = \mu - T(\partial\mu/\partial T) - p(\partial\mu/\partial p),$$

and since [see Part I, Eqs. (18), (19)]

$$\mu = kT \ln (\Lambda z),$$

$$\ln \lambda_0(s, \nu) = \tfrac{1}{2}\nu - \ln z,$$

one finds

$$\epsilon/kT = \tfrac{1}{2}\nu - (\nu/\lambda_0)(\partial\lambda_0/\partial\nu)_s + \tfrac{1}{2},$$

which, together with

$$\frac{\partial\lambda_0}{\partial\nu} = \iint\limits_{-\infty}^{+\infty} dx\, dy\, \frac{\partial K_s(x, y)}{\partial\nu}\, \psi_0(x)\psi_0(y)$$

$$= \frac{\lambda_0}{2\nu^{\frac{1}{2}}} \int_{-\infty}^{+\infty} dx\, x\psi_0^2(x),$$

reduces (41) to (42).

The virial theorem (39a) can be verified in a similar manner. We omit the details, because in a way these verifications are simply a rearrangement of the general thermodynamic argument. The question remains how to derive the basic identities like Eq. (42), which can also be written in the form

$$\frac{\lambda_0(s)}{2\nu^{\frac{1}{2}}} \int_{-\infty}^{+\infty} dx\, x\psi_0^2(x, s) - \frac{\lambda_0(s)}{2}$$

$$= \iint\limits_{-\infty}^{+\infty} dx\, dy\, \psi_0(x, s)\psi_0(y, s) R_{s+\gamma}\left(x, y; \frac{1}{\lambda_0(s)}\right),$$

directly from the Kac integral equation. Such a derivation is given in Appendix B.

IV. THE VAN DER WAALS LIMIT OF THE TWO-POINT DISTRIBUTION FUNCTION; THE SHORT-RANGE BEHAVIOR

To investigate in the range x of order δ, the behavior of $\bar{n}_2(x; l)$ in the van der Waals limit, i.e. for $\gamma \to 0$ after setting $\nu = \nu_0\gamma$, it is simplest to start from Eq. (28a). The first step is to "tame" the kernel $K_{s+\sigma}(x, y)$ as in Part I, Sec. III, by the substitution

$$x = x' + \eta(2/\gamma)^{\frac{1}{2}}, \qquad y = y' + \eta(2/\gamma)^{\frac{1}{2}},$$

where $\eta(s)$ is determined by Eq. (29) in Part I. The contribution of the first term of the resolvent series (29), to Eq. (28a) then becomes

$$\frac{1}{\lambda_0(s)} \iint dx'\, dy'\, h(x')h(y') \left[\frac{W(x')}{W(y')}\right]^{\frac{1}{2}} \cdot \int_\delta^\infty d\tau\, e^{-(s+\sigma)\tau}$$

$$\times P_\gamma(x' \mid y', \tau) \exp \{\tfrac{1}{2}(\nu_0\gamma)^{\frac{1}{2}}(x' + y' + 2\eta[2/\gamma]^{\frac{1}{2}})$$

$$- [\eta^2/\gamma + \eta(x' + y')/(2\gamma)^{\frac{1}{2}}] \tanh (\tfrac{1}{2}\gamma\tau)\},$$

where $h(x')$ is defined by Eq. (34) in Part I. One must now substitute the expansions (36) in Part I, for $h(x')$ and $\lambda_0(s)$, and expand everything in powers of γ. Because of the taming, the zeroth approximation is very simple, since for $\gamma \to 0$, $P_\gamma(x' \mid y', \tau \to \delta(x' - y')$, and since $h^{(0)}(x')$ is normalized to unity, one obtains for $\gamma \to 0$,

$$\frac{e^{\eta(2\nu_0)^{\frac{1}{2}}}}{\omega(s)} \int_\delta^\infty d\tau \exp [-(s + \sigma)\tau - \tfrac{1}{2}\eta^2\tau]$$

$$= \frac{\exp [\eta(2\nu_0)^{\frac{1}{2}} - (s + \sigma + \frac{1}{2}\eta^2)\delta]}{\omega(s)(s + \sigma + \frac{1}{2}\eta^2)} \equiv \frac{A}{\omega(s)}, \tag{43}$$

or one can say that for $\gamma \to 0$, $K_{s+\sigma}(x, y)$ can be replaced by $A\delta(x' - y') = A\delta(x - y)$ where A is defined by (43). Hence $K_{s+\sigma}^{(2)}(x, y) \to A^2\delta(x - y)$, etc., and one obtains

$$l \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2(x; l)$$

$$= \frac{A}{\omega} + \frac{A^2}{\omega^2} + \frac{A^3}{\omega^3} + \cdots = \frac{1}{[1 + \sigma(l - \delta)]e^{\sigma\delta} - 1},$$

using $s + (\frac{1}{2}\eta^2) = 1/(l - \delta)$ which follows from I, Eqs. (30) and (31).

In zeroth approximation, one obtains therefore, exactly the same result as for a gas of hard rods [see Eq. (31)]. This would of course be expected, since for small γ, the attractive force at distances of order δ is very weak and, in zeroth approximation, will not affect the arrangement of the molecules, which arrangement will be determined only by the repulsive core.

In the first approximation, the attractive force will have an influence even at distances of order δ. To calculate this effect, one must collect all terms of order γ in the resolvent series. One then finds

$$l \int_0^\infty dx\, e^{-\sigma x} \bar{n}_2(x, l) = \frac{1}{[1 + \sigma(l - \delta)]e^{\sigma\delta} - 1}$$

$$+ \frac{\gamma\nu_0(l - \delta)^4}{lB} \frac{\sigma^2 e^{2\sigma\delta}}{\{[1 + \sigma(l - \delta)]e^{\sigma\delta} - 1\}^3} + \cdots . \tag{44}$$

See Appendix C for some of the details of the lengthy calculation. The results derived in Part I, Sec. III must be used.

As mentioned previously in the introduction, it is interesting to check these results with the virial theorem in the form of Eq. (40a). To do this, one must find $\bar{n}_2(\delta^+; l)$ from Eq. (44). Multiply both sides of (44) by $\sigma e^{\sigma\delta}$ and then go to the limit $\sigma \to \infty$. The left-hand side, (with $x' = x - \delta$) becomes

$$\lim_{\sigma\to\infty} \sigma \int_0^\infty dx'\, e^{-\sigma x'} \bar{n}_2(x' + \delta; l)$$

$$\cong \bar{n}_2(\delta^+; l)\sigma \int_0^\infty dx'\, e^{-\sigma x'} = \bar{n}_2(\delta^+; l),$$

and by calculating the limit of the right-hand side, one obtains

$$\bar{n}_2(\delta^+; l) = 1/l(l - \delta) + \gamma\nu_0(l - \delta)/l^2 B + \cdots . \tag{45}$$

Consider first the zeroth approximation, and substitute in (40a). One obtains

$$\frac{p}{kT} = \frac{1}{l - \delta} - \nu_0\gamma^2 \int_\delta^\infty dx\, x\, e^{-\gamma x} \bar{n}_2(x, l),$$

If we introduce $\gamma x = x'$ into the integral, then since in the limit $\gamma \to 0$, $\bar{n}_2(x'/\gamma; l) = 1/l^2$, the integral becomes

$$-\frac{\nu_0}{l^2} \int_0^\infty dx'\, x' e^{-x'} = -\frac{\nu_0}{l^2},$$

so that the van der Waals equation is obtained once more. The second term in (45) leads to a part of the correction to the van der Waals equation of order γ mentioned at the end of Part I, Sec. IV. For the complete correction, one must know also the γ correction to the long-range behavior of $n_2(x; l)$, and this is also needed to resolve the difficulty of the apparent *nonagreement* of the fluctuation theorem [Eq. (36)] and the first term of (44) with van der Waals' equation. In fact, from the first term of (44) one finds

$$\int_0^\infty dx \left[\bar{n}_2(x; l) - \frac{1}{l^2}\right] = -\frac{1}{2l} + \frac{(l - \delta)^2}{2l^3}, \tag{46}$$

which agrees with (36) if $p/kT = 1/(l - \delta)$. We shall see that the long-range behavior of $\bar{n}_2(x; l)$, which is of order γ, gives in the fluctuation integral, a zeroth-order contribution, which brings Eq. (36) into agreement with the van der Waals equation.

V. THE VAN DER WAALS LIMIT OF THE TWO-POINT DISTRIBUTION FUNCTION; THE LONG-RANGE BEHAVIOR

To determine the behavior of $\bar{n}_2(x; l)$ for x of order $1/\gamma$, we use Eq. (9a) for $\bar{n}_2(x; l)$. Replace σ by $\sigma\gamma$ and then expand the right-hand side in powers of γ. First consider the matrix element

$$\langle 0, s \mid n, s + \sigma\gamma\rangle$$

$$= \int_{-\infty}^{+\infty} dx\; \psi_0(x, s, \gamma)\psi_n(x, s + \sigma\gamma, \gamma). \tag{47}$$

With $x = x' + \eta(s)(2/\gamma)^{\frac{1}{2}}$, we know that

$$\psi(x, s, \gamma) \equiv h(x', s, \gamma)$$

$$= h^{(0)}(x', s) + \gamma^{\frac{1}{2}} h^{(1)}(x', s) + \cdots ,$$

where the $h^{(k)}(x', s)$ are determined in Part I, Sec. III. Therefore,

$$\psi_n(x, s + \sigma\gamma, \gamma)$$

$$= h_n(x - \eta(s + \sigma\gamma)(2/\gamma)^{\frac{1}{2}}, s + \sigma\gamma, \gamma)$$

$$= h_n^{(0)}(x', s) + \gamma^{\frac{1}{2}}$$

$$\times \left[h_n^{(1)}(x', s) - 2^{\frac{1}{2}}\sigma \frac{d\eta}{ds} \frac{\partial h_n^{(0)}(x', s)}{\partial x'}\right] + O(\gamma).$$

Since $h_n^{(1)}$ is orthogonal to $h_0^{(0)}$ for $n > 0$, then for $n > 0$ [using Eqs. (38) and (39) in Part I], one finds

$$\langle 0, s \mid n, s + \sigma\gamma\rangle = -\sigma\left(\frac{\gamma B}{2l}\right)^{\frac{1}{2}} \frac{d\eta}{ds}\, \delta_{n1} + O(\gamma). \tag{48}$$

For $n = 0$, one obtains

$$\langle 0, s \mid 0, s + \sigma\gamma\rangle = 1 - \sigma^2 \frac{\gamma B}{4l} \left(\frac{d\eta}{ds}\right)^2 + O(\gamma^{\frac{3}{2}}). \tag{49}$$

Note that (48) and (49) are consistent up to order γ with the completeness requirement

$$\sum_{n=0}^{\infty} \langle 0, s \mid n, s + \sigma\gamma \rangle^2 = 1.$$

Next we consider the eigenvalues. We know that

$$\lambda_n(s, \gamma) = \omega(s)[1 + \gamma\mu_n^{(1)}(s) + O(\gamma^2)], \tag{50}$$

where $\mu_n^{(1)}$ is given by Eq. (39) in Part I. Therefore,

$$\lambda_n(s + \sigma\gamma, \gamma) = \omega(s) \times \left\{1 + \gamma\left[\sigma\frac{\omega'(s)}{\omega(s)} + \mu_n^{(1)}(s)\right] + O(\gamma^2)\right\}. \tag{51}$$

Using all this one obtains from Eq. (9a),

$$l\int_0^\infty dx\, e^{-\sigma\gamma x}\bar{n}_2(x; l) = -\frac{\omega}{\gamma\sigma\omega'} - 1 + \frac{\omega}{\sigma\omega'}\left[\frac{\sigma}{2}\frac{\omega''}{\omega'} + \frac{\omega}{\omega'}\frac{d\mu_0^{(1)}}{ds}\right] + \frac{\sigma^2 B}{2l}\left(\frac{d\eta}{ds}\right)^2 \times \left[\frac{\omega}{\sigma\omega'} + \frac{1}{-\sigma(\omega'/\omega) + \mu_0^{(1)} - \mu_1^{(1)}}\right] + \cdots. \tag{52}$$

Now there is the following complication: One would be inclined to replace $\omega'(s)/\omega(s)$ by $(-l)$ according to Part I, Eq. (31), but this is *not* correct. The expansion of the eigenfunctions and eigenvalues was done at constant s, while the Laplace transform of $\bar{n}_2(x; l)$ is taken for a fixed value of $l = -\lambda_0'(s)/\lambda_0(s)$. Since $\lambda_0(s)$ and $\omega(s)$ differ by a quantity of order γ [see Eq. (50)], one has

$$-l = \frac{\lambda_0'(s)}{\lambda_0(s)} = \frac{\omega'}{\omega}\left[1 + \gamma\frac{\omega}{\omega'}\frac{d\mu_0^{(1)}}{ds} + \cdots\right],$$

and so up to order γ,

$$\frac{\omega'}{\omega} = -l\left[1 + \frac{\gamma}{l}\frac{d\mu_0^{(1)}}{ds}\right]. \tag{53}$$

This γ correction must be taken into account in the first term in Eq. (52), but can of course be neglected in the other terms. Since in zeroth order

$$\frac{\omega''}{\omega'} = -l + \frac{1}{l}\frac{\partial l}{\partial s} = -l - \frac{l(l-\delta)^2}{B^2}$$

$$\eta(s) = \frac{(2\nu_0)^{\frac{1}{2}}}{l}; \qquad \left(\frac{d\eta}{ds}\right)^2 = \frac{2\nu_0(l-\delta)^4}{B^4}$$

$$\mu_0^{(1)} - \mu_1^{(1)} = B; \qquad l^2 - B^2 = \frac{2\nu_0(l-\delta)^2}{l},$$

one can simplify (52) to

$$\int_0^\infty dx\, e^{-\sigma\gamma x}\bar{n}_2(x; l) = \frac{1}{\gamma\sigma l^2} - \frac{1}{2l} + \frac{(l-\delta)^2}{2l^3} + \frac{\nu_0(l-\delta)^4}{l^4 B}\cdot\frac{1}{B + \sigma l}.$$

Since for a gas of hard rods one finds [see Eq. (46)], up to zeroth order in γ,

$$\int_0^\infty dx\, e^{-\sigma\gamma x}\bar{n}_2^{\text{h.c.}}(x; l) = \frac{1}{\gamma\sigma l} - \frac{1}{2l} + \frac{(l-\delta)^2}{2l^3},$$

one obtains

$$\int_0^\infty dx\, e^{-\sigma\gamma x}[\bar{n}_2(x; l) - \bar{n}_2^{\text{h.c.}}(x; l)] = \frac{\nu_0(l-\delta)^4}{l^4 B}\cdot\frac{1}{B + \sigma l}.$$

Hence by inverting the Laplace transform one concludes

$$\bar{n}_2(x; l) = \bar{n}_2^{\text{h.c.}}(x; l) + \gamma\frac{\nu_0(l-\delta)^4}{l^5 B}\exp[-(B/l)\gamma x]. \tag{54}$$

This holds for x of order $1/\gamma$, so that $\bar{n}_2^{\text{h.r.}}(x; l)$ should be replaced by $1/l^2$. However in the form (54), it can be seen that our result connects with the short-range expression (44) derived in the previous section, since from (44) follows that for $\sigma \to 0$,

$$\int_0^\infty dx\, e^{-\sigma x}\bar{n}_2(x, l) = \frac{1}{\sigma}\left[\frac{1}{l^2} + \frac{\gamma\nu_0(l-\delta)^4}{l^5 B}\right] + \cdots,$$

so that for $x \to \infty$, we obtain

$$\bar{n}_2(x; l) = \frac{1}{l^2} + \frac{\gamma\nu_0(l-\delta)^4}{l^5 B},$$

and the second term is just the amplitude of the long-range exponential decay in (54). Note also that if one substitutes (54) into the fluctuation theorem (36), one obtains [using (46)]

$$\int_0^\infty dx\left[\bar{n}_2(x, l) - \frac{1}{l^2}\right] = -\frac{1}{2l} + \frac{(l-\delta)^2}{2l^3} + \frac{\nu_0(l-\delta)^4}{l^4 B^2} = -\frac{1}{2l} + \frac{(l-\delta)^2}{2lB^2}$$

as is expected since according to the van der Waals equation

$$-\frac{kT}{2l^3}\frac{\partial l}{\partial p} = -\frac{1}{2l^3}\frac{\partial l}{\partial s} = \frac{(l-\delta)^2}{2lB^2}.$$

It is also easy to verify that, (54) together with (45) substituted into the virial theorem (40a), gives the complete γ correction to the van der Waals equation.

We have also calculated the terms of order γ^2 in the long-range behavior of $\bar{n}_2(x; l)$. Because the calculation is straightforward although very lengthy, we will record only the result since it is needed in Part III of this series. Call the inverse Laplace transform of the right-hand side of Eq. (44) $\bar{n}_2(x; l)_{\text{short range}}$, which consists therefore of $\bar{n}_2^{\text{h.r.}}(x; l)$ plus the first correction due to the attractive force. Then we find

$$\bar{n}_2(x;\,l) = \bar{n}_2(x;\,l)_{\text{short range}} + \frac{\gamma\nu_0(l-\delta)^4}{l^5B}\,(e^{-B\gamma x/l}-1)$$
$$+\frac{\nu_0^3(l-\delta)^8}{l^8B^5}\left[-\delta(2l-3\delta)+\frac{2}{3}\frac{\nu_0(l-\delta)^2}{l}\right]\gamma^3\,xe^{-B\gamma x/l}-\frac{2\nu_0^2(l-\delta)^6}{l^4B^6}$$
$$\times\left[\delta(2l-3)-\frac{\nu_0(l-\delta)^2(4l^2+18l\delta-27\delta^2)}{6l^3}+\frac{\nu_0^2(l-\delta)^4(11l^2-12l\delta+18\delta^2)}{9l^6}\right]\gamma^2e^{-B\gamma x/l}$$
$$+\frac{\nu_0^2(l-\delta)^6(l-3\delta)^2}{2l^4B^6}\left\{1-\frac{8\nu_0(l-\delta)^2}{3l^2}\right\}^2\gamma^2e^{-2B\gamma x/l}. \qquad (55)$$

As a check, one can place this expression in the fluctuation integral, and obtain the expected result with $\partial l/\partial p$ computed from the van der Waals equation, plus the correction of order γ. The most interesting feature of (55) is the appearance of the exponential with half the range of the exponential occurring in first approximation.[13]

VI. THE DISTRIBUTION FUNCTIONS IN THE TWO-PHASE REGION

Since at the condensation value $\bar{z}$ of the fugacity z, the specific volume v is a discontinuous function of z, all the grand canonical distribution functions $\bar{p}_s(\mathbf{r}_1\cdots\mathbf{r}_s,\,z)$ are discontinuously changing from $\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;\,v_1)$ to $\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;\,v_2)$, where v_1 and v_2 are the specific volumes of the saturated vapor and liquid. In the condensation region, the functions $\bar{p}_s$ therefore lose their meaning, but we can still ask for the meaning of the canonical distribution functions $\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;v)$. Following Mayer, we assert that for any finite s, one should expect

$$\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;v) = (1/v)[\xi_1v_1\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;v_1) + \xi_2v_2\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;v_2)], \qquad (56)$$

where ξ_1 and ξ_2 are the mole fractions of the vapor and the liquid phase, so that $v = \xi_1v_1 + \xi_2v_2$. The reason is that Eq. (56) expresses the geometrical separation of the two phases because of the following argument: Physically, since there is no outside force field, one must expect that in the equilibrium state the condensed phase is in the form of a large sphere surrounded by the vapor phase and that the position of the sphere is purely random. Of course, since we are discussing the thermodynamic limit exclusive of surface phenomena, this cannot be proved in detail, but one might expect that all results are in harmony with this picture. This is the case if the $\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;\,v)$ fulfill Eq. (56). The first factor $(1/v)$ in (56) is the probability per unit volume of finding one particle say at $\mathbf{r}_1$; it is independent of whether the particle is in the liquid or vapor phase because the position of the large liquid sphere is random. However *if* the first particle is in the liquid or vapor phase, then all remaining $(s-1)$ particles will be in the same phase, because the chance that some of them are in the other phase will be proportional to the ratio of surface to volume of the liquid sphere and is therefore negligible in the thermodynamic limit. Since $v_1\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;\,v_1)$ and $v_2\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;\,v_2)$ are the conditional probabilities to find $(s-1)$ particles in phase 1 and 2 if the first particle is in the same phase, and since ξ_1 and ξ_2 are the *a priori* probabilities to find the first particle in phase 1 or 2, this accounts for the second factor in Eq. (56).

Several points should be noted:

(a) The $\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;\,v)$ are still spatially homogeneous, although there are two phases. This is clearly again due to the fact that the position of the liquid sphere is random.

(b) The $\bar{n}_s(\mathbf{r}_1\cdots\mathbf{r}_s;\,v)$ do *not* have the product property. The presence of the two phases produce correlations even when the particles are far apart. In particular,

$$\bar{n}_2(\mathbf{r}_1,\mathbf{r}_2;v)\to\frac{1}{v}\left(\frac{\xi_1}{v_1}+\frac{\xi_2}{v_2}\right)$$

if the two particles are far apart, and since

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[13] We have also calculated from Eq. (28b), the long-range behavior of the three-particle distribution function. Up to order γ one finds

$$\bar{n}_3(x,\,y;\,l) = \bar{n}_3^{\text{h.c.}}(x,\,y;\,l) + \frac{\gamma\nu(l-\delta)^4}{l^6B}\left\{\exp\left[-\frac{B}{l}\gamma(x+y)\right] + \exp\left[-\frac{B}{l}\gamma x\right] + \exp\left[-\frac{B}{l}\gamma y\right]\right\}.$$

In the far range we have therefore up to $O(\gamma)$ the superposition principle

$$\bar{n}_3(t_1,\,t_2,\,t_3;\,l) = l^3\bar{n}_2(t_1,\,t_2;\,l)\bar{n}_2(t_1,\,t_3;\,l)\bar{n}_2(t_2,\,t_3;\,l),$$

which should be contrasted with the form of the superposition principle for the hard core given by Eq. (31a).

$$\frac{1}{v}\left(\frac{\xi_1}{v_1}+\frac{\xi_2}{v_2}\right)-\frac{1}{v^2}=\frac{\xi_1\xi_2(v_2-v_1)^2}{v^2v_1v_2}>0,$$

the fluctuation integral will go to infinity, which is in accord with the constant vapor pressure.

(c) If one substitutes (56) for $s = 2$ into the virial theorem [Eq. (39)], then since

$$\begin{aligned}\frac{1}{6}\int d\mathbf{r}\, r\frac{d\varphi}{dr}\bar{n}_2(r;v) &= \frac{1}{6v}\int d\mathbf{r}\, r\frac{d\varphi}{dr}\left[\xi_1v_1\bar{n}_2(r;v_1)+\xi_2v_2\bar{n}_2(r;v_2)\right]\\ &= \frac{\xi_1v_1}{v}\left(\frac{kT}{v_1}-p_s\right)+\frac{\xi_2v_2}{v}\left(\frac{kT}{v_2}-p_s\right)\\ &= \frac{kT}{v}-p_s,\end{aligned}$$

using the virial theorem for each of the two phases separately, one obtains that the pressure p is really constant and equal to p_s.

Thus far, all these general statements are of course not really proved. It is therefore of great interest that for our one-dimensional model, the relations (56) follow strictly in the van der Waals limit. This can easily be seen from Eqs. (28a) and (28b). We know from Part I, Sec. IV, that in the two-phase region, the maximum eigenvalue in the van der Waals limit is doubly degenerate and that the two eigenfunctions for small $\gamma\delta$ do not overlap. Since we also showed that corresponding to a given $l = \xi_1l_1 + \xi_2l_2$, the eigenfunction is given by

$$\psi_0(x;l)=\xi_1^{\frac{1}{2}}\psi_0(x;l_1)+\xi_2^{\frac{1}{2}}\psi_0(x;l_2),$$

one immediately sees from (28a) and (28b) that $\bar{n}_2(x;\, l)$ and $\bar{n}_3(x,\, y;\, l)$ fulfill the one-dimensional form of Eq. (56) for $s = 2$ and $s = 3$. Equations (28a) and (28b) are so obviously generalizable that there is little doubt that Eq. (56) also holds for arbitrary s.

VII. THE RELATION TO THE ORNSTEIN–ZERNIKE THEORY

To show the connection between our results and the Ornstein–Zernike theory, we will first present the one-dimensional version of this theory. We start with an integral equation connecting the correlation function $g(t_1, t_2)$ defined by

$$g(t_1,t_2)\equiv g(x)=l[\bar{n}_2(x;l)-1/l^2], \qquad (57)$$

with the so-called direct correlation function $c(t_1, t_2) \equiv c(x)$. Both functions depend only on the absolute value of the distance $x = t_2 - t_1$ between the two particles at t_1 and t_2, and in the one phase region they both go to zero for $x \to \infty$. The equation is:

$$g(t_1,t_2)=c(t_1,t_2)+\int_{-\infty}^{+\infty}dt_3\, g(t_1,t_3)c(t_3,t_2), \qquad (58)$$

and to make it plausible one can argue as follows: The correlation in position of two particles is in the first instance caused by the direct interaction between the two molecules and this is expressed by the term $c(t_1, t_2)$. In addition, there is an indirect effect through the action of a third particle in the neighborhood of the two particles, and this is described by the second term in (58). We do not try to give a formal derivation of (58).[14] From the way in which Eq. (58) is used, it seems clear that it is valid only in some asymptotic sense and for long-range attractive forces. Note that one can write (58) in the form:

$$g(x)=c(x)+\int_{-\infty}^{+\infty}dy\, g(x-y)c(y), \qquad (58a)$$

which implies that for the Fourier transforms, one has the simple relation

$$\tilde{g}(k)=\tilde{c}(k)+\tilde{g}(k)\tilde{c}(k). \qquad (59)$$

We now observe that near the critical point the range of $g(x)$ is magnified because of the small compressibility of the gas. This follows from the fluctuation theorem, which gives

$$\int_{-\infty}^{+\infty}dx\, g(x)=\tilde{g}(0)=-1-\frac{kT}{l^2}\left(\frac{\partial l}{\partial p}\right)_T. \qquad (60)$$

However the range of the direct correlation function $c(x)$ should *not* increase near the critical point since it is determined by the attractive force. This is confirmed by the relation

$$\begin{aligned}\int_{-\infty}^{+\infty}c(x)\,dx=\tilde{c}(0)&=\frac{\tilde{g}(0)}{1+\tilde{g}(0)}\\ &=1+\frac{l^2}{kT}\left(\frac{\partial p}{\partial l}\right)_T,\end{aligned} \qquad (61)$$

which follows from (59) and (60).

In the critical region, therefore, Ornstein and Zernike develop in Eq. (58a), $g(x - y)$ in powers of y up to y^2. Since in the range we are concerned with $g(x) \gg c(x)$, one can neglect $c(x)$, and using the fact that $c(x) = c(-x)$, one obtains the differential equation

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[14] In a second paper, ("Statistical Thermodynamics of Non-Uniform Fluids" (Preprint) (to be published), J. L. Lebowitz and J. K. Percus have given a formal derivation of the Ornstein–Zernike equation (58) which they claim to be exact. However, at present it is not yet clear whether this leads to a successive approximation method which would start with Eq. (69) as first approximation.

$$d^2g/dx^2 - \kappa^2 g = 0, \tag{62}$$

with

$$\kappa^2 = \frac{2\left[1 - \int_{-\infty}^{+\infty} dy\, c(y)\right]}{\int_{-\infty}^{+\infty} dy\, y^2 c(y)} = \frac{-\left(\dfrac{2l^2}{kT}\right)\left(\dfrac{\partial p}{\partial l}\right)_T}{\int_{-\infty}^{+\infty} dy\, y^2 c(y)}, \tag{63}$$

which has the solution [using (60)]

$$g(x) = \kappa\left(-\frac{kT}{2l^2}\frac{\partial l}{\partial p}\right)e^{-\kappa x}. \tag{64}$$

This can now be compared with the long-range behavior of $\bar{n}_2(x;\, l)$ discussed in Sec. VI. Clearly, the first approximation (54), agrees with (64) both in form and in the dependence on the compressibility $\partial p/\partial l$. Since κ depends on the unknown function $c(x)$, we cannot proceed further. However, as Lebowitz and Percus (see reference 7) have pointed out, one can analyze the Ornstein–Zernike equation (58a) in more detail by using the basic ideas of the theory of van der Waals. In the first place, it is clear that for large x, $c(x)$ should be proportional to the potential of the attractive force $\varphi(x)$, and that only for x close to zero will $c(x)$ deviate from $\varphi(x)$ due to the hard core. Then, since according to van der Waals the equation of state has the form

$$p = p^{\mathrm{h.c.}} - \alpha_0/l^2 \tag{65}$$

with

$$\alpha_0 = -\int_0^{\infty} dx\, \varphi(x) = -\tfrac{1}{2}\tilde{\varphi}(0),$$

and since $\tilde{c}(0)$ has to fulfill Eq. (61), a very plausible ansatz for $\tilde{c}(k)$ is

$$\tilde{c}(k) = \tilde{c}^{\mathrm{h.c.}}(0) - \tilde{\varphi}(k)/lkT, \tag{66}$$

with

$$\tilde{c}^{\mathrm{h.c.}}(0) = 1 + (l^2/kT)(\partial p^{\mathrm{h.c.}}/\partial l). \tag{67}$$

From Eq. (66), we obtain $\tilde{g}(k)$ by (59), and if we now define the long-range behavior of $\tilde{g}(k)$ by

$$\tilde{g}^{\mathrm{l.r.}}(k) = \tilde{g}(k) - \tilde{g}^{\mathrm{h.c.}}(0), \tag{68}$$

where

$$\tilde{g}^{\mathrm{h.c.}}(0) = \tilde{c}^{\mathrm{h.c.}}(0)/[1 - \tilde{c}^{\mathrm{h.c.}}(0)],$$

one finds

$$\tilde{g}^{\mathrm{l.r.}}(k) = \frac{lkT}{\tilde{\varphi}(0) + l^3(\partial p/\partial l)} \times \frac{\tilde{\varphi}(k)}{\tilde{\varphi}(k) - \tilde{\varphi}(0) - l^3(\partial p/\partial l)}, \tag{69}$$

which is the result of Lebowitz and Percus. It is easy to verify that for our model, where

$$\varphi(x) = -\alpha_0 e^{-\gamma|x|}; \qquad \tilde{\varphi}(k) = -2\alpha_0\gamma/(\gamma^2 + k^2),$$

one obtains from (69) *exactly* the first approximation to the long-range behavior of $\bar{n}_2(x,\, l)$ derived in Sec. V. *For low density,* $l^3(\partial p/\partial l) \cong -lkT$ is very large, and Eq. (69) therefore becomes

$$\tilde{g}^{\mathrm{l.r.}}(k) \cong -\tilde{\varphi}(k)/lkT,$$

which is in agreement with the expected result

$$\bar{n}_2(x,\, l) \cong \frac{1}{l^2}e^{-\varphi(x)/kT} \cong \frac{1}{l^2}\left[1 - \frac{\varphi(x)}{kT}\right]. \tag{70}$$

Near the critical point $\partial p/\partial l$ is very small, and Eq. (69) can then be approximated for small k by

$$\tilde{g}^{\mathrm{l.r.}}(k) \cong lkT/[\tfrac{1}{2}\tilde{\varphi}''(0)k^2 - l^3(\partial p/\partial l)]$$

which gives

$$\tilde{g}^{\mathrm{l.r.}}(x) \cong \frac{lkT}{2R}\left(-2\alpha_0 l^3\frac{\partial p}{\partial l}\right)^{-\frac{1}{2}} \times \exp\left[-\frac{x}{R}\left(-\frac{l^3}{2\alpha_0}\frac{\partial p}{\partial l}\right)^{\frac{1}{2}}\right], \tag{71}$$

where R is defined by

$$R^2 = \frac{\tfrac{1}{2}\int_{-\infty}^{+\infty} x^2\varphi(x)\, dx}{\int_{-\infty}^{+\infty} dx\, \varphi(x)} = \frac{\tilde{\varphi}''(0)}{4\alpha_0}. \tag{72}$$

This has precisely the same form as the Ornstein–Zernike result (64) except that now the range $1/\kappa$ is expressed in the intermolecular potential. In fact (64) becomes (71) by setting

$$\kappa = \frac{1}{R}\left(-\frac{l^3}{2\alpha_0}\frac{\partial p}{\partial l}\right)^{\frac{1}{2}}. \tag{73}$$

We believe that Eq. (69) is an exact result in the sense that it gives the long-range behavior of the correlation function in first approximation for *any* long-range potential, and for the whole range of density from the ideal gas to the critical region. We are able to confirm this belief by generalizing the discussion in Sec. V to the case that the attractive potential is the sum of exponentials as in Part I, Eq. (52). We found again that Eq. (69) is fulfilled exactly. Since the calculations follow the same lines as for one exponential, we will present only an outline of the proof. For a potential

$$\varphi_{\mathrm{attr}}/kT = -\gamma\sum_{i=1}^{m}\nu_i \exp(-\sigma_i\gamma x),$$

where $\nu_i = \alpha_i/kT$, the Kac integral equation is in

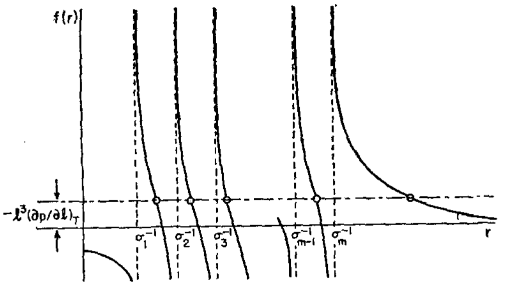

FIG. 1. Graphical determination of the ranges from Eq. (84).

m variables, and the kernel is given by

$$K_s(x_1 \cdots x_m, y_1 \cdots y_m) = \int_0^\infty d\tau\, e^{-s\tau} \prod_{i=1}^m \left[\frac{W(x_i)}{W(y_i)}\right]^{\frac{1}{2}} \exp\left[\frac{\nu_i^{\frac{1}{2}}}{2}(x_i + y_i)\right] \times P_{\sigma_i\gamma}(x_i \mid y_i, \tau).$$

To investigate the approach to the limit $\gamma \to 0$, one has to "tame" the integral equation by the substitutions

$$x_i = x_i' + \eta_i(2/\gamma\sigma_i)^{\frac{1}{2}}, \qquad y = y_i' + \eta_i(2/\gamma\sigma_i)^{\frac{1}{2}},$$

where

$$\eta_i = \frac{\eta(\nu_i/\sigma_i)^{\frac{1}{2}}}{[\sum_i (\nu_i/\sigma_i)]^{\frac{1}{2}}},$$

with η defined as in Part I, Eq. (33). In zeroth approximation one then obtains, instead of Eq. (37) in Part I, the differential equation

$$\sum_i \frac{\partial^2 H^{(0)}}{\partial z_i^2} + \left[\sum_i \frac{\sigma_i}{l} - \frac{\mu^{(1)}}{l} - \tfrac{1}{4}\sum_{i,j} M_{ij} z_i z_j\right] \times H^{(0)}(z_1 \cdots z_m) = 0, \tag{74}$$

where $z_i = x_i'(\sigma_i)^{-\frac{1}{2}}$, and the matrix M is given by

$$M_{ij} = \sigma_i^2 \delta_{ij} - \sigma_i\sigma_j(c_i c_j)^{\frac{1}{2}}, \tag{75}$$

with

$$c_i = 2\nu_i(l - \delta)^2/\sigma_i l^3. \tag{76}$$

Since by an orthogonal transformation $z_i = \sum_k a_{ik} y_k$, one can diagonalize the matrix M, so that

$$\sum_{i,j} M_{ij} z_i z_j = \sum_k A_k y_k^2; \tag{77}$$

one finds in this approximation,

$$H^{(0)}_{n_1 \cdots n_m} = \prod_{i=1}^m N_{n_i} D_{n_i}(y_i A_i^{\frac{1}{4}}), \tag{78}$$

$$\lambda_{n_1 \cdots n_m} = \omega(s)\left\{1 + \gamma l\left[\sum_i \frac{\sigma_i}{2} - \sum_i (n_i + \tfrac{1}{2}) A_i^{\frac{1}{2}}\right] + \cdots\right\},$$

with $N_{n_i} = (n_i!)^{-\frac{1}{2}}(2\pi\sigma_i)^{-\frac{1}{4}}$. Since the maximum eigenvalue is still $\omega(s)$, one again obtains the van der Waals equation of state as already noted in Part I. The van der Waals constant α_0 is given by [see Part I, Eq. (53)]

$$\nu_0 \equiv \frac{\alpha_0}{kT} = -\frac{1}{kT}\int_0^\infty dx\, \varphi_{\text{attr.}}(x) = \sum_i \frac{\nu_i}{\sigma_i}, \tag{79}$$

so that

$$\sum_i c_i = 1 - (B/l)^2, \tag{80}$$

where B is given by Eq. (38) in Part I.

With these results, the generalization of the calculation of the long-range behavior of $\bar{n}_2(x; l)$ is straightforward and we find

$$\bar{n}_2(x; l) = \bar{n}_2^{\text{h.c.}}(x; l) + \frac{\gamma l(l - \delta)^2}{2B^4} \times \sum_{k=1}^m s_k^2 A_k^{3/2} \exp[-A_k^{1/2}\gamma x], \tag{81}$$

where

$$s_k = \sum_{i=1}^m a_{ik}(c_i^{1/2}/\sigma_i). \tag{82}$$

In the derivation one must use the identity

$$\sum_{k=1}^m A_k s_k^2 = \frac{B^2(l^2 - B^2)}{l^4}, \tag{83}$$

which follows immediately from (77) by setting $y_k = c_k^{\frac{1}{2}}/\sigma_k$. For the discussion of Eq. (81), the A_k are needed. It is now easy to show that the secular determinant of the matrix M can be written in the form

$$||M_{ij} - A\,\delta_{ij}|| = \prod_{i=1}^m (\sigma_i^2 - A)\left(1 - \sum_{i=1}^m \frac{c_i\sigma_i^2}{\sigma_i^2 - A}\right).$$

Hence the A_k are the m real roots of the equation

$$\sum_{i=1}^m \frac{c_i\sigma_i^2}{\sigma_i^2 - A} = 1.$$

By putting in the expression for c_i, and by using Eq. (79) and the expression for B, one can write this as

$$f(r) \equiv \sum_{i=1}^m \frac{(2\alpha_i/\sigma_i)}{(r\sigma_i)^2 - 1} = -l^3\left(\frac{\partial p}{\partial l}\right)_T, \tag{84}$$

where $r = A^{-\frac{1}{2}}$. From (81) it can be seen that the m roots r_i of this equation are the ranges of the exponentials in $\bar{n}_2(x; l)$. The function $f(r)$ is plotted in Fig. 1. For low densities $-l^3\partial p/\partial l \cong lkT$, and thus it becomes very large. Then $r_i \to 1/\sigma_i$ and since $c_i \to 0$, one sees from (75) that the orthogonal matrix $a_{ij} \to \delta_{ij}$, and from (82) it follows that the amplitudes $s_k^2 A_k^{\frac{3}{2}}$ of the exponentials in (81) become $2\nu_k/l$, so that $\bar{n}_2(x; l)$ approaches the expected form (70). Near the critical point, $-l^3\partial p/\partial l$ is very small, and from Fig. 1 we see that r_m becomes very large, while all the other ranges remain finite. From (84) we find that in this limit, r_m is determined by

$$\frac{1}{r_m^2}\sum_i \frac{2\alpha_i}{\sigma_i^3} = -l^3\frac{\partial p}{\partial l},$$

which can be rewritten as

$$\frac{1}{r_m} = A_m^{1/2} = \frac{1}{\gamma R}\left(-\frac{l^3}{2\alpha_0}\frac{\partial p}{\partial l}\right)^{\frac{1}{2}}, \tag{85}$$

where R is defined by (72). The range of the mth exponential becomes therefore the Ornstein–Zernike range (73). To show that also the amplitude checks with Eq. (71), notice that since according to (80), near the critical point $\sum_i c_i \to 1$, the eigenvector a_{im} must approach the value

$$a_{im}^{(0)} = \frac{c_i^{1/2}/\sigma_i}{\left(\sum_i (c_i/\sigma_i^2)\right)^{\frac{1}{2}}},$$

because this will give the eigenvalue zero to which A_m approaches. From (82) then follows

$$s_m^2 \to \sum_i \frac{c_i}{\sigma_i^2} = \frac{2\nu_0(l-\delta)^2}{l^3}\gamma^2 R^2, \tag{86}$$

which leads to the amplitude of Eq. (71). Finally, we can show that not only the ranges, but also the amplitudes of the remaining $(m-1)$ exponentials, remain finite near the critical point. This follows from the identity (83), since it allows us to conclude that

$$\sum_{k=1}^{m-1} A_k s_k^2 = \frac{B^2}{l^2} - \frac{B^4}{l^4} - A_m s_m^2 = O(B^4),$$

using (85) and (86), and noting that near the critical point $(-l^3/2\alpha_0)(\partial p/\partial l) \cong B^2/l^2$. Hence, since all the A_k are positive, all the s_k^2 must go to zero at least as B^4, and from (81) it then follows that all amplitudes except the mth remain finite at the critical point.

We have seen therefore that Eq. (81) behaves in the same way as the Lebowitz–Percus result (69) in the ideal gas and in the critical region. To show that the Fourier transform of (81) fulfills (69) exactly, requires the proof of the identity

$$\sum_{j=1}^{m}\frac{A_j^2 s_j^2}{k^2+A_j} = \left(1-\sum_{i=1}^{m} c_i\right)^2 \frac{\Phi(k)}{1-\Phi(k)}, \tag{87}$$

where

$$\Phi(k) = \sum_{i=1}^{m}\frac{c_i\sigma_i^2}{\sigma_i^2+k^2},$$

which is given in Appendix D.

VIII. CONCLUDING REMARKS

Although we have restricted ourselves mainly to the one-dimensional case, it is clear that several aspects of the discussion can be generalized to three dimensions.

1. The connection between the virial theorem and the van der Waals equation discussed in Sec. IV can be discussed in the same way for the three-dimensional case. For a weak but long-range attractive force, the virial theorem in the form of Eq. (40) shows that one can separate, in zeroth approximation, the effect of the hard core from the effect of the attractive force. The $\bar{n}_2(d^+; v)$ will be determined by the hard-sphere repulsion, while in the last term in Eq. (40), the $\bar{n}_2(r; v)$ can be replaced by the asymptotic value $1/v^2$; this leads to

$$p = p^{\text{h.c.}} - a/v^2 \tag{88}$$

with

$$a = \tfrac{2}{3}\pi\int_0^\infty dr\, r^3\frac{d\varphi_{\text{attr}}}{dr} = -\tfrac{1}{2}\int d\mathbf{r}\,\varphi_{\text{attr}}(r),$$

which agrees with the value $C/2$ derived in Part I, Sec. V. Of course, $\bar{n}_2(d^+; v)$ for a gas of hard spheres is *not* known, so that as in Part I, Sec. V one can only conclude that the equation of state is van der Waals-like. One should note also that this derivation is completely equivalent to the original considerations by van der Waals and Lorentz.

2. The Ornstein–Zernike theory and especially Eq. (69) are clearly valid in any number of dimensions. The first approximation of the long-range behavior of $\bar{n}_2(r; v)$, which this theory gives, agrees with the van der Waals-like equation (88) through the fluctuation theorem, and it gives a correction to the inner pressure $(-a/v^2)$ through the virial theorem. If one could still find a physical (and therefore generalizable) argument for (a) the next approximation to the short-range behavior of $\bar{n}_2(r, v)$, corresponding to the last term in Eq. (44), and (b) the higher approximations to the long-range behavior of $\bar{n}_2(r; v)$, corresponding to Eq. (55), then it would be possible, through the fluctuation and virial theorem, to develop a successive approximation method for the equation of state which would start from (88) as the zeroth approximation.

3. We believe that the linear relations (56) for the distribution functions in the two-phase region are also valid in any number of dimensions. We have shown in Sec. VI that through the virial theorem, these relations lead to the constant vapor pressure in the two-phase region. Of course this does not prove that there *are* two phases. The linear functional equation (like the Kac equation), whose maximum eigenvalue is doubly degenerate in the condensation region with nonoverlapping eigenfunctions, is lacking in the three-dimensional

theory. Whether it will be possible to construct such a functional equation from the set of distribution functions as Mayer has tried to do, and whether the degeneracy of the maximum eigenvalue and the relations (56) can then be shown rigorously, remains to be seen.

APPENDIX A—COMPLETION OF THE PROOF OF EQ. (9b)

We must solve the integral equation (25) by a perturbation calculation with the parameters $\epsilon_i^{\frac{1}{2}}$. Setting

$$\begin{aligned}\Psi &= \Psi^{(000)} + \sum_{klm} \epsilon_1^{k/2}\epsilon_2^{l/2}\epsilon_3^{m/2}\Psi^{(klm)},\\ \Lambda &= \Lambda^{(000)} + \sum_{klm} \epsilon_1^{k/2}\epsilon_2^{l/2}\epsilon_3^{m/2}\Lambda^{(klm)},\end{aligned} \tag{A1}$$

one finds immediately that in zeroth order the eigenfunctions and eigenvalues are given by

$$\begin{aligned}\Psi_{\mathbf{n}}^{(000)}(\mathbf{x}) &= \psi_n(x; s + n_1\sigma_1 + n_2\sigma_2 + n_3\sigma_3)\\ &\qquad \times \prod_{i=1}^{3} N_{n_i} D_{n_i}(x_i),\\ \Lambda_{\mathbf{n}}^{(000)} &= \lambda_n(s + n_1\sigma_1 + n_2\sigma_2 + n_3\sigma_3),\end{aligned}$$

where $\mathbf{n} = (n, n_1, n_2, n_3)$. The $\Lambda_{0000}^{(klm)}$ and especially $\Lambda_{0000}^{(222)}$, are needed. Since the calculation is lengthy, we will only list the intermediate results which are required for the final result. One easily sees that $\Psi^{(100)} = \Psi^{(010)} = \Psi^{(001)} = 0$ and that in Λ, only the integral powers of ϵ_i contribute. One finds

$$\Psi_{0000}^{(110)}(\mathbf{x}) = \sum_{n=0}^{\infty} a_n^{(110)}\Psi_{n110}^{(000)}(\mathbf{x}),$$

with

$$a_n^{(110)} = \frac{1}{2}\frac{\lambda_0(s) + \lambda_n(s + \sigma_1 + \sigma_2)}{\lambda_0(s) - \lambda_n(s + \sigma_1 + \sigma_2)} \times \langle 0, s \mid n, s + \sigma_1 + \sigma_2\rangle,$$

and similar expressions for $\Psi_{0000}^{(101)}$ and $\Psi_{0000}^{(011)}$. In the order ϵ_1, one obtains

$$\begin{aligned}\Lambda_{0000}^{(200)} &= \tfrac{1}{2}\Lambda_{0000}^{(000)} = \tfrac{1}{2}\lambda_0(s),\\ \Psi_{0000}^{(200)}(\mathbf{x}) &= \sum_{n=0}^{\infty} a_n^{(200)}\Psi_{n200}^{(000)}(\mathbf{x}),\end{aligned} \tag{A2}$$

with

$$a_n^{(200)} = \frac{1}{4}\frac{\lambda_0(s) + \lambda_n(s + 2\sigma_1)}{\lambda_0(s) - \lambda_n(s + 2\sigma_1)}\langle 0, s \mid n, s + 2\sigma_1\rangle,$$

and similar formula for the terms of order ϵ_2 and ϵ_3.

Then in the order $\epsilon_1\epsilon_2$ one finds

$$\Lambda_{0000}^{(220)} = \lambda_0(s)\left[\frac{1}{4} + \sum_{n=0}^{\infty}\frac{\lambda_n(s + \sigma_1 + \sigma_2)}{\lambda_0(s) - \lambda_n(s + \sigma_1 + \sigma_2)} \times \langle 0, s \mid n, s + \sigma_1 + \sigma_2\rangle^2\right]. \tag{A3}$$

The only thing we need know about the eigenfunction $\Psi_{0000}^{(220)}(x)$ is the fact that the integral

$$\int d\mathbf{x}\, \Psi_{0000}^{(220)}\Psi_{\mathbf{n}}^{(000)}$$

is proportional to $\delta_{n,0}$.

In the order $\epsilon_1(\epsilon_2\epsilon_3)^{\frac{1}{2}}$, one obtains for the development coefficients, $a_n^{(211)}$ of $\Psi_{0000}^{(211)}$ in $\Psi_{n011}^{(000)}$, that is, for the integral

$$a_n^{(211)} = \int d\mathbf{x}\, \Psi_{0000}^{(211)}\Psi_{n011}^{(000)},$$

the expression

$$\begin{aligned}a_n^{(211)} &= -\tfrac{1}{4}\langle 0, s \mid n, s + \sigma_2 + \sigma_3\rangle\\ &+ \frac{1}{2}\frac{\lambda_0(s) + \lambda_n(s + \sigma_2 + \sigma_3)}{\lambda_0(s) - \lambda_n(s + \sigma_2 + \sigma_3)}\\ &\times \sum_{m=0}^{\infty}\Big[\langle n, s + \sigma_2 + \sigma_3 \mid m, s + \sigma_1 + \sigma_2\rangle\\ &\times \frac{\lambda_m(s + \sigma_1 + \sigma_2)}{\lambda_0(s) - \lambda_m(s + \sigma_1 + \sigma_2)}\langle m, s + \sigma_1 + \sigma_2 \mid 0, s\rangle\\ &+ \langle n, s + \sigma_2 + \sigma_3 \mid m, s + \sigma_1 + \sigma_3\rangle\\ &\times \frac{\lambda_m(s + \sigma_1 + \sigma_3)}{\lambda_0(s) - \lambda_m(s + \sigma_1 + \sigma_3)}\langle m, s + \sigma_1 + \sigma_3 \mid 0, s\rangle\Big].\end{aligned}$$

No other development coefficients are needed. This leads finally in the order $\epsilon_1\epsilon_2\epsilon_3$, to

$$\begin{aligned}\frac{\Lambda_{0000}^{(222)}}{\lambda_0(s)} = \frac{1}{8} + \frac{1}{2}\sum_{n=0}^{\infty}\Bigg[&\frac{\lambda_n(s + \sigma_1 + \sigma_2)}{\lambda_0(s) - \lambda_n(s + \sigma_1 + \sigma_2)}\langle 0, s \mid n, s + \sigma_1 + \sigma_2\rangle^2\\ &+ \frac{\lambda_n(s + \sigma_1 + \sigma_3)}{\lambda_0(s) - \lambda_n(s + \sigma_1 + \sigma_3)}\langle 0, s \mid n, s + \sigma_1 + \sigma_3\rangle^2 + \frac{\lambda_n(s + \sigma_2 + \sigma_3)}{\lambda_0(s) - \lambda_n(s + \sigma_2 + \sigma_3)}\\ &\times \langle 0, s \mid n, s + \sigma_2 + \sigma_3\rangle^2\Bigg] + 2\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\Bigg[\langle 0, s \mid n, s + \sigma_2 + \sigma_3\rangle\\ &\times \frac{\lambda_n(s + \sigma_2 + \sigma_3)}{\lambda_0(s) - \lambda_n(s + \sigma_2 + \sigma_3)}\langle n, s + \sigma_2 + \sigma_3 \mid m, s + \sigma_1 + \sigma_2\rangle\frac{\lambda_m(s + \sigma_1 + \sigma_2)}{\lambda_0(s) - \lambda_m(s + \sigma_1 + \sigma_2)}\\ &\times \langle m, s + \sigma_1 + \sigma_2 \mid 0, s\rangle + 2 \text{ similar terms with } (\sigma_2, \sigma_3), (\sigma_1, \sigma_2), \text{ replaced by } (\sigma_1, \sigma_3),\\ &(\sigma_1, \sigma_2), \text{ and by } (\sigma_1, \sigma_3), (\sigma_2, \sigma_3)\Bigg].\end{aligned} \tag{A4}$$

To calculate the left-hand side of Eq. (24), one must still expand Eq. (27) by substituting for s in the expansion for $\Lambda_{0000}(s)$,

$$\begin{aligned} s = \tilde{p}/kT &= \tilde{\bar{\chi}}(z, \epsilon_1, \epsilon_2, \epsilon_3) \\ &= \bar{\chi}(z) + \sum_{k,l,m} \epsilon_1^{k/2}\epsilon_2^{l/2}\epsilon_3^{m/2}\bar{\chi}^{(klm)}. \end{aligned}$$

By equating in (27), equal powers of the ϵ_i, one can then express the $\bar{\chi}^{(klm)}$ in terms of the $\Lambda_{0000}^{(klm)}(s)$, where now $s = p/kT = \bar{\chi}(z)$. One finds

$$\bar{\chi}^{(200)} = \bar{\chi}^{(020)} = \bar{\chi}^{(002)} = 0,$$

$$l\bar{\chi}^{(220)} = \frac{1}{\lambda_0(s)} \Lambda_{0000}^{(220)}(s) - \tfrac{1}{4},$$

and finally

$$\begin{aligned} l\bar{\chi}^{(222)} &= \frac{1}{4} + \frac{1}{\lambda_0(s)} \\ &\times \{\Lambda_{0000}^{(222)} - \tfrac{1}{2}[\Lambda_{0000}^{(220)} + \Lambda_{0000}^{(202)} + \Lambda_{0000}^{(022)}]\}. \qquad \text{(A5)} \end{aligned}$$

Substituting in this equation the results (A3) and (A4), one finds that $l\bar{\chi}^{(222)}$ is exactly equal to the double sum in Eq. (A4). Since this double sum is symmetric in σ_1, σ_2, σ_3, all the six terms on the right-hand side of (24) are equal to each other, so that one can write Eq. (24) in the form

$$6l \iint_0^\infty dx\, dy\, \bar{\rho}_3(x, y; z) e^{-\sigma_1 x - \sigma_2 y - \sigma_3(x+y)} = l\bar{\chi}^{(222)}. \qquad \text{(A6)}$$

Since the Laplace transform is over the two relative distances x and y, we need only two σ variables. Setting

$$\sigma_2 = \sigma_3 = \tfrac{1}{2}\sigma', \qquad \sigma_1 = \sigma - \tfrac{1}{2}\sigma',$$

one easily verifies that the three terms under the double sum in (A4) become equal to each other and hence that (A6) reduces to Eq. (9b).

APPENDIX B—PROOF OF THE IDENTITY (42)

From Eqs. (8) and (9) in Part I of this series, one can easily verify that the kernel $K_s(x, y)$ of the Kac integral equation fulfills the identity

$$\begin{aligned} &\partial K_{s+\gamma}/\partial y + \partial K_s/\partial x \\ &\qquad = (\tfrac{1}{2}\nu^{1/2})(K_{s+\gamma} + K_s) + \tfrac{1}{2}yK_{s+\gamma} - \tfrac{1}{2}xK_s. \end{aligned}$$

Multiply this equation with $\psi_k(y; s)\psi_n(x; s + \gamma)$, and integrate over x and y. In each term, one of the integrations can be performed. After a partial integration of the second term, the result can be written in the form

$$\begin{aligned} &\frac{1}{2}\frac{\lambda_k(s) + \lambda_n(s+\gamma)}{\lambda_k(s) - \lambda_n(s+\gamma)} \int_{-\infty}^{+\infty} dx\, \psi_n(x; s+\gamma)\psi_k(x; s) \\ &\qquad = \frac{1}{2\nu^{1/2}} \int_{-\infty}^{+\infty} dx\, x\psi_n(x; s+\gamma)\psi_k(x; s) \\ &\qquad\quad + \frac{1}{\nu^{1/2}} \int_{-\infty}^{+\infty} dx\, \psi_n(x; s+\gamma) \frac{\partial}{\partial x} \psi_k(x; s). \end{aligned}$$

Multiply this equation with

$$\int_{-\infty}^{+\infty} dy\, \psi_n(y; s+\gamma)\psi_k(y; s),$$

and sum over all n. On the right-hand side, use the completeness relation

$$\sum_{n=0}^{\infty} \psi_n(x; s+\gamma)\psi_n(y; s+\gamma) = \delta(x - y).$$

The term with $\partial/\partial x$ then vanishes and one is left with

$$\begin{aligned} &\frac{1}{2}\sum_{n=0}^{\infty} \frac{\lambda_k(s) + \lambda_n(s+\gamma)}{\lambda_k(s) - \lambda_n(s+\gamma)} \\ &\qquad \times \left[\int_{-\infty}^{+\infty} dx\, \psi_k(x; s)\psi_n(x; s+\gamma)\right]^2 \\ &= \frac{1}{2\nu^{1/2}} \int_{-\infty}^{+\infty} dx\, x\psi_k^2(x; s). \end{aligned}$$

This holds for all k. By letting $k = 0$ and by using (9a), Eq. (42) follows. We leave it to the reader to prove, in a similar way, the identity implied by the virial theorem (40a).

APPENDIX C—PROOF OF EQ. (44)

After the "taming" substitution and after expanding up to $O(\gamma)$, the contribution of the nth term of the resolvent series (29) to Eq. (28a), can be written in the form

$$\begin{aligned} &\frac{\exp[n\eta(2\nu_0)^{1/2}]}{\lambda_0^n(s)} \iint_{-\infty}^{+\infty} dx'\, dy'\, h(x')h(y') \\ &\qquad \times \left[\frac{W(x')}{W(y')}\right]^{1/2} \int_{-\infty}^{+\infty}\cdots\int dz_1' \cdots dz_{n-1}' \\ &\times \int_{\delta}^{\infty}\cdots\int dt_1' \cdots dt_n' \prod_{i=1}^{n} e^{-\alpha t_i}[1 + \gamma^{1/2}a_i(z_{i-1}' + z_i') \\ &+ \tfrac{1}{2}\gamma a_i^2(z_{i-1}' + z_i')^2]P_\gamma(z_{i-1}' \mid z_i', t_i), \end{aligned}$$

where

$$\alpha = s + \sigma + \tfrac{1}{2}\eta^2; \qquad a_i = \tfrac{1}{2}\eta(\tfrac{1}{2}\gamma)^{1/2}(l - t_i);$$

$$z_0' \equiv x', \qquad z_n' \equiv y',$$

and where for $\lambda_0(s)$, $h(x')$ and $h(y')$, one should still substitute the expansions (36) of Part I. We have already seen that in zeroth order, one obtains $(A/\omega)^n$

with

$$A = (1/\alpha) \exp[-\alpha\delta + \eta(2\nu_0)^{\frac{1}{2}}].$$

There are six sources of terms proportional to γ.

1. In zeroth order, $s + \frac{1}{2}\eta^2 = 1/(l - \delta)$. Since one develops at constant l, one obtains up to first order,

$$s + \tfrac{1}{2}\eta^2 = 1/(l + \Delta l - \delta),$$

with $\Delta l = \gamma\, d\mu_0^{(1)}/ds$, where $\mu_0^{(1)}(s)$ is given by Eq. (39) in Part I. From the zeroth approximation one therefore obtains the contribution

$$-P^n n\sigma\Delta l/[1 + \sigma(l - \delta)],$$

where

$$P = e^{-\sigma\delta}/[1 + (l - \delta)].$$

2. From the $\lambda_0^n(s)$, one clearly obtains the contribution

$$-P^n n\gamma\mu_0^{(1)} = -\tfrac{1}{2}n\gamma(l - B)P^n.$$

3. From the γ terms in the square brackets one obtains

$$nP^n \frac{\gamma\nu_0 l}{2B}\left\{1 - \frac{2}{l}\left(\delta + \frac{1}{\alpha}\right) + \frac{1}{l^2}\left(\delta^2 + \frac{2\delta}{\alpha} + \frac{2}{\alpha^2}\right)\right\}.$$

4. From the $\gamma^{\frac{1}{2}}$ terms in the square brackets combined with the correction of $O(\gamma^{\frac{1}{2}})$ in the eigenfunctions $h(x')$ and $h(y')$, one obtains

$$nP^n \frac{2\nu_0\gamma}{l^2}\left(l - \delta - \frac{1}{\alpha}\right)\frac{(l - \delta)^2}{B} \times \left[1 - \frac{l}{2B} + \frac{\nu_0 l}{2B^2}\left(1 - 4\frac{\delta}{l} + 3\frac{\delta^2}{l^2}\right)\right].$$

5. From the product of two $\gamma^{\frac{1}{2}}$ terms in the square brackets, one obtains

$$\tfrac{1}{2}n(n - 1)P^n \frac{\nu_0\gamma}{lB}(l - \delta - 1/\alpha)^2.$$

6. In all these contributions, the function $P_\gamma(z'_{i-1} \mid z'_i, t_i)$ was replaced by the zeroth approximation, which is $\delta(z'_i - z'_{i-1})$. One must therefore still calculate the contribution due to the deviation of P_γ from the δ function. All other factors can now be replaced by the zeroth approximation. From the Markoff property of P_γ all the z'_i integrals can be performed immediately. One then carries out the y' integral using the result that up to $O(\gamma)$,

$$\int_{-\infty}^{+\infty} dy'\, F(y')P_\gamma(x' \mid y', t) = F(x') - \gamma x' t F'(x') + \gamma t F''(x').$$

The x' integral can be performed and one finally obtains

$$nP^n \frac{\gamma}{2}\left(\delta + \frac{1}{\alpha}\right)\left[1 - \frac{l}{B} + \frac{\nu_0(l - \delta)^2}{l^2 B}\right].$$

Combining all these results, and summing over n then leads to Eq. (44). Here, as in many of the other calculations, a principle of maximum simplification seemed to be operative. If the final answer was not simple, we invariably found that we had made some algebraic errors!

APPENDIX D—PROOF OF THE IDENTITY (87)

For the proof we are indebted to Dr. J. H. Halton of the Brookhaven National Laboratory. The first step is to develop the left-hand side of (87) in inverse powers of k^2. Using the fact that

$$\sum_{i,j} (M^{r+2})_{ij} z_i z_i = \sum_j A_j^{r+2} y_j^2,$$

from which follows by putting $z_i = c_i^{\frac{1}{2}}/\sigma_i$,

$$\sum_{i,j} (M^{r+2})_{ij} \frac{(c_i c_j)^{1/2}}{\sigma_i \sigma_j} = \sum_j A_j^{r+2} s_j^2;$$

one obtains for the left-hand side

$$\frac{1}{k^2}\sum_{r=0}^{\infty} \frac{(-1)^r}{k^{2r}} \sum_{i,j} (M^{r+2})_{ij} \frac{(c_i c_j)^{1/2}}{\sigma_i \sigma_j}. \qquad \text{(A7)}$$

It is now slightly more convenient to introduce instead of the matrix M [given by (75)], the matrix

$$L_{ik} = \frac{1}{\sigma_i \sigma_k}\left(\frac{c_k}{c_i}\right)^{1/2} M_{ik} = \delta_{ik} - c_k.$$

In this way, (A7) can be written

$$\frac{1}{k^2}\sum_{r=0}^{\infty} \frac{(-1)^r}{k^{2r}} \sum_{i,i_1\cdots i_{r+1},j} c_i L_{ii_1} L_{i_1 i_2} \cdots L_{i_{r+1} j} \times \sigma_{i_1}^2 \sigma_{i_2}^2 \cdots \sigma_{i_{r+1}}^2.$$

The summation over i and j can be performed immediately and give the factor

$$c_{i_1}(1 - \sum_j c_j)^2.$$

Call $\rho_i = -\sigma_i^2/k^2$, and for convenience of writing, set $c_i = -d_i$. It is then easily seen that the identity (87) can be written in the form

$$\sum_{r=1}^{\infty} \sum_{i_1, i_2 \cdots i_r} d_{i_1} L_{i_1 i_2} L_{i_2 i_3} \cdots L_{i_{r-1} i_r} \times \rho_{i_1}\rho_{i_2} \cdots \rho_{i_r} = \frac{\Phi}{1 - \Phi}, \qquad \text{(A8)}$$

where now

$$\Phi = \sum_i d_i \frac{\rho_i}{1 - \rho_i}, \qquad L_{ij} = \delta_{ij} + d_j.$$

By substituting L and by working out the product, one can verify that the sum over the i_1, $i_2 \cdots i_r$ can be written as

$$\sum_{s=1}^{r}\sum_{i_1 i_2\cdots i_s}\sum'_{r_1,r_2\cdots r_s}\prod_{k=1}^{s} d_{i_k}\rho_{i_k}^{r_k},$$

where the summation over the integers r_k go from 1 to $(r-1)$, and are restricted by the condition (denoted by the prime)

$$r_1 + r_2 \cdots + r_s = r.$$

Interchanging in (A8) the summations over r and s, the left-hand side of (A8) becomes

$$\sum_{s=1}^{\infty}\sum_{i_1\cdots i_s}\sum_{r_1\cdots r_s}\prod_{k=1}^{s} d_{i_k}\rho_{i_k}^{r_k},$$

where the summation over the r_k are now unrestricted and go from one to infinity. One therefore obtains

$$\sum_{s=1}^{\infty}\sum_{i_1\cdots i_s}\prod_{k=1}^{s}\frac{d_{i_k}\rho_{i_k}}{1-\rho_{i_k}} = \sum_{s=1}^{\infty}\left(\sum_i \frac{d_i\rho_i}{1-\rho_i}\right)^s = \frac{\Phi}{1-\Phi},$$

which verifies Eq. (A8).

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Asymptotic Behavior of the Radial Distribution Function*

J. L. LEBOWITZ
Belfer Graduate School of Science, Yeshiva University, New York, New York
AND
J. K. PERCUS
Courant Institute of Mathematical Sciences, New York University, New York, New York

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The pair distribution function in a uniform classical fluid is equivalent to the one-body density when one particle is fixed. An implicit relation for this nonuniform density is found by a functional expansion of the difference of chemical potential and external potential about its value for a system of uniform density. A linearization of this expansion, followed by retention of, at most, second derivatives of the inhomogenity, reproduces the Ornstein–Zernicke relations for the asymptotic pair correlation. Linearization alone calls for the sum of internal potential and direct correlation function to vanish asymptotically. This relation is developed for the case of weak long-range forces, resulting in the Debye–Huckel expression for an electron gas, and reproducing the asymptotic correlations of the Kac–Uhlenbeck–Hemmer one-dimensional model. The relation is also shown to follow from the virial expansion for the direct correlation function.

1. INTRODUCTION

THE qualitative properties of the radial distribution function in a uniform classical fluid are still incompletely understood. Whereas the short-range character must depend explicitly upon the interaction potential, presumably in a quite complicated fashion, it has been suggested[1] on numerous occasions that the form of the radial distribution function well outside the range of the potential is essentially universal, with at most a few parameters determined by the potential. Indeed, as a critical point is approached, and random fluctuations predominate, the specific form of the potential might be completely masked in the asymptotic region. There are however only a few instances[2,3] in which the asymptotic correlation function has been rigorously determined.

It is the aim of this paper to consider the problem of asymptotic correlations from the point of view of local characterizations of nonuniform systems, which we have previously presented.[4] This enables us to discuss the assumptions of the basic Ornstein–Zernicke theory,[5] and to weaken these assumptions, giving rise to a formulation of particular use in the case of weak long-range potentials. A comparison with the rigorously derived correlations of the Kac–Uhlenbeck model[3] provides support for the essential validity of the approach used.

2. REVIEW OF FORMALISM

A method previously developed[4] for examination of distributions and thermodynamic parameters of nonuniform classical systems will be used here. In this study, it was shown that if

$$\begin{aligned}\gamma(\mathbf{r}) &= \lambda + \beta\mu - \beta U(\mathbf{r}),\\ \lambda &= \tfrac{3}{2}\ln\,(2\pi mkT/h^2), \qquad (2.1)\\ \beta &= (kT)^{-1},\end{aligned}$$

for a system with external potential U, chemical potential μ in a grand canonical ensemble, then the multiparticle distribution functions are obtainable by successive variational differentiation of the one-body density $n(\mathbf{r})$:

$$\hat{\mathfrak{F}}_1(\mathbf{r}_1) = n(\mathbf{r}_1) \qquad (2.2\text{a})$$

$$\begin{aligned}\hat{\mathfrak{F}}_2(\mathbf{r}_1,\mathbf{r}_2) &= n_2(\mathbf{r}_1,\mathbf{r}_2) - n(\mathbf{r}_1)n(\mathbf{r}_2)\\ &\quad + n(\mathbf{r}_1)\delta(\mathbf{r}_1-\mathbf{r}_2) \qquad (2.2\text{b})\\ &= \delta n(\mathbf{r}_1)/\delta\gamma(\mathbf{r}_2)\end{aligned}$$

$$\hat{\mathfrak{F}}_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \delta\hat{\mathfrak{F}}_2(\mathbf{r}_1,\mathbf{r}_2)/\delta\gamma(\mathbf{r}_3), \cdots . \qquad (2.2\text{c})$$

Here $\hat{\mathfrak{F}}_s$ is the sth Ursell function,[4] in which however the component ordinary distributions are allowed to refer to identical particles:

$$\hat{n}(\mathbf{r}_1) = n(\mathbf{r}_1), \quad \hat{n}_2(\mathbf{r}_1,\mathbf{r}_2) = n_2(\mathbf{r}_1,\mathbf{r}_2) + n(\mathbf{r}_1)\delta(\mathbf{r}_1-\mathbf{r}_2),$$

$$\begin{aligned}\hat{n}_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) &= n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) + n_2(\mathbf{r}_1,\mathbf{r}_2)\delta(\mathbf{r}_2-\mathbf{r}_3)\\ &\quad + \cdots + n(\mathbf{r}_1)\delta(\mathbf{r}_2-\mathbf{r}_3)\delta(\mathbf{r}_3-\mathbf{r}_1).\end{aligned}$$

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[4] J. L. Lebowitz and J. K. Percus, J. Math. Phys. **4**, 116 (1963), hereafter referred to as I.

[5] L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam **17**, 793 (1914).

The principal technique for examining nonuniform systems consisted of transforming from an initial (uniform) $n_0(\mathbf{r})$ to the final desired $n(\mathbf{r})$ by a functional Taylor expansion

$$f[n] = f[n_0] + \int \frac{\delta f[n]}{\delta n(\mathbf{r}_1)}\bigg|_0 \Delta n(\mathbf{r}_1)\, d\mathbf{r}_1 + \frac{1}{2}\iint \frac{\delta^2 f[n]}{\partial n(\mathbf{r}_1)\,\delta n(\mathbf{r}_2)}\bigg|_0 \Delta n(\mathbf{r}_1)\Delta n(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 + \cdots, \tag{2.3}$$

where

$$\Delta n(\mathbf{r}) = n(\mathbf{r}) - n_0(\mathbf{r}).$$

The required density derivatives were obtained in terms of known γ derivatives by the chain rule

$$\frac{\delta}{\delta n(\mathbf{r}_1)} = \int \frac{\delta\gamma(\mathbf{r}_2)}{\delta n(\mathbf{r}_1)} \frac{\delta}{\delta\gamma(\mathbf{r}_2)}\, d\mathbf{r}_2. \tag{2.4}$$

The quantity $\delta\gamma(\mathbf{r}_2)/\delta n(\mathbf{r}_1)$ was written as

$$\frac{\delta\gamma(\mathbf{r}_2)}{\delta n(\mathbf{r}_1)} \equiv \frac{\delta(\mathbf{r}_1 - \mathbf{r}_2)}{n(\mathbf{r}_1)} - X(\mathbf{r}_1, \mathbf{r}_2), \tag{2.5}$$

and, as the matrix inverse to (2.26), thereby satisfied[6]

$$\frac{n_2(\mathbf{r}_1, \mathbf{r}_3)}{n(\mathbf{r}_1)n(\mathbf{r}_2)} - 1 = X(\mathbf{r}_1, \mathbf{r}_2) + \int \left[\frac{n_2(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)n(\mathbf{r}_3)} - 1\right] n(\mathbf{r}_3) X(\mathbf{r}_3, \mathbf{r}_2)\, d\mathbf{r}_3, \tag{2.6}$$

so that X is to be identified with the generalization to nonuniform systems of the direct correlation function of Ornstein and Zernicke.[5]

3. ASYMPTOTIC FORM OF RADIAL DISTRIBUTIONS

We now make use of our general formalism to investigate some properties of uniform fluids. This will be done by considering the response of the fluid to an external potential $U(\mathbf{r})$ induced by keeping a fluid particle fixed at $\mathbf{r} = 0$,[7] i.e. $U(\mathbf{r}) = \varphi(\mathbf{r})$, the intermolecular potential. Then $n(\mathbf{r})$ becomes the density of particles at $\mathbf{r}$ when it is known that there is a particle at the origin:

$$n(\mathbf{r}) = \rho_2(\mathbf{r})/\rho = \rho + G(\mathbf{r}), \tag{3.1}$$

where ρ and $\rho_2(\mathbf{r})$ are the singlet and pair densities, and $G(\mathbf{r})$ the normalized radial correlation function in the *uniform* fluid.

An implicit equation for the density $G(\mathbf{r})$ can now be obtained by applying (2.3) to $\gamma(\mathbf{r})$ of (2.1), which is known to within the constant chemical potential μ. If the uniform comparison system is that at density ρ, then μ is unaltered by the potential, and we have, from (2.2)–(2.5), with $\Delta n(\mathbf{r}) = G(\mathbf{r})$,

$$\begin{aligned}\gamma(\mathbf{r}) - \beta\mu - \lambda &= -\beta\varphi(\mathbf{r})\\ &= \int [\rho^{-1}\delta(\mathbf{r} - \mathbf{x}) - X(\mathbf{r} - \mathbf{x})]G(\mathbf{x})\, d\mathbf{x}\\ &\quad - \frac{1}{2}\int \cdots \int \mathfrak{F}_3(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2)\\ &\quad \times [\rho^{-1}\delta(\mathbf{r}_1 - \mathbf{x}_1) - X(\mathbf{r}_1 - \mathbf{x}_1)]\\ &\quad \times [\rho^{-1}\delta(\mathbf{r}_2 - \mathbf{x}_2) - X(\mathbf{r}_2 - \mathbf{x}_2)]\\ &\quad \times [\rho^{-1}\delta(\mathbf{r} - \mathbf{x}) - X(\mathbf{r} - \mathbf{x})]\\ &\quad \times G(\mathbf{r}_1)G(\mathbf{r}_2)\, d\mathbf{r}_1 \cdots d\mathbf{x}_2 + \cdots .\end{aligned} \tag{3.2}$$

A superior expansion for many purposes, using a generally smaller expansion parameter, is obtained by taking the uniform comparison system for evaluation of $\gamma(\mathbf{r})$ as that at the local density $n(\mathbf{r})$. Then

$$\Delta n(\mathbf{x}) = n(\mathbf{x}) - n(\mathbf{r}) = G(\mathbf{x}) - G(\mathbf{r}), \tag{3.3}$$

so that

$$\begin{aligned}&\gamma(\mathbf{r}) - \lambda = \\ &\beta\mu - \beta\varphi(\mathbf{r}) = \beta\mu_0(\rho + G(\mathbf{r})) + \int [n^{-1}(\mathbf{r})\delta(\mathbf{r} - \mathbf{x})\\ &\quad - X_0(\mathbf{r} - \mathbf{x})][G(\mathbf{x}) - G(\mathbf{r})]\, d\mathbf{x}\\ &\quad - \frac{1}{2}\int \cdots \int \hat{\mathfrak{F}}_{30}(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2)[n^{-1}(\mathbf{r})\delta(\mathbf{r} - \mathbf{x})\\ &\quad - X_0(\mathbf{r} - \mathbf{x})][n^{-1}(\mathbf{r})\delta(\mathbf{r}_1 - \mathbf{x}_1) - X_0(\mathbf{r}_1 - \mathbf{x}_1)]\\ &\quad \times [n^{-1}(\mathbf{r})\delta(\mathbf{r}_2 - \mathbf{x}_2) - X_0(\mathbf{r}_2 - \mathbf{x}_2)][G(\mathbf{r}_1) - G(\mathbf{r})]\\ &\quad \times [G(\mathbf{r}_2) - G(\mathbf{r})]\, d\mathbf{r}_1 \cdots d\mathbf{x}_2 + \cdots ,\end{aligned} \tag{3.4}$$

where subscript zero indicates that the quantity is to be taken in a uniform system of density $n(\mathbf{r}) = \rho + G(\mathbf{r})$.

To the extent that X_0 and $\mathfrak{F}_{30}$ of (3.4) are short range, $G(\mathbf{x}) - G(\mathbf{r})$ may be expanded in a Taylor series about $\mathbf{r}$ within the integrals, and we find

$$\beta\mu = \beta\varphi(\mathbf{r}) + \beta\mu_0(\rho + G) - \frac{1}{6}\frac{\Lambda_0^2\beta}{(\rho + G)^2\chi_0}\nabla^2 G - \frac{1}{6}\frac{l_0^2}{(\rho + G)^4}\left(\frac{\beta}{\chi_0}\right)^2(\nabla G)^2 + \cdots, \tag{3.5a}$$

where

$$\Lambda_0^2 = \int x^2 X_0(\mathbf{x})\, d\mathbf{x} \bigg/ \int [n^{-1}(\mathbf{r})\delta(\mathbf{x}) - X_0(\mathbf{x})]\, d\mathbf{x}$$

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[6] Equations (2.5) and (2.6) are identical to Eqs. (2.10) and (2.12) of I with the relation between X and C (used in I) given in Eq. (4.1) of I.

[7] See, e.g., J. K. Percus, Phys. Rev. Letters **8**, 462 (1962).

$$= (n^2\chi_0/\beta) \int x^2 X_0(\mathbf{x})\, d\mathbf{x}$$

$$= \int x^2 G_0(\mathbf{x})\, d\mathbf{x} \Big/ \int [\delta(\mathbf{x}) + G_0(\mathbf{x})]\, d\mathbf{x}, \qquad (3.5\text{b})$$

$$l_0^2 = \int \hat{\mathfrak{F}}_{30}(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2)[n^{-1}(\mathbf{r})\delta(\mathbf{x}) - X_0(\mathbf{x})]\mathbf{x}_1 \cdot \mathbf{x}_2\, d\mathbf{x}\, d\mathbf{x}_1\, d\mathbf{x}_2. \qquad (3.5\text{c})$$

Here $\chi_0 = n^{-1} (\partial p/\partial n)^{-1} |_0$ is the isothermal compressibility, entering through the relation

$$\int [n^{-1}(\mathbf{r})\delta(\mathbf{x}) - X_0(\mathbf{x})]\, d\mathbf{x} = \beta/(n^2\chi_0). \qquad (3.6)$$

The earliest work on the asymptotic behavior of $G(\mathbf{r})$, where $G(\mathbf{r})$ is small compared to ρ, was done by Ornstein and Zernike[5] (O.Z.), and is essentially equivalent to (a) keeping only terms linear in G, and (b) cutting off the series in (3.5) after the ∇^2 term. This yields

$$\frac{\partial\mu_0(\rho)}{\partial\rho} G_a(\mathbf{r}) - \frac{1}{6}\frac{\Lambda^2}{\rho^2\chi} \nabla^2 G_a(\mathbf{r}) = -\varphi(\mathbf{r}), \qquad (3.7)$$

where G_a is the asymptotic value of G. Since $\varphi(\mathbf{r})$ is the intermolecular potential, it will generally have a short range, i.e., it will vanish in the region in which G assumes its asymptotic form, and the right-hand side of (3.7) can be set equal to zero. This leads at once to the usual O–Z equation (noting $\rho\partial\mu/\partial\rho = \partial p/\partial\rho$)

$$\nabla^2 G_a = (6/\Lambda^2)G_a. \qquad (3.8)$$

The "advantage" of our analysis over a purely macroscopic derivation of Eq. (3.8) is that we have here an explicit expression for the coefficient of $\nabla^2 G_a$, in terms of G (but not necessarily of G_a), an advantage shared by other treatments as well.[8]

The solution of (3.8) in three dimensions is

$$G_a = Ar^{-1} \exp[-(6^{\frac{1}{2}}/\Lambda)r], \qquad (3.9)$$

and in one dimension, where the factor 6 in (3.5), (3.8) should be replaced by two,

$$G_a = A \exp[-(2^{\frac{1}{2}}/\Lambda)r]. \qquad (3.10)$$

It is easily verified that the use of G_a itself for computing Λ in (3.5b) leads to a contradiction which becomes less severe when the integral of G_a, which in this approximation would be proportional to the compressibility, is very large. This is consistent with the O–Z theory which was developed for the vicinity of the critical point, where the compressibility is indeed very large, (see also Sec. 6 and reference 11).

4. LONG-RANGE POTENTIALS

We may attempt to minimize the assumptions leading to (3.7) by avoiding assumption (b) and supposing only that (3.4) can be linearized in G. This leads directly to the result

$$-\beta\varphi(\mathbf{r}) = \beta(\partial\mu_0(\rho)/\partial\rho)G + \int [\rho^{-1}\delta(\mathbf{r} - \mathbf{x}) - X(\mathbf{r} - \mathbf{x})][G(\mathbf{x}) - G(\mathbf{r})]\, d\mathbf{x}$$
$$= X_1(\mathbf{r}), \qquad (4.1)$$

where the subscript one indicates the result of linearization in G. If one again restricts attention to the asymptotic region, in order to justify retaining only linear terms in G, then, for a short range $\varphi(\mathbf{r})$, (4.1) implies that $X(\mathbf{r})$ also vanishes asymptotically. This arises from the fact that in (3.4), it is not sufficient to know $G_a(\mathbf{r})$ alone even where r is large, since G appears in integrals over the whole domain of r. Indeed there may be no general way of separating the asymptotic part of G. However, when the intermolecular forces are weak everywhere, i.e., when φ is always small, then (4.1) does become correct, representing the lowest order in φ in an expansion of X. In fact, a virial expansion of X starts with the term $X = e^{-\beta\varphi} - 1$, which is precisely what one obtains by expanding $\exp[\gamma(\mathbf{r})]$ rather than γ in Eq. (3.2) or (3.4) [see Appendix].

When φ is not only small but also has a finite range, the corresponding G must also assume the form $G = -\rho\beta\varphi \sim \rho(e^{-\beta\varphi} - 1)$. It is only when φ has a very large range, i.e. the moments of φ are not small even though φ is, that we get an interesting situation. This can be seen most easily by going over to the Fourier transform of X and G. We have then from (4.1)

$$X_1(\mathbf{k}) = -\beta\varphi(\mathbf{k}), \qquad (4.2)$$

but since from (2.6)

$$G(\mathbf{k}) = \rho X(\mathbf{k})/[1 - \rho X(\mathbf{k})], \qquad (4.3)$$

then correspondingly

$$G_1(\mathbf{k}) = -\beta\rho\varphi(\mathbf{k})/[1 + \beta\rho\varphi(\mathbf{k})]. \qquad (4.4)$$

If $\varphi(\mathbf{r})$ has a finite range, then $\varphi(\mathbf{k})$ will be small everywhere and (4.4) can again be expanded to give $G_1(\mathbf{k}) = -\beta\rho\varphi(\mathbf{k})$. However where $\varphi(\mathbf{r})$ has

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[8] See, e.g., L. J. Goldstein in *Symposium on the Many-Body Problem,* edited by J. K. Percus, (Interscience Publishers, Inc., New York, 1963), Chap. XIX.

a long range, $\varphi(\mathbf{k})$ will be large near $\mathbf{k} = 0$, and such an expansion cannot be made.

The Electron Gas

An example of the foregoing is the case of an electron gas embedded in a uniform positive background. Here

$$\varphi(\mathbf{r}) = (4\pi\epsilon_0)^{-1}e^2/r, \tag{4.5}$$

$$\varphi(\mathbf{k}) = \begin{cases} (e^2/\epsilon_0)\ 1/k^2 & \mathbf{k} \neq 0 \\ 0 & \mathbf{k} = 0. \end{cases} \tag{4.6}$$

Thus

$$G_1(\mathbf{k}) = -[1 + (\epsilon_0/\beta\rho e^2)k^2]^{-1}, \tag{4.7}$$

and

$$G_1(\mathbf{r}) = -\rho(\beta e^2/4\pi\epsilon_0)r^{-1}e^{-r/D} = \rho(g - 1),$$

where

$$D = (\epsilon_0/\beta\rho e^2)^{\frac{1}{2}}, \tag{4.8}$$

and g is the radial distribution function. Equation (4.8) is the well-known Debye–Huckel[9] form of G to lowest order in e^2. As is also well-known, (4.8) does not give a sensible result near $r = 0$, i.e., for $r < (4\pi\epsilon_0/\beta e^2) = r_0$. This is not surprising since $\varphi(\mathbf{r})$ near the origin is not only not small but is in fact infinite.

The difficulty of infinite $\varphi(\mathbf{r})$ and correspondingly infinite $-\gamma(\mathbf{r})$ can be overcome as previously mentioned if the expansion (3.4) of $\gamma(\mathbf{r})$ is replaced by an expansion of $e^{\gamma(\mathbf{r})}$. Doing so, (4.4) is replaced by

$$G_1(\mathbf{k}) = \rho f(\mathbf{k})/[1 - \rho f(\mathbf{k})],$$

where

$$f(\mathbf{r}) = e^{-\beta\varphi(\mathbf{r})} - 1, \tag{4.9}$$

but the anomaly of a negative g is still not eliminated, for the "effective" $\beta\varphi$, while not infinite, does reach unity at the origin. Indeed, (4.8) is expected to be correct at most asymptotically, i.e., for $r \geq D \gg r_0$. Furthermore, in a real system, φ is strongly modified near the origin. It is thus more reasonable to consider the case of an intermolecular potential made up of two parts: a strong short-range part and a weak long-range part.

5. THE KAC MODEL

An example of a potential with strong short-range and weak long-range parts has recently been studied in detail by Kac, Uhlenbeck, and Hemmer (K–U–H).[3] This one-dimensional model is of great interest because it can be solved rigorously (with great skill and great labor), and it leads to a first-order phase transition, something never before found rigorously. The potential has the form

$$\begin{aligned} \varphi(x) &= \varphi_h(x) + \varphi_l(x), \\ \varphi_h(x) &= \begin{cases} \infty & |x| < \delta \\ 0 & |x| > \delta \end{cases}, \\ \varphi_l(x) &= -\alpha_0\gamma e^{-\gamma x}, \end{aligned} \tag{5.1}$$

where x is now a one-dimensional variable and $\gamma\delta \ll 1$. The asymptotic region is defined by $x \geq \gamma^{-1}$ and there is a parameter of smallness $\gamma\delta$. In the limit $\gamma \to 0$, this model exhibits a phase change described by the van der Waals equation:

$$\begin{aligned} p &= \beta^{-1}\rho/(1 - \rho\delta) - \alpha_0\rho^2 \\ &= \beta^{-1}/(l - \delta) - \alpha_0/l^2. \end{aligned} \tag{5.2}$$

If (4.1) is now considered in the asymptotic region, where G and X are small, then $X_1(r)$, which we shall now call $X_a(r)$, has the form

$$X_a(r) = -\beta\varphi_l = \alpha_0\beta\gamma e^{-\gamma r} \tag{5.3}$$

and

$$X_a(k) = 2\beta\alpha_0/(1 + \gamma^{-2}k^2). \tag{5.4}$$

It is seen from (5.3) and (5.4) that the even moments of $X_a(r)$ will be of order $(1/\gamma^2)^m$. Stated differently, if we expand $X_a(k)$ in a power series in k, we find

$$X_a(k) = 2\beta\alpha_0[1 - (k^2/\gamma^2) + (k^2/\gamma^2)^2 + \cdots]. \tag{5.5}$$

Hence all coefficients in the series (5.5), except for the zeroth, will be very large. The correct $X(k)$ would presumably have a power series expansion whose coefficients, except for the zeroth-order term, are essentially the same as those given in (5.5). This would, for example, be the result of a virial expansion of X (or G). (It is a peculiarity of this type of potential that the moments of G or X, other than zero, diverge for all densities in the limit $\gamma \to 0$, which may limit the inferences that can be drawn from it.)

For the purpose of finding the asymptotic form of G, for $x \geq \gamma^{-1}$, it is thus sufficient to modify

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[9] P. Debye and E. Huckel, Z. Physik 24, 185 (1923).

$X_a(k)$ at $k = 0$ to have its correct value there[10]:

$$X(k) = X_a(k) + [X(0) - X_a(0)]$$
$$= 2\beta\alpha_0/(1 + \gamma^{-2}k^2) + \rho^{-1}s. \qquad (5.6)$$

Using (5.6) to find $G(k)$, in order to obtain the asymptotic form of G, yields

$$G(k) = \rho X(k)/(1 - \rho X(k)]$$
$$= \frac{s}{1-s} + \frac{2\beta\rho\alpha_0}{(1-s)^2}\left[\frac{k^2}{\gamma^2} + \frac{1 - s - 2\beta\rho\alpha_0}{1-s}\right]^{-1} \qquad (5.7)$$

and this in turn leads to

$$G_a(r) = \frac{\beta\rho\alpha_0\gamma}{(1-s)^2}\left(\frac{1 - s - 2\beta\rho\alpha_0}{1-s}\right)^{\frac{1}{2}}$$
$$\times \exp\left[-\gamma r\left(\frac{1 - s - 2\beta\rho\alpha_0}{1-s}\right)^{\frac{1}{2}}\right]. \qquad (5.8)$$

We now employ Eqs. (3.6) and (5.2) for $X(0)$ and p to find s:

$$s = (X(0) - X_a(0)\rho = (1 - \beta dp/d\rho) - 2\beta\rho\alpha_0$$
$$= 1 - (1 - \rho\delta)^{-2} = 1 - \beta\delta p_h/\delta\rho, \qquad (5.9)$$

where p_h is the part of the pressure which comes from the hard core alone. There finally results

$$G_a(r) = \gamma\frac{(l-\delta)^4}{l^4}\beta\alpha_0\left[\frac{dp_h}{dl}\Big/\frac{dp}{dl}\right]^{\frac{1}{2}}$$
$$\times \exp\left[-\gamma r\left[\frac{dp}{dl}\Big/\frac{dp_h}{dl}\right]^{\frac{1}{2}}\right], \qquad (5.10)$$

which is precisely the expression obtained by K–U–H. when the system is not too close to the critical point, at which dp/dl vanishes. Had we taken s to be a function of k, independent or weakly dependent on γ, with the correct value for $k = 0$, the exponent and coefficient in (5.10) would have been modified by terms which vanish when $\gamma \to 0$.[11]

We may perhaps understand the region of breakdown near the critical point by considering that in the derivation of (4.1) from (3.4) we have neglected terms of order G^2 compared to $(\partial\mu_0(\rho)/\partial\rho)G$. Near the critical point, dp/dl and, hence, $d\mu/d\rho$, of course vary as $(l - l_c)^2$, and as $T - T_c$, where l_c and T_c are critical volume and temperature. Since $G \sim \gamma(dp/dl)^{-\frac{1}{2}}$, we are assuming (in suitable units) that $\gamma^2(dp/dl)^{-1} \ll \gamma(dp/dl)^{\frac{1}{2}}$, or $\gamma \ll (dp/dl)^{\frac{3}{2}}$. We are thus limited to the region $\gamma \ll (l - l_c)^3$, $\gamma \ll (T - T_c)^{\frac{3}{2}}$, which are the same as the limits found by K–U–H.

6. DISCUSSION

G_a as given in (5.10) is of the same form, exponential, as that given by the O–Z theory for a short-range potential, Eq. (3.10). It is clear, however, that (1) when the O–Z theory, Eq. (3.7), is applied to this potential, it will yield a G_a which is the sum of two exponentials with the wrong exponents and coefficients, and (2) the simple exponential form of (5.10) is here due entirely to the precise form of the assumed long-range part of φ. This is certainly so if our method of arriving at (5.10) is essentially valid and can be used as well for other forms of φ_l. It is easy to construct φ_l's—shallow square-well sum of exponentials—for which G_a would be a sum of exponentials, or decaying oscillatory exponentials, or change from one to the other as a function of density. We may also surmise that the single exponential form is not universal from the fact that (5.10) may be expanded in a virial series the lowest-order term of which $-\rho\beta\varphi_l$ is given correctly by the usual expansion; presumably the higher-order terms also follow correctly. This would not be true if G_a were a single exponential, but φ_l were not.[12]

There remains the question of the validity of the linearization of (3.4). If we are interested in the asymptotic region from the outset, we may equally well use (3.2) as our starting point. Combining terms as before, this reduces to

$$-\beta\varphi(\mathbf{r}) = X(\mathbf{r}) - \frac{1}{2}\iiint \hat{\mathfrak{F}}_3(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2,)X(\mathbf{x}_1)X(\mathbf{x}_2)$$
$$\times [\rho^{-1}\delta(\mathbf{r}-\mathbf{x}) - X(\mathbf{r}-\mathbf{x})]\, d\mathbf{x}\, d\mathbf{x}_1\, d\mathbf{x}_2 + \cdots, \qquad (6.1)$$

and this may profitably be rewritten as

$$-\beta\varphi(\mathbf{r}) = X(\mathbf{r}) - \frac{1}{2}\iint [\delta\hat{\mathfrak{F}}_2(\mathbf{x}_1, \mathbf{x}_2)/\delta n(\mathbf{r})]$$
$$\times X(\mathbf{x}_1)X(\mathbf{x}_2)\, d\mathbf{x}_1\, d\mathbf{x}_2 + \cdots. \qquad (6.2)$$

Keeping the Kac–Uhlenbeck model in mind as prototype, it is clear that for large r, the regions $x_1 \sim x_2 \sim r$; $x_1 \sim r$, x_2 far from r; and $x_2 \sim r$, x_1 far from r in the second term of (6.2) all con-

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[10] The corresponding modification in the case of the electron gas would yield corrections to G_a of higher order in e^2.

[11] Note added in proof: The *ad hoc* prescription given here for obtaining G_a from X_a, to lowest order in γ, can be made rigorous and generalized to obtain also higher-order terms in G_a from a limited knowledge of X. It is interesting to note from Eq. (5.10) that when α_0 is negative, i.e., we have a weak long-range repulsive potential, then, the range of the radial distribution function is smaller than that of the direct correlation function.

[12] P. C. Hemmer has shown: (1) that our analysis yields the correct result for G_a when φ_l consists of a sum of exponentials and (2) that near the critical point (but still $(l - l_c)^3 \gg \gamma$, $(T - T_c)^{\frac{3}{2}} \gg \gamma$) one exponential will dominate the long-range part of G. There is thus approximate agreement with the O–Z theory in this range, though there is no way of determining both A & Λ appearing in (3.10) from the O–Z theory alone, c.f. discussion at the end of Sec. 3.

tribute $0(\gamma^2)$. In the first case both $X(x_1)$ and $X(x_2)$ would be of order γ while in the second case $\hat{\mathfrak{F}}_2$ and one of the X's would be of order γ. We still have to show that when x_1 and x_2 are both far from r then $\delta\hat{\mathfrak{F}}_2(\mathbf{x}_1, \mathbf{x}_2)/\delta n(\mathbf{r})$ is of order γ^2. To do this we consider an expansion of $\gamma(\mathbf{r})$, similar to (3.2), with the nonuniform density $n(\mathbf{r})$ caused by keeping *two* fluid particles fixed at $\mathbf{x}_1$ and $\mathbf{x}_2$. In this case,

$$n(\mathbf{r}) = \rho_3(\mathbf{r}, \mathbf{x}_1, \mathbf{x}_2)/\rho_2(\mathbf{x}_1, \mathbf{x}_2), \tag{6.3}$$

where, as in section three, ρ_l refers to the l-particle distribution in a uniform system of density ρ. Thus, to lowest order,

$$-\beta[\varphi(\mathbf{r} - \mathbf{x}_1) + \varphi(\mathbf{r} - \mathbf{x}_2)] = \int [\rho^{-1}\delta(\mathbf{r} - \mathbf{x}) - X(\mathbf{r} - \mathbf{x})] \times \left[\frac{\rho_3(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2)}{\rho_2(\mathbf{x}_1, \mathbf{x}_2)} - \rho\right] d\mathbf{x} + \cdots . \tag{6.4}$$

After some manipulation, started by expressing ρ_3 in terms of $\hat{\mathfrak{F}}_3$, Eq. (6.4) may be put in the form

$$\frac{\delta\hat{\mathfrak{F}}_2(\mathbf{x}_1, \mathbf{x}_2)}{\delta n(\mathbf{r})} = -\hat{\mathfrak{F}}_2(\mathbf{x}_1 - \mathbf{x}_2)\{X(\mathbf{r} - \mathbf{x}_1) + \beta\varphi(\mathbf{r} - \mathbf{x}_1) + X(\mathbf{r} - \mathbf{x}_2) + \beta\varphi(\mathbf{r} - \mathbf{x}_2) + \rho^{-1}[\delta(\mathbf{r} - \mathbf{x}_1) + \delta(\mathbf{r} - \mathbf{x}_2)]\} + \delta(\mathbf{r} - \mathbf{x}_1)\delta(\mathbf{r} - \mathbf{x}_2). \tag{6.5}$$

We see that taking $X(\mathbf{y}) = -\beta\varphi(\mathbf{y}) + 0(\gamma^2)$ for $y \gg \delta$ leads to $\delta\hat{\mathfrak{F}}_2(\mathbf{x}_1, \mathbf{x}_2)/\delta n(\mathbf{r}) \sim 0(\gamma^2)$ for $\mathbf{r}$ far from $\mathbf{x}_1$ and $\mathbf{x}_2$ which in turn makes the second term in (6.2) of $0(\gamma^2)$. We have also verified this explicitly for the lowest order in the density.

The virial expansion of $X(\mathbf{r})$ may actually be used to verify (4.1) directly to lowest order in γ. As is well-known, all the clusters appearing in the virial series for X must be at least doubly connected. In fact,[13]

$$X(\mathbf{r}_{12}) = f(\mathbf{r}_{12}) + \sum_{k=2}^{\infty} \frac{\rho^{k-1}}{(k-1)!} \times \int S_k(1, 2, \cdots, k+1)\, d\mathbf{r}_3 \cdots d\mathbf{r}_{k+1},$$

where S_k is the irreducible cluster sum of the f's connecting (at least doubly) $k + 1$ particles. It is easy to convince oneself that for r_{12} large, i.e. of order γ^{-1}, all the terms in the sum will be of order γ^2 at least. Thus the term proportional to ρ is

$$f(\mathbf{r}_{12}) \int f(\mathbf{r}_{13})f(\mathbf{r}_{23})\, d\mathbf{r}_3 .$$

For large $\mathbf{r}_{12}$, $f(\mathbf{r}_{12})$ will be of order ν and so will the integral. In general it is sufficient to look at the ring diagrams for clearly none of the other clusters will give (lower)-order γ contributions. In the term proportional to ρ^3 there will be a ring diagram which contains $f(\mathbf{r}_{12})$ and this will behave essentially like the three-particle ring. Similar considerations show that the term

$$\int f(\mathbf{r}_{13})f(\mathbf{r}_{14})f(\mathbf{r}_{23})f(\mathbf{r}_{24})\, d\mathbf{r}_3\, d\mathbf{r}_4$$

is again of order γ^2, for r_{12} large (we simply have to enumerate all the possibilities: $\mathbf{r}_3$, $\mathbf{r}_4$ close to $\mathbf{r}_1$ or $\mathbf{r}_2$; $\mathbf{r}_3$ close $\mathbf{r}_4$ far, etc.) and the same holds for all other ring clusters.[14] The same analysis will also apply to the case where φ_l is the sum of exponentials.[12]

ACKNOWLEDGMENTS

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APPENDIX. ALTERNATE EXPANSIONS

We describe here several alternate expansions to the one developed in Sec. 3 for obtaining the properties of a uniform system in terms of a nonuniform system with an external potential induced by keeping one of the particles fixed at the origin. We have already referred to the expansion of $e^{\gamma(\mathbf{r})}$. This yields according to (2.2)–(2.5) with

$$\Delta n(\mathbf{r}) = G(\mathbf{r}), \tag{A1}$$

$$\frac{\delta e^{\gamma(\mathbf{r})}}{\delta n(\mathbf{x})} = e^{\gamma(\mathbf{r})} \frac{\delta\gamma(\mathbf{r})}{\delta n(\mathbf{x})}, \tag{A2}$$

$$(e^{-\beta\varphi(\mathbf{r})} - 1) \equiv f(\mathbf{r}) = X(\mathbf{r}) + \frac{1}{2!} X^2(\mathbf{r}) - \frac{1}{2!} \int \frac{\delta\hat{\mathfrak{F}}(\mathbf{x}_1, \mathbf{x}_2)}{\delta n(\mathbf{r})} X(\mathbf{x}_1)X(\mathbf{x}_2)\, d\mathbf{x}_1\, d\mathbf{x}_2 + \cdots . \tag{A3}$$

It is interesting to note that the series in (A3) can be partially summed to start with $(e^{X(\mathbf{r})} - 1)$.

We consider next the inverse process of Eqs. (3.2) and (A3), i.e., instead of expanding $\gamma(\mathbf{r})$ or $e^{\gamma(\mathbf{r})}$ in a Taylor series in $\Delta n(\mathbf{r}')$ we expand $n(\mathbf{r})$ in a series in $\Delta\gamma(\mathbf{r}')$ or $\Delta e^{\gamma(\mathbf{r}')}$ (cf. Sec. 3 in I). In

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[13] M. J. von Leeuwen, J. Growenweld, and J. de Boer, Physica **25**, 792 (1959); F. H. Stillinger and F. P. Buff, J. Chem. Phys. **37**, 1 (1962).

[14] Note added in proof: Similar results for the lowest γ order in X_a were also obtained by E. Helfand and M. Fischer. We have also obtained a very simple expression for the γ^2 term in X_a from graphical consideration. This agrees with the second-order term in G_a obtained by Uhlenbeck, Kac and Hemmer, first from their integral equation, and later from direct graphical analysis of G_a.

the first case we find for

$$\begin{aligned} n(\mathbf{r}) &= G(\mathbf{r}) + \rho, \\ \Delta\gamma(\mathbf{r}) &= -\beta\varphi(\mathbf{r}), \end{aligned} \tag{A4}$$

$$\begin{aligned} G(\mathbf{r}) &= -\beta \int \hat{\mathfrak{F}}_2(\mathbf{r}, \mathbf{x})\varphi(\mathbf{x})\, d\mathbf{x} \\ &\quad + \frac{\beta^2}{2!}\int \hat{\mathfrak{F}}_3(\mathbf{r}, \mathbf{x}_1, \mathbf{x}_2)\varphi(\mathbf{x}_1)\varphi(\mathbf{x}_2)\, d\mathbf{x}_1\, d\mathbf{x}_2 + \cdots \\ &= -\beta\rho\varphi(\mathbf{r}) - \beta\rho \int G(\mathbf{r} - \mathbf{x})\varphi(\mathbf{x})\, d\mathbf{x} \\ &\quad + \frac{\beta^2}{2}\int \hat{\mathfrak{F}}_3(\mathbf{r}, \mathbf{x}_1, \mathbf{x}_2)\varphi(\mathbf{x}_1)\varphi(\mathbf{x}_2)\, d\mathbf{x}_1\, d\mathbf{x}_2 + \cdots \end{aligned} \tag{A5}$$

When φ is both weak and short range then, to lowest-order $G = \beta\rho\varphi$, as discussed in Sec. 4, which results from the first term in (A5). For the electron gas where φ is assumed weak everywhere but is long range, the first two terms in (A5) would again yield the Debye–Huckel result. For the Kac potential, however, where $\varphi(x)$ is long range and in addition is infinite for $|x| < \delta$, (A5) cannot be used at all even for r large. This indicates that we try expanding $n(\mathbf{r})$ in $\Delta e^{\gamma(\mathbf{r})} = e^{\lambda+\beta\mu}f(\mathbf{r})$. Writing thus

$$\frac{\delta n(\mathbf{r})}{\delta e^{\gamma(\mathbf{x})}} = e^{-\gamma(\mathbf{x})}\,\frac{\delta n(\mathbf{r})}{\delta\gamma(\mathbf{x})}, \tag{A6}$$

we find

$$\begin{aligned} G(\mathbf{r}) &= \int \hat{\mathfrak{F}}_2(\mathbf{r}, \mathbf{x})f(\mathbf{x})\, d\mathbf{x} + \frac{1}{2!}\left\{-\int \hat{\mathfrak{F}}_2(\mathbf{r}, \mathbf{x})f^2(\mathbf{x})\, d\mathbf{x}\right. \\ &\quad \left. + \int \hat{\mathfrak{F}}_3(\mathbf{r}, \mathbf{x}_1, \mathbf{x}_2)f(\mathbf{x}_1)f(\mathbf{x}_2)\, d\mathbf{x}_1\, d\mathbf{x}_2\right\} + \cdots \\ &= \rho f(\mathbf{r}) + \rho\int G(\mathbf{r} - \mathbf{x})f(\mathbf{x})\, d\mathbf{x} \\ &\quad - \tfrac{1}{2}\rho f^2(\mathbf{r}) - \tfrac{1}{2}\rho\int G(\mathbf{r} - \mathbf{x})f^2(\mathbf{x})\, d\mathbf{x} \\ &\quad + \frac{1}{2!}\int \hat{\mathfrak{F}}_3(\mathbf{r}, \mathbf{x}_1, \mathbf{x}_2)f(\mathbf{x}_1)f(\mathbf{x}_2)\, d\mathbf{x}_1\, d\mathbf{x}_2 + \cdots . \end{aligned} \tag{A7}$$

It is seen from (A7) that, unlike (4.1), the higher terms in the Taylor expansion will contain terms of order γ, so that terminating the expansion after one or two terms will not yield G_a correctly even to the lowest order in γ. This agrees with our analysis of Secs. 5 and 6.

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Variational Statistical Mechanics in Terms of "Observables" for Normal and Superfluid Systems

C. De Dominicis
Service de Physique Mathématique C.E.N. de Saclay, (S.O.), France

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Thermodynamical functions are expressed by perturbation theory as stationary functionals of the 1-, and 2-body potentials; the stationary conditions yield the 1-, and 2-body correlation functions in terms of the potentials. Through the use of diagramatic methods, it is possible to *explicitly* invert these relations and express the potentials in terms of the correlation functions; in turn the thermodynamical functions become stationary functionals of the correlation functions. This procedure is carried out for normal (quantum and classical) systems. For superfluid systems, $\frac{1}{2}$-, $\frac{3}{2}$-body potentials, and correlation functions need also be considered and the above procedure becomes imperative to eliminate the nonphysical $\frac{1}{2}$-, $\frac{3}{2}$-body potentials. Its first two steps are illustrated, and various features of this formulation and its usefulness are discussed.

I. INTRODUCTION

We are concerned with equilibrium statistical mechanics of classical and quantum systems. First we discuss how the thermodynamical functions can be considered as the solutions of a variational problem and then we explicitly construct these functions. Equilibrium statistical mechanics may be viewed variationally in several different ways.

1. For definiteness we consider a system the Hamiltonian of which is the sum of a one-body potential[1] v_1 and a two-body potential v_2. Perturbation theory expresses the grand partition function

$$Z = \operatorname{Tr} e^{-\beta H},$$

or rather its logarithm $\operatorname{Log} Z = W$ as an explicit expansion in powers of βv_1 and βv_2,

$$W\{\beta v_1, \beta v_2\}, \tag{1a}$$

and the one- and two-particle distribution functions G_1, G_2 are then defined by

$$G_i = -(\delta/\delta\beta v_1) W\{\beta v_1, \beta v_2\}. \tag{1b}$$

Instead of W, one may consider

$$F = W\{\beta v_1, \beta v_2\} + \int \beta v_1 G_1, \tag{1a$'$}$$

$$S = W\{\beta v_1, \beta v_2\} + \sum_{i=1}^{2} \int \beta v_i G_i, \tag{1a$''$}$$

where S is the entropy and F (although slightly differing from its usual definition) is considered as a free energy. These expressions, for *fixed values of G_1 or G_1 and G_2* satisfy

$$(\delta/\delta\beta v_1)F = 0, \tag{1b$'$}$$

$$(\delta/\delta\beta v_i)S = 0. \tag{1b$''$}$$

These relations express, for example, that the right hand side of (1a$''$), considered as a functional of $\beta\bar{v}_i$, becomes equal to the entropy S for the particular values $\beta\bar{v}_i = \beta v_i$ which satisfy Eq. (1b$''$) and, for fixed values of G_i, render that functional stationary. In a short but less precise way, we state that for fixed values of G_i, S is a stationary functional of the potentials βv_i.

2. A partially *reciprocal* point of view is obtained by considering the free energy as expressed in terms of G_1 and βv_1:

$$F\{G_1, \beta v_2\}, \tag{2a}$$

which satisfies

$$\beta v_1 = (\delta/\delta G_1) F\{G_1, \beta v_2\}. \tag{2b}$$

We then have

$$W = F\{G_1, \beta v_2\} - \int \beta v_1 G_1, \tag{2a$'$}$$

which, for a *fixed value of v_1*, is such that

$$(\delta/\delta\beta v_1)W = 0, \tag{2b$'$}$$

i.e., W, for a fixed value of v_1, is a stationary functional of G_1.

Equation (1.b$'$) expresses the one-particle distribution function in terms of the potentials; Eq. (2b) expresses the one-body potential v_1 in terms of the one-particle distribution function, an ex-

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[1] In which we include the kinetic energy minus the chemical potential μ.

pansion first found for classical systems by Yvon[2] in 1935. The stationarity property, Eqs. (2a′, b′), was first pointed out by Lee and Yang[3] in connection with quantum systems. Formulations involving not the one-particle distribution function, but the one-particle Green's function [4,5,6] lead to explicit[7] expansions of (2a, b).

Yvon[2,9] had previously pointed out the usefulness of Eq. (2b) in relation to phase transitions in classical systems, and (2a′) involves only a slight rewriting of the virial expansion for inhomogeneous systems derived by Yvon. *Self-consistent* approximations are constructed by approximating (2a) with

$$F^{(0)}\{G_1, \beta v_2\}, \tag{2c}$$

and determining G_1 by the implicit equation

$$\beta v_1 = (\delta/\delta G_1)F^{(0)}\{G_1, \beta v_2\}. \tag{2d}$$

Thus a generalization to nonzero temperature of the Hartree–Fock approximation is obtained by keeping in $F^{(0)}$, terms up to first power in v_2.

3. The fully *reciprocal* point of view is obtained by considering the entropy as expressed in terms of

$$S\{G_1, G_2\}. \tag{3a}$$

Clearly we also have

$$\beta v_i = (\delta/\delta G_i)S\{G_1, G_2\}. \tag{3b}$$

If we now write

$$W = S\{G_1, G_2\} - \sum_{i=1}^{2} \int \beta v_i G_i \tag{3a′}$$

for fixed values of the potentials v_i, we obtain

$$(\delta/\delta G_i)W = 0. \tag{3b′}$$

Explicit forms of (3a, b) have been derived for classical systems[10,11] and, in the Green's function formulation, for quantum systems.[11] The entropy functional is free from any reference to equilibrium, which may be an interesting point in relation to nonequilibrium situations; it is also free from any reference to the Hamiltonian. Practically speaking, the self-consistent approximations formulated by limiting the expansion of $S\{G_1, G_2\}$ to a certain class of terms $S^{(0)}\{G_1, G_2\}$ [and calculating G_1, G_2 through (3b)], are expected to be particularly interesting in the case of singular potentials. Convergence of the expansions is also expected to improve when going from (1a) to (2a) and from (2a) to (3a).

4. The case for a reciprocal point of view becomes even more compelling with *anomalous systems*. By definition we call anomalous the class of systems for which the prescription given by Bogoliubov[12] applies, i.e., systems for which the usual grand ensemble must be replaced by a more general one where the possible degeneracies are removed. Paul Martin has discussed at this conference the kind of new ensemble suited to describe Bose systems in the condensation region, so that we only mention the essential features: the Hamiltonian is supplemented by a source term potential $v_{\frac{1}{2}}$ (and a sink term potential $v^*_{\frac{1}{2}}$) which is eventually set equal to zero. Such terms lead, for example, to nonvanishing averages of single annihilation (or creation) operators. These averages are called $G_{\frac{1}{2}}$ (or $G^*_{\frac{1}{2}}$). If one goes now to a *reciprocal* point of view, expressing for example $v_{\frac{1}{2}}$ as a functional of $G_{\frac{1}{2}}$ and $G^*_{\frac{1}{2}}$, it becomes possible for nonvanishing solutions for $G_{\frac{1}{2}}$, $G^*_{\frac{1}{2}}$ to persist, even after $v_{\frac{1}{2}}$ is set equal to zero. In this way one constructs the quasi-averages of Bogoliubov which remain nonvanishing in the "degeneracy" region i.e., below the transition temperature. Paul Martin has shown how to write *generating equations* which construct order-by-order expansions of the reciprocal formulations e.g., the expansion of $v_{\frac{1}{2}}$ in terms of $G_{\frac{1}{2}}$, $G^*_{\frac{1}{2}}$ (and v_1, v_2). Here we use *diagram techniques*,[13] which offer the ad-

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[2] J. Yvon, Actualités Sc. et Ind. **203** (1935).

[3] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959); **117**, 22 (1960).

[4] E. Montroll and J. Ward, Phys. Fluids **1**, 55 (1958).

[5] P. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959). A. Abrikosov, L. Gorkov, and I. Dzyaloshinsky, Soviet Phys.—JETP **36**, 900 (1959).

[6] J. Luttinger, J. Ward, Phys. Rev. **118**, 1417 (1960).

[7] It should be pointed out that for quantum systems, no *explicit* expansion of F or v_1, in terms of the one-particle distribution function (average occupation number) is known so far. Formulations of references 3 and 8 lead to explicit functionals of the occupation number, but the kinetic energy at least, is still explicitly present. Expansions (2.a) and (2b) could of course be constructed *term by term* through the type of iterative process described by Paul Martin.

The Green's function formulation on the other hand, leads to explicit expansions for (2a, b) but through the use of (time-dependent) Green's function instead of the more physical occupation number; as a consequence one loses the maximal property of W which is a feature of the formulations of references 3 and 8.

[8] R. Balian, C. Bloch, and C. De Dominicis, Nuclear Phys. **25**, 529 (1961); **27**, 294 (1961).

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[10] T. Morita and K. Hiroike, Progr. Theoret. Phys. (Kyoto) **25**, 537 (1961).

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[12] N. Bogolubov, Physica **26**, S1 (1960); T. D. Lee and C. N. Yang [Phys. Rev. **117**, 897 (1960)] had also introduced an extended ensemble to treat condensed Bose systems through the condensation point and succeeded in expressing the thermodynamical functions in terms of the condensate density and the average occupation number. However the transformation to the reciprocal forms is more conventiently carried out[7] in terms of the Green's function formulation.

[13] Such techniques have been standard in field theory for many years; more recent approaches use "anomalous" diagrams of the type considered here (J. Goldstone, private communication).

vantage of immediately displaying the character of the general term in the expansions.

5. In the following, we examine first the case of anomalous systems and calculate the thermodynamical functions (and distribution functions) in the partial reciprocal formulation (where the $v_{\frac{1}{2}}$ and v_1 variables are replaced by $G_{\frac{1}{2}}$ and G_1). We sketch how to obtain the complete reciprocal formulation and quote some results for the normal case. Finally, we mention the corresponding results for classical systems. At each stage of the transformation into the reciprocal formulation, we display explicitly the variational properties of the thermodynamical functions.

An expanded version of the new material presented here will appear as part of a joint publication with Paul Martin.

II. ANOMALOUS SYSTEMS: PERTURBATION THEORY

We consider a Bose system characterized by its Hamiltonian in momentum representation ($2m = 1$), and second-quantized form

$$\begin{aligned} H = {} & \sum_{\mathbf{k}} (\mathbf{k}^2 - \mu + u_1(\mathbf{k}))a^+_{\mathbf{k}}a_{\mathbf{k}} \\ & + \tfrac{1}{2} \sum_{\mathbf{klmn}} v_2(\mathbf{k}, \mathbf{l}; \mathbf{m}, \mathbf{n})a^+_{\mathbf{k}}a^+_{\mathbf{l}}a_{\mathbf{m}}a_{\mathbf{n}} \qquad (2.1) \\ & + \sum_{\mathbf{k}} (v_{\frac{1}{2}}(\mathbf{k})a^+_{\mathbf{k}} + v^*_{\frac{1}{2}}(\mathbf{k})a_{\mathbf{k}}); \end{aligned}$$

eventually we let $v_{\frac{1}{2}}(\mathbf{k}) \to 0$, the nonvanishing part of the Hamiltonian being translationally invariant. With the notations of previous paragraph, we have

$$v_1(\mathbf{k}; \mathbf{l}) = \delta_{\mathbf{kl}}(\mathbf{k}^2 - \mu + u_1(\mathbf{k})).$$

$\delta_{\mathbf{kl}}u_1(\mathbf{k})$ and $v_2(\mathbf{kl}; \mathbf{mn})$ are the matrix elements in momentum space of a one-body (diagonal) external potential and a two-body interaction potential respectively. We recall now the results of pertubation theory as applied in the Green's function formulation.[4,5,6]

Wick's theorem establishes a one-to-one correspondence between algebraic terms of the perturbation expansion and a set of diagrams to each element of which, algebraic factors are associated according to well defined rules.

Diagrams are built with α vertices ($\alpha = \frac{1}{2}$, 1, 2) represented as shown below

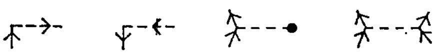

FIG. 1

and solid lines with a single arrow (unperturbed propagator) connecting the various vertices. They are *Feynmann* diagrams: two diagrams are considered distinct only if their topology is different (i.e., if the *connections* between various vertices are different; the relative *position* of the vertices is irrelevant). To each ζ diagram (diagram with 2ζ external lines), an algebraic contribution calculated with the following set of rules (rule A) is associated:

(Ai) to each α vertex ($\alpha = \frac{1}{2}$, 1, 2), associate $-\beta v^*_{\frac{1}{2}}(\mathbf{k})$ or $-\beta v_{\frac{1}{2}}(\mathbf{k})$, $-\beta u_1(\mathbf{k})$, $-\beta v_2(\mathbf{k}, \mathbf{l}; \mathbf{m}, \mathbf{n})$ respectively.

(Aii) to each line j, which is characterized by a momentum $\mathbf{k}_j$ and an energy ω_j, associate the unperturbed propagator

$$G^0_1(\mathbf{k}_j, \omega_j) = [\beta\mathbf{k}^2_j - \omega_j - \beta\mu]^{-1}, \qquad (2.2)$$

where

$$\omega_j = 2ni\pi \qquad n = 0, \pm 1, \pm 2 \cdots.$$

(Aiii) keep fixed momenta and energies to the 2ζ external lines, sum over momenta and energies relative to internal lines, with (a) conservation of energy at each α vertex (i.e., a line j ending at or emerging from a 1 vertex has $\omega_j = 0$). (b) conservation of momenta[14] at each "physical" α vertex ($\alpha = 1, 2$).

A weight s^{-1} where s is the symmetry number of the diagram,[15] is also associated with each diagram.

Perturbation expansion around the unperturbed system ($v_{\frac{1}{2}} = u_1 = v_2 = 0$) gives

$$Z/Z_0 = \Sigma \text{ (all distinct 0 diagrams)}, \qquad (2.3)$$

$$W - W_0 = \Sigma \text{ (all distinct, connected, 0 diagrams)}. \qquad (2.4)$$

We also consider average values over the ensemble defined by

$$\langle A \rangle = \operatorname{Tr} e^{-\beta H}A.$$

1. Let

$$G^*_{\frac{1}{2}}(\mathbf{k}_1, w_1) = \langle \hat{a}^+_{\mathbf{k}_1}(w_1) \rangle, \qquad (2.5)$$

where

$$\hat{a}^+_{\mathbf{k}_1}(w_1) = e^{w_1 H}\, a^+_{\mathbf{k}_1} e^{-w_1 H}$$

is the Heisenberg representation of the creation operator $a^+_{\mathbf{k}_1}$, w_1 playing the role of a "time" ($0 \le w_1 \le 1$).

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[14] If we had chosen a translationally invariant source term

$$v_{1/2}(\mathbf{k}) = \delta_{\mathbf{k},0}\, v_{1/2},$$

momentum conservation would also hold at $\frac{1}{2}$ vertices (i.e., a line j ending up at or emerging from a $\frac{1}{2}$ vertex would have $\mathbf{k}_j = 0$).

[15] Alternatively one could label all vertices with labels 1, 2 $\cdots$ n; the weight for such labeled diagrams would then be $(n!)^{-1}$, a procedure which is most convenient for carrying out proofs. The representation adopted in the text also implies an extra factor ($\frac{1}{2}$) for each symmetrical (ladder-like) diagram.

Consider its Fourier-series transform

$$G^*_{\frac{1}{2}}(\mathbf{k}_1, \omega_1) = \int_0^1 dw_1 e^{w_1 \omega_1} G^*_{\frac{1}{2}}(\mathbf{k}_1, w_1), \tag{2.6}$$

which due to translational invariance in time, can be written

$$G^*_{\frac{1}{2}}(\mathbf{k}_1, \omega_1) = \delta_{\omega_1, 0} G^*_{\frac{1}{2}}(\mathbf{k}_1); \tag{2.7}$$

we then have from perturbation theory,

$$G_{\frac{1}{2}}(\mathbf{k}_1) = \Sigma \text{ (all distinct, connected } \tfrac{1}{2} \text{ diagrams with one outgoing external line)}, \tag{2.8}$$

$$G^*_{\frac{1}{2}}(\mathbf{k}_1) = \Sigma \text{ (all distinct, connected } \tfrac{1}{2} \text{ diagrams with one incoming external line)}, \tag{2.9}$$

expansions which could also have been derived from Eq. (2.4) by noting that

$$G_{\frac{1}{2}}(\mathbf{k}_1) = [\delta/\delta(-\beta v^*_{\frac{1}{2}}(k_1))] W\{-\beta v_{\frac{1}{2}}, -\beta v^*_{\frac{1}{2}}\}. \tag{2.10}$$

2. The usual Green's function is defined by

$$\langle T \hat{a}\mathbf{k}'_1 \, (w'_1) \hat{a}^+_{\mathbf{k}_1}(w_1) \rangle \tag{2.11}$$

where T stands for the usual T product. This Green's function depends upon only $w_1 - w'_1$ (not upon w_1 and w'_1 separately) and its Fourier series transform can be written as

$$G_1(\mathbf{k}'_1\omega_1, \mathbf{k}_1\omega_1) = \Sigma \text{ (all distinct, connected 1 diagrams with one incoming line 1 and one outgoing line 1')} + \delta_{\omega_1, 0} G_{\frac{1}{2}}(\mathbf{k}'_1) G^*_{\frac{1}{2}}(\mathbf{k}_1), \tag{2.12}$$

with the usual relation to the total number of particles

$$N = \sum_{\mathbf{k}_1, \omega_1} G_1(\mathbf{k}_1\omega_1, \mathbf{k}_1\omega_1). \tag{2.13}$$

The separation in Eq. (2.12) between a part containing completely connected diagrams and a part containing diagrams disconnected into two parts (one connected to the incoming line 1, the other to the outgoing line 1′), corresponds to the separation into cumulants made by Paul Martin at this conference;

$$\langle \hat{a}_{1'} \hat{a}^+_1 \rangle = \langle (\hat{a}_{1'} - \langle \hat{a}_{1'} \rangle)(\hat{a}^+_1 - \langle \hat{a}^+_1 \rangle) \rangle, \tag{2.14}$$

i.e., it corresponds to the splitting of the one-particle density matrix for superfluid systems as introduced by Onsager and Penrose.[16]

III. ANOMALOUS SYSTEMS: FIRST RECIPROCAL FORMULATION

Perturbation theory has allowed us to write the thermodynamical functions and the average values of a number of basic operators (a^+ and a) in terms of the potentials $v_{\frac{1}{2}}$, u_1, v_2. Here we wish to express the same quantities in terms of $G_{\frac{1}{2}}$, u_1, v_2.

1. To do this, we analyze ζ diagrams (diagrams with 2ζ external lines):

An articulation line is such that by cutting it, a connected ζ diagram falls into two disconnected parts (a single $\frac{1}{2}$ vertex is not considered as a separate part).

A *$\frac{1}{2}$-irreducible ζ diagram* is such that it has no *articulation line.* We call $\mathcal{K}\{-G^0_1\beta v_{\frac{1}{2}}, -G^0_1\beta v^*_{\frac{1}{2}}\}$ the *contribution* of *all the $\frac{1}{2}$-irreducible* 0 *diagrams.* Such a functional contains both normal diagrams (containing no $\frac{1}{2}$ vertices $v_{\frac{1}{2}}$ or $v^*_{\frac{1}{2}}$) and anomalous diagrams (containing an equal number of $\frac{1}{2}$ vertices $v_{\frac{1}{2}}$ and $v^*_{\frac{1}{2}}$). The contribution of all the $\frac{1}{2}$-irreducible $\frac{1}{2}$ diagrams with a single outgoing line e.g., is expressed in terms of the functional derivative

$$[\delta/\delta(-G^0_1\beta v^*_{\frac{1}{2}})] \mathcal{K}^{(\frac{1}{2})}\{-G^0_1\beta v_{\frac{1}{2}}, -G^0_1\beta v^*_{\frac{1}{2}}\} = K^{(\frac{1}{2})}_{\frac{1}{2}}\{\mathbf{k}_1; G_{\frac{1}{2}}, G^*_{\frac{1}{2}}\} \tag{3.1}$$

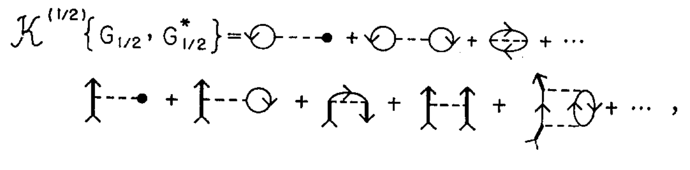
as

$$G^0_1(\mathbf{k}_1, 0) K^{(\frac{1}{2})}_{\frac{1}{2}}\{\mathbf{k}_1; G_{\frac{1}{2}}, G^*_{\frac{1}{2}}\}. \tag{3.2}$$

The general $\frac{1}{2}$ diagram with a single outgoing line, (besides the trivial $\frac{1}{2}$ diagram of first order in $v_{\frac{1}{2}}$) is then generated by replacing inside the $\frac{1}{2}$-irreducible $\frac{1}{2}$ diagram and each $\frac{1}{2}$ vertex (and its attached line) by the most general $\frac{1}{2}$ diagram, i.e., replacing $-G^0_1\beta v_{\frac{1}{2}}$ or $-G^0_1\beta v^*_{\frac{1}{2}}$ by $G_{\frac{1}{2}}$ or $G^*_{\frac{1}{2}}$ respectively. This operation yields

$$G_{\frac{1}{2}}(\mathbf{k}_1) = G^0_1(\mathbf{k}_1, 0)[-\beta v_{\frac{1}{2}}(\mathbf{k}_1) + K^{(\frac{1}{2})}_{\frac{1}{2}}\{\mathbf{k}_1; G_{\frac{1}{2}}, G^*_{\frac{1}{2}}\}]. \tag{3.3}$$

$\mathcal{K}^{(\frac{1}{2})}$, $K^{(\frac{1}{2})}_{\frac{1}{2}}$ (and $K^{(\frac{1}{2})*}_{\frac{1}{2}}$) are now functionals of $G_{\frac{1}{2}}$, $G^*_{\frac{1}{2}}$ and are represented by all distinct, connected $\frac{1}{2}$ irreducible, 0 or $\frac{1}{2}$ diagrams, i.e.,



(3.4)

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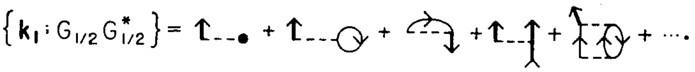
[16] O. Penrose, L. Onsager, Phys. Rev. **104**, 576 (1956).

$$K^{(1/2)}\{\mathbf{k}_1 ; G_{1/2}G^*_{1/2}\} =$$  (3.5)

Associated contributions are now calculated with rule B differing from rule A through point (*i*)

(Bi) to each incoming or outgoing (heavy) half-line associated factor $G^*_{\frac12}$ or $G_{\frac12}$; to each 1- or 2-vertex associate $-\beta u_1$, $-\beta v_2$.

Naturally, instead of (3.1) we now have

$$[\delta/\delta G^*_{\frac12}(\mathbf{k}_1)]\mathcal{K}^{(\frac12)}\{G_{\frac12}, G^*_{\frac12}\} = K^{(\frac12)}_{\frac12}\{\mathbf{k}_1; G_{\frac12}, G^*_{\frac12}\}. \quad (3.6)$$

The inversion of relation (2.10) is thus achieved in (3.3) which we may rewrite

$$\beta v_{\frac12}(\mathbf{k}_1) = -[G^0_1(\mathbf{k}_1, 0)]^{-1}G_{\frac12}(\mathbf{k}_1) + K^{(\frac12)}_{\frac12}\{\mathbf{k}_1; G_{\frac12}, G^*_{\frac12}\}. \quad (3.7)$$

2. We now express W as a functional of $G_{\frac12}$, $G^*_{\frac12}$. Although this may be done by direct functional integration of (3.7) over $G^*_{\frac12}$, we use a more detailed analysis.[17]

Consider the three following expressions:

$$\text{(a)} \qquad -\sum_{\mathbf{k}_1} [\beta v_{\frac12}(\mathbf{k}_1)G^*_{\frac12}(\mathbf{k}_1) + \beta v^*_{\frac12}(\mathbf{k}_1)G_{\frac12}(\mathbf{k}_1)]: \quad (3.8)$$

This quantity may be thought of as represented by all connected 0 diagrams (calculated with rule A) but with *one ½ vertex distinguished*. The contribution to (3.8) of a class of 0 diagrams containing $N(\frac12\, v)$ ½ vertices is thus $N(\frac12\, v)$ times its contribution to W.

$$\text{(b)} \qquad \mathcal{K}^{(\frac12)}\{G_{\frac12}, G^*_{\frac12}\}: \quad (3.9)$$

This quantity may be represented by all 0 diagrams (calculated with rule A but with *one ½ irreducible part distinguished*. The contribution to Eq. (3.9) of 0 diagrams with $N(\mathcal{K}^{(\frac12)})$ ½-irreducible parts (i.e., 0 diagrams falling into $N(\mathcal{K}^{(\frac12)})$ parts after suppression of all articulation lines) is $N(\mathcal{K}^{(\frac12)})$ times the contribution of the same diagram to W.

(c) Consider finally a general 0 diagram where we *distinguish one ½-irreducible part* and *one ½ vertex* (*or one articulation line*) attached to it. This may be generated by taking a ½-irreducible part, replacing the marked ½ vertex (and its attached line) by the most general ½ diagram ($G_{\frac12}$ or $G^*_{\frac12}$) and then performing the same operation with the other ½ vertices, i.e., we have

$$\sum_{\mathbf{k}_1} G_{\frac12}(\mathbf{k}_1)K^{(\frac12)*}_{\frac12}\{\mathbf{k}_1; G_{\frac12}, G^*_{\frac12}\} + G^*_{\frac12}(\mathbf{k}_1)K^{(\frac12)}_{\frac12}\{\mathbf{k}_1; G_{\frac12}, G^*_{\frac12}\}. \quad (3.10)$$

Let $N(\mathcal{K}^{(\frac12)}\cdot m)$ be, in a 0 diagram, the number of ways in which the above distinction can be performed;[18] $N(\mathcal{K}^{(\frac12)}\cdot m)$ is also the extra weight carried by the distinguished diagrams contributing to (3.10) as compared with their contribution to W.

We now consider the following relation, which is easily proven by induction and holds between the three different weights introduced

$$\tfrac12[N(\tfrac12\, v) - N(\mathcal{K}^{(\frac12)}\cdot m)] + N(\mathcal{K}^{(\frac12)}) = +1. \quad (3.11)$$

This relation allows immediately to construct the proper weight for 0 diagrams contributing to W;

$$W - W_0 = -\tfrac12 \sum_{\mathbf{k}_1} [\beta v_{\frac12}(\mathbf{k}_1)G^*_{\frac12}(\mathbf{k}_1) + \beta v^*_{\frac12}(\mathbf{k}_1)G_{\frac12}(\mathbf{k}_1) + G_{\frac12}(\mathbf{k}_1)K^{(\frac12)*}_{\frac12}\{\mathbf{k}_1; G_{\frac12}, G^*_{\frac12}\} + G^*_{\frac12}(\mathbf{k}_1)K^{(\frac12)}_{\frac12}\{\mathbf{k}_1; G_{\frac12}, G^*_{\frac12}\}] + \mathcal{K}^{(\frac12)}\{G_{\frac12}, G^*_{\frac12}\}. \quad (3.12)$$

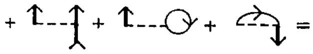
Equation (3.12) is verified to be stationary under changes of $K^{(\frac12)}_{\frac12}$ [$G_{\frac12}$ itself being expressed in terms of $K^{(\frac12)}_{\frac12}$ through Eq. (3.3)] and this stationarity property is easily traced back to the structure of the diagrams (tree structure).[17]

Using Eq. (3.6), one can eliminate $K^{(\frac12)}_{\frac12}$ and rewrite Eq. (3.12) as

$$W - W_0 = -\sum_{\mathbf{k}_1} [\beta v_{\frac12}(\mathbf{k}_1)G^*(\mathbf{k}_1) + \beta v^*_{\frac12}(\mathbf{k}_1)G_{\frac12}(\mathbf{k}_1) + [G^0_1(\mathbf{k}_1, 0)]^{-1}G_{\frac12}(\mathbf{k}_1)G^*_{\frac12}(\mathbf{k}_1)] + \mathcal{K}^{(\frac12)}\{G_{\frac12}G^*_{\frac12}\}, \quad (3.13)$$

an expression which, with Eq. (3.7), is now stationary with respect to variations of $G_{\frac12}$ (or $G^*_{\frac12}$). Also, the second variation is easily shown to be *negative definite*.

3. In the ensemble considered, $v_{\frac12}$ and $v^*_{\frac12}$ are eventually set equal to zero, and Eq. (3.7) (and its complex conjugate) becomes a homogenous equation determining $G_{\frac12}$. A normal system would lead only to the trivial solution $G_{\frac12} = 0$; a nontrivial solution characterizes an anomalous system (in this case, a Bose system below its transition temperature). The lowest order approximation to (3.7) is the Hartree–Fock approximation:

$$\beta(\mathbf{k}_1^2 - u_1(\mathbf{k}_1) - \mu)G_{1/2}(\mathbf{k}_1) +$$  $= 0.$ (3.14)

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[17] cf. the method used in references 8 and 11 and C. Bloch, Physica **26**, S62 (1960).

[18] i.e. the number of ½-irreducible parts each one weighted by the number m of its attached articulation lines or ½ vertices.

When the density of the condensate $|G_{\frac{1}{2}}(\mathbf{k}_1)|^2$ is considered close to the total density (small depletion), one may neglect the last two terms, and the equation obtained is then identical to one presented at this conference by Gross, for the wavefunction of the condensate. For zero depletion, $G_{\frac{1}{2}}$ is normalized to the number of particles N; otherwise we have (2.12), and (2.13) which may be rewritten

$$N = \sum_{\mathbf{k}_1} |G_{\frac{1}{2}}(\mathbf{k}_1)|^2 + \sum_{\mathbf{k}_1,\omega_1} G_1(\mathbf{k}_1,\omega_1;\mathbf{k}_1\omega_1). \qquad (3.15)$$

If one assumes that the overall space translational invariance is to be preserved, then only the component $\mathbf{k}_1 = 0$ is allowed, momentum is conserved at *all* vertices and (3.7) becomes an equation for μ, i.e., (when $G_{\frac{1}{2}} \neq 0$),

$$\beta\mu = [G_{\frac{1}{2}}]^{-1} K^{(\frac{1}{2})}\{\mathbf{k}_1 = 0; G_{\frac{1}{2}}, G^*_{\frac{1}{2}}\}. \qquad (3.16)$$

This is an expression for the chemical potential which is the natural extension at nonzero temperature of Belyaev's[19] results.

IV. SECOND RECIPROCAL TRANSFORMATION (MASS RENORMALIZATION)

Here we want to transform explicitly, from a functional dependence upon the 1-vertex u_1, (or rather v_1, as introduced in Sec. I) into a functional dependence upon the reciprocal function, i.e., the one-particle Green's function. This transformation is the analog of the mass-renormalization operation as used in field theories.

1. First we recall how this transformation is performed for *normal* systems. The same procedure as used in Sec. III leads to consider in the expression of W, the class of 1-irreducible 0 diagrams $\mathcal{K}^{(1)}\{G_1^0\}$ i.e., 0 diagrams such that by cutting two lines, one cannot obtain two different pieces (the diagram of first order in u_1 is not included in that class). The corresponding class of 1-irreducible 1 diagrams is then given by

$$G_1^0(\mathbf{k}_1,\omega_1)K_1^{(1)}\{\mathbf{k}_1,\omega_1;G_1^0\}G_1^0(\mathbf{k}_1,\omega_1),$$

where

$$K_1^{(1)}\{\mathbf{k}_1,\omega_1;G_1^0\} = [\delta/\delta G_1^0(\mathbf{k}_1,\omega_1)]\mathcal{K}^{(1)}\{G_1^0\},$$

and the most general 1 diagram is then generated by

(a) making the most general insertion in each internal line, i.e., replacing the unperturbed Green's function G_1^0 by the exact G_1 in the argument of $\mathcal{K}^{(1)}$, $K_1^{(1)}$;

(b) iterating this new mass operator; i.e., by writing the analog of Dyson's equation for statistical mechanics,

$$G_1(\mathbf{k}_1,\omega_1) = G_1^0(\mathbf{k}_1,\omega_1) + G_1^0(\mathbf{k}_1,\omega_1) \times [-\beta u_1(\mathbf{k}_1) + K_1^{(1)}\{\mathbf{k}_1\omega_1;G_1\}]G_1(\mathbf{k}_1,\omega_1). \qquad (4.2)$$

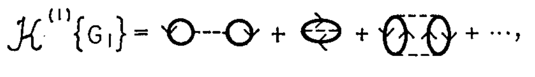
This equation expresses v_1 as a functional of G_1.

$$\beta v_1(\mathbf{k}_1) = \beta(\mathbf{k}_1^2 + u_1(\mathbf{k}_1) - \mu) = \omega_1 + [G_1(\mathbf{k}_1,\omega_1)]^{-1} + K_1^{(1)}\{\mathbf{k}_1,\omega_1;G_1\}. \qquad (4.3)$$

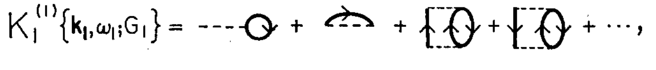
The same proof as used above,[17] or direct integration,[6] leads to W in its stationary form:

$$W = \sum_{\mathbf{k}1,\omega 1} [\log [G_1(\mathbf{k}_1,\omega_1)] + [\omega_1 - \beta v_1(\mathbf{k}_1)]G_1(\mathbf{k}_1,\omega_1)] + \mathcal{K}^{(1)}\{G_1\}, \qquad (4.4)$$

With



(4.5)



(4.6)

where the associated contributions are calculated with a rule C differing from rule A through points (i) (ii)

(Ci) to each 2 vertex, associate a matrix element of $-\beta v_2$.

(Cii) to each heavy line j, associate a function $G_1(\mathbf{k}_j, \omega_j)$.

Notice that here the second variation of Eq. (4.4) with respect to G_1 no longer has a definite sign.[7]

2. For *anomalous* systems the procedure is similar. Here however we also have nonvanishing average values of pairs of creation or annihilation operators. For example the Fourier series transform of

$$\langle T\hat{a}^+_{\mathbf{k}'_1}(w'_1)\hat{a}^+_{\mathbf{k}_1}(w_1)\rangle$$

is represented by

a. the sum of all distinct connected 1 diagrams with two outgoing external lines 1 and 1′ (their energies are ω_1, $-\omega_1$ respectively due to trans-

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[19] S. Belyaev, J.E.T.P. 7 289, 299 (1958).

lational invariance in time). Associated contributions are calculated with rule A (or with rule B if the first reciprocal transformation has been performed).

b. the sum of all distinct 1 diagrams disconnected into two $\frac{1}{2}$ diagrams, each one connected to an external outgoing line 1 or 1′ i.e., contributing

$$\delta_{\omega_1,0} G^*_{\frac{1}{2}}(\mathbf{k}_1') G^*_{\frac{1}{2}}(\mathbf{k}_1).$$

The possible average values of two operators or rather their *connected* part are usually written in a matrix form

$$(G_1(1', 1))_{\mu\nu}$$
$$= \text{F.T.}\ \langle (\hat{\eta}^{(\mu)}_{\mathbf{k}_1'} - \langle \hat{\eta}^{(\mu)}_{\mathbf{k}_1'} \rangle)(\hat{\eta}^{(\nu)}_{\mathbf{k}_1} - \langle \hat{\eta}^{(\nu)}_{\mathbf{k}_1} \rangle) \rangle. \tag{4.7}$$

We use variables 1, 1′ for $k_1\omega_1$, $k_1'\omega_1'$ with the appropriate conservation laws of energy (and momentum) implied; for simplicity here we keep the anomalous terms off diagonal by choosing

for μ: $\hat{\eta}^{(1)} = \hat{a}$, $\hat{\eta}^{(2)} = \hat{a}^+$,

for ν: $\hat{\eta}^{(1)} = \hat{a}^+$, $\hat{\eta}^{(2)} = \hat{a}$.

The complete Green's function matrix, (i.e., including the contribution of diagrams made of two disconnected parts) is, with obvious notations,

$$(G_1(1', 1))_{\mu\nu} = (\tilde{G}_1(1', 1))_{\mu\nu} + (G_{\frac{1}{2}}(1'))_\mu (G^*_{\frac{1}{2}}(1))_\nu$$

or

$$\mathbf{G}_1(1', 1) = \tilde{\mathbf{G}}_1(1', 1) + \mathbf{G}_{\frac{1}{2}}(1')\mathbf{G}^*_{\frac{1}{2}}(1).$$

Corresponding to the possibility of these nonvanishing values in the anomalous case, one must keep two arrows on the lines (propagators), one arrow for each of the two operators. Thus the average values occuring in (4.7) are respectively represented by the heavy double-arrowed lines

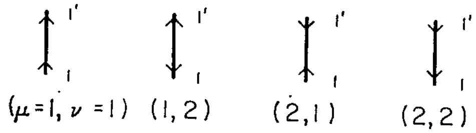


FIG. 2

The corresponding average values over the unperturbed ensemble would be represented by thin double-arrowed lines

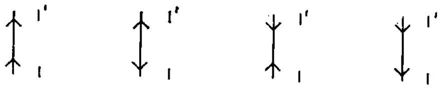


FIG. 3

To thin lines of the type (1, 2) or (2, 1) in a diagram, is of course associated a vanishing contribution, and to thin lines of the type (1, 1), (2, 2) an unperturbed propagator (rather its cumulant part $\tilde{G}_1^0$). The matrix form of this unperturbed propagator would be, e.g., for a translationally invariant system,

$$\tilde{\mathbf{G}}_1^0(1', 1) = \mathbf{G}_1^0(1', 1)$$
$$= \begin{pmatrix} [\beta\mathbf{k}_1^2 - \omega_1 - \beta\mu]^{-1} & 0 \\ 0 & [\beta(-\mathbf{k}_1)^2 + \omega_1 - \beta\mu]^{-1} \end{pmatrix} \delta_{1'1}.$$

Consider however, among all the 0 diagrams constructed with heavy half lines ($G_{\frac{1}{2}}$, $G^*_{\frac{1}{2}}$), 1 and 2 vertices joined by *all* the possible double-arrowed thin lines, the class of 1-irreducible 0 diagrams. It corresponds to a well defined functional of $(\tilde{G}_1^0)_{\mu\nu}$ [it is irrelevant for our purpose that the *actual value* of a large number of terms of that functional vanish with $(\tilde{G}_1^0)_{12}$ and $(\tilde{G}_1^0)_{21}$].

Let this functional be

$$\mathcal{K}^{(1)}\{\tilde{\mathbf{G}}_1^0\}.$$

Also the sum of all connected 1-irreducible 1 diagrams, classified according to the nature of their two external lines is given by

$$\sum_{2',2} \tilde{\mathbf{G}}_1^0(1', 2')\mathbf{K}_1^{(1)}\{2', 2; \tilde{\mathbf{G}}_1^0\}\tilde{\mathbf{G}}_1^0(2, 1),$$

where

$$[\delta/\delta\tilde{\mathbf{G}}_1^0(2', 2)]\mathcal{K}^{(1)}\{\tilde{\mathbf{G}}_1^0\} = \mathbf{K}_1^{(1)}\{2', 2; \tilde{G}_1^0\}, \tag{4.8}$$

the elements of the 2 × 2 matrix $(K_1^{(1)})_{\mu\nu}$ being thus obtained by functional derivation of $\mathcal{K}^{(1)}$ with respect to the matrix element $(\tilde{G}_1^0)_{\mu\nu}$.

The sum of all distinct, connected 1 diagrams is then generated by

(a) making in each internal (double-arrowed) line, the most general insertion, i.e., replacing the matrix elements of $\tilde{\mathbf{G}}_1^0$ by the corresponding elements of $\tilde{\mathbf{G}}_1$ in the arguments of $\mathbf{K}_1^{(1)}$;

(b) iterating this new mass operator $\mathbf{K}_1^{(1)}$ i.e., by writing a generalization of Belyaev's equation to nonzero temperature,

$$\tilde{\mathbf{G}}_1(1', 1) = \tilde{\mathbf{G}}_1^0(1', 1) + \sum_{2,2'} \tilde{\mathbf{G}}_1^0(1', 2')$$
$$\times \left[\begin{pmatrix} \beta u_1(\mathbf{k}_2) & 0 \\ 0 & \beta u_1(-\mathbf{k}_2) \end{pmatrix} \delta_{2'2} + \mathbf{K}_1^{(1)}\{2', 2; \tilde{\mathbf{G}}_1 G_{\frac{1}{2}}\} \right]$$
$$\times \tilde{\mathbf{G}}_1(2, 1). \tag{4.9}$$

This equation is readily solved for v_1 as a functional of $\tilde{\mathbf{G}}_1$ (and $\mathbf{G}_{\frac{1}{2}}$). In matrix form we have,

$$\begin{pmatrix} \beta v_1(\mathbf{k}_1) & 0 \\ 0 & \beta v_1(-\mathbf{k}_1) \end{pmatrix} \delta_{11'} = \begin{pmatrix} \omega_1 & 0 \\ 0 & -\omega_1 \end{pmatrix} \delta_{11'}$$
$$+ [\tilde{\mathbf{G}}_1(1', 1)]^{-1} + \mathbf{K}_1^{(1)}\{1', 1; \tilde{\mathbf{G}}_1\mathbf{G}_{\frac{1}{2}}\}. \tag{4.10}$$

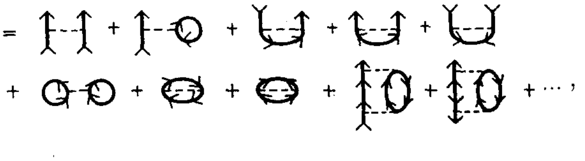
As in Sec. III and above, by direct integration or through the use of a topological relation, one obtains W in its stationary form:

$$W = \frac{1}{2}\operatorname{Tr}\left[\log(\tilde{\mathbf{G}}_1) + \begin{pmatrix}\omega_1+\beta v_1(\mathbf{k}_1) & 0\\ 0 & -\omega_1+\beta v_1(-\mathbf{k}_1)\end{pmatrix}[\tilde{\mathbf{G}}_1+\mathbf{G}_{\frac12}\mathbf{G}^*_{\frac12}]\right]$$

$$+\sum_{\mathbf{k}_1}[\beta v_{\frac12}(\mathbf{k}_1)G^*_{\frac12}(\mathbf{k}_1)+\beta v^*_{\frac12}(\mathbf{k}_1)G_{\frac12}(\mathbf{k}_1)]+\mathcal{K}^{(1)}\{\mathbf{G}_{\frac12},\tilde{\mathbf{G}}_1\}. \qquad (4.11)$$

Here

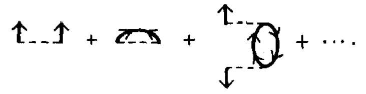
$$\mathcal{K}^{(1)}\{G_{1/2},\tilde{G}_1\} =$$



(4.12)

and, for example,

$$\left(K^{(1)}\{1',1;G_{1/2},\tilde{G}_1\}\right)_{1,2} =$$



(4.13)

The above equations display *explicitly*, the general terms of the expansions. Expression (4.11) for W is now stationary with respect *to variations of* $G_{\frac12}$, $G^*_{\frac12}$ *and* $(\tilde{G}_1)_{\mu\nu}$; the stationarity with respect to $\tilde{\mathbf{G}}_1$ implies Eq. (4.10) and with respect to $G^*_{\frac12}$, it implies a modified version of Eq. (3.7), namely

$$\beta v_{\frac12}(\mathbf{k}_1) = -\beta v_1(\mathbf{k}_1)G_{\frac12}(\mathbf{k}_1) + (\delta/\delta G^*_{\frac12})\mathcal{K}^{(1)}\{\mathbf{G}_{\frac12},\tilde{\mathbf{G}}_1\}. \qquad (4.14)$$

Again the quadratic form of the second variations has no definite sign.

Systematic matrix notations would simplify equation writing and diagram representation. We keep it here to a minimum to avoid introducing a machinery disproportionate to short exposé.

3. For the ensemble considered, $v_{\frac12}$ is eventually set equal to zero. Self-consistent approximations are generated by keeping only a certain class of terms in the functional $\mathcal{K}^{(1)}$, leading with Eqs. (4.10) and (4.14) to an approximate but self-consistent pair of coupled equations defining the approximations for $\mathbf{G}_{\frac12}$ and $\tilde{\mathbf{G}}_1$. Following the pioneer work of Bogoliubov[20] ($\beta = \infty$, small depletion), the first-order approximation has been studied particularly by Girardeau and Arnowitt[21] ($\beta = \infty$), and Tolmachev[22]; the second-order has been worked out in 1958 (for $\beta = \infty$) by Belyaev[19] and has been studied more generally by Martin and Hohenberg[23] using the generating equation method discussed at this conference by Paul Martin.

V. THE COMPLETE RECIPROCAL TRANSFORMATION (VERTEX-RENORMALIZATION)

Now we would like to perform the last steps of the reciprocal transformation, i.e., explicitly transform the functional dependence upon the 2 vertex (and the "effective" 3 vertices such as $v_2G_{\frac12}$) into a functional dependence upon the reciprocal functions; i.e., the average value of three operators $\mathbf{G}_{\frac32}$, and four operators $\mathbf{G}_2$. This operation leads eventually to an explicit expression of the entropy in terms of $\mathbf{G}_{\frac12}$, $\mathbf{G}_1$, $\mathbf{G}_{\frac32}$, $\mathbf{G}_2$ (or rather the corresponding cumulants) where there is no trace left of μ, β or $v_{\frac12}$, v_1, v_2. This functional is then *fourfold stationary* (with the appropriate constraints) under variations of $\mathbf{G}_{\frac12}$, $\mathbf{G}_1$, $\mathbf{G}_{\frac32}$, $\mathbf{G}_2$ leading to four coupled self-consistent equations to determine these functions (matrices). For clarity, we shall here consider only *normal* systems where the algebra is much simpler and leave the results pertinent to the anomalous systems for separate publication.

1. In normal systems the only further reciprocal quantity involved is the usual two body Green's function,

$$\langle T\hat{a}_{\mathbf{k}_1'}(w_1')\hat{a}_{\mathbf{k}_2'}(w_2')\hat{a}^+_{\mathbf{k}_1}(w_1)\hat{a}^+_{\mathbf{k}_2}(w_2)\rangle,$$

and its Fourier series transform $(G_2(1'2', 12)$ which is represented by the sum of all connected 2 diagrams with two incoming lines 1, 2 and two outgoing lines 1′, 2′. We separate diagrams made of two disconnected parts from the completely connected dia-

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[20] N. Bogolubov, J. Phys. Moscow **11**, 23 (1947).

[21] M. Girardeau and R. Arnowitt, Phys. Rev. **113**, 755 (1959).

[22] V. Tolmachev, Doklady **135**, 41, 825, (1960).

[23] P. Martin and P. Hohenberg, to be published; P. Hohenberg, Thesis, Harvard University, Cambridge, Massachusetts, 1962.

grams and we write (for the translationally invariant system)

$$G_2(1'2', 1\,2) = G_1(1)G_1(2)[\delta_{11'}\delta_{22'} + \delta_{12'}\delta_{21'}] + G_1(1')G_1(2')C_2(1'2', 1\,2)G_1(1)G_1(2). \qquad (5.1)$$

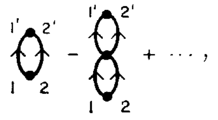
C_2 is a two particle correlation function and $G_1(1) = G_1(1,\ 1)$ the nonvanishing, diagonal part of the one-body Green's function. The analysis proceeds in very much the same way as in Sec. III and we shall just quote two results from reference 10 (Sec. II iii).

The inversion formula for the two-body potential becomes

$$\beta v_2(1'2', 1\,2) = -C_2(1'2', 1\,2) + L_2\{1'2', 1\,2; G_1, C_2\} + N_2\{1'2', 1\,2; G_1, C_2\} + K_2^{(2)}\{1'2', 1\,2; G_1C_2\}, \qquad (5.2)$$

where L_2 is represented by ladder 2 diagrams (with alternate sign):

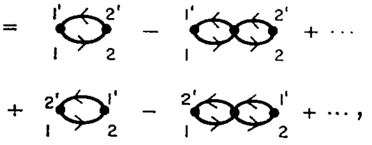
$L_2\{1', 2', 1, 2; G_1, C_2\} =$



(5.3)

N_2 by nodal (or ring) 2 diagrams (with alternate sign):

$N_2\{1', 2', 1, 2; G_1, C_2\} =$

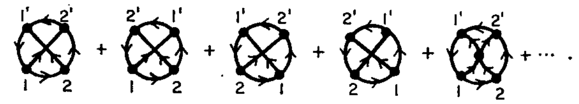


(5.4)

$K_2^{(2)}$ by 2-irreducible 2 diagrams:

$K_2^{(2)}\{1', 2', 1, 2; G_1, C_2\}$

$=$



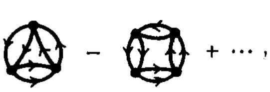
(5.5)

Finally, the entropy may be written

$$S = \sum_{1} [\log (G_1(1)) + \omega_1 G_1(1)] - \tfrac{1}{2} \sum_{1'2',12} [G_1(1')G_1(2')C_2(1'2', 1\,2)G_1(1)G_1(2)C_2(1\,2, 1'2')] + \mathcal{L}\{G_1, C_2\} + \mathfrak{N}\{G_1, C_2\} + \mathcal{K}^{(2)}\{G_1, C_2\}, \qquad (5.6)$$

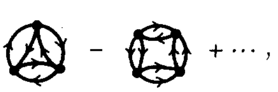
where

$\mathcal{L}\{G_1, C_2\} =$



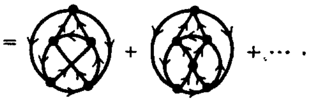
(5.7)

$\mathcal{N}\{G_1, C_2\} =$



(5.8)

$\mathcal{K}^{(2)}\{G_1, C_2\} =$



(5.9)

$\mathcal{K}^{(2)}$ represents the sum of all 2-irreducible[24] 0 diagrams, i.e., 0 diagrams which cannot be separated into two disconnected parts by cutting four lines (a single 2 vertex is not considered as a separate part).

These diagrams are calculated with a rule D differing from rule A through points (i), (ii)[25]

(Di) to each vertex, associate a matrix element of the correlation function C_2,

(Dii) to each line j, associate the one particle Green's function $G_1(j)$.

Clearly, L_2, N_2, $K_2^{(2)}$ are functional derivatives of $\mathcal{L}$, $\mathfrak{N}$, $\mathcal{K}^{(2)}$ with respect to C_2—more precisely,

$$G_1(1')G_1(2')L_2(1'2', 1\,2)G_1(1)G_1(2) = 4[\delta/\delta C_2(1'2', 1\,2)]\mathcal{L}\{G_1, C_2\}, \text{ etc } \cdots . \qquad (5.10)$$

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[24] Strictly speaking, a rigorous definition of 2 irreducibility requires a more detailed analysis of 0 diagrams. The definition given here will be complete if it is further required that the 2 diagram, obtained by cutting out a 2 vertex, is such that it cannot be separated into two pieces by cutting two more lines. Notice that the definition of 2-irreducible diagrams of reference 11 [Section II (ii)] is incorrect.

[25] Counting factors are also slightly different since we use now 2-vertices where exchange is not distinguished (C_2 is symmetrical under exchange of 1, 2, or 1′, 2′). Instead of the extra factor $\frac{1}{2}$ accompanying each ladder, one has now an extra factor $(2)^{-q}$ where q is the number of pairs of parallel lines in the diagram ($q = p - 1$ in L_2, $q = p$ in $\mathcal{L}$; $q = 0$ elsewhere, p is the order of the diagram).

Under the constraints of constant energy and particle number, S is stationary with respect to changes in C_2, implying Eq. (5.2). Stationarity with respect to changes in G_1 implies the first equation of the hierarchy of equations satisfied by Green's functions. Similarly, for anomalous systems, stationarity of the final form of the entropy with respect to $\mathbf{G}_{\frac{1}{2}}$ and $\tilde{\mathbf{G}}_1$ would lead to the first two equations of the corresponding hierarchy for anomalous systems.

2. A number of self-consistent approximations can be generated by truncating the functional form of the entropy. Thus, if besides the first line of Eq. (5.6) one keeps $\mathcal{L}$, $\mathfrak{N}$ or $\mathcal{L} + \mathfrak{N}$, one obtains self-consistent ladder, ring, or hypernetted approximations. A word of caution is perhaps necessary here concerning the approximations generated by truncation of the functionals. In these approximations the usual functional relations between successive Green's functions no longer hold exactly (i.e., relations between successive functional derivatives of W with respect to the potentials, remain only approximately true) and in cases where these functional relations are required to hold, a compromise between the self-consistent and the perturbative approach must be worked out.

Finally, before turning to classical systems, it may be remarked that anomalous Fermi systems, i.e., superfluid or superconducting Fermi systems, can be generally treated with the same method as used for anomalous Bose systems.

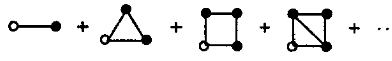
VI. CLASSICAL SYSTEMS

1. The same methods may be applied to classical systems. The first reciprocal transformation leads to the Yvon equation,[2,26]

$$\begin{aligned}\beta v_1(1) &= \beta \mathbf{p}_1^2 + \beta u_1(\mathbf{r}_1) - \beta\mu] \\ &= -\log \mu_1(1) + K_1^{(1)}\{1;\mu_1\}, \qquad (6.1)\end{aligned}$$

where the one-particle distribution function in configuration space is called[27] $\mu_1(\mathbf{r}_1, \mathbf{p}_1) = \mu_1(1)$. Diagram representations are in terms of *Yvon–Mayer ζ diagrams,* i.e., sets points, (ζ of which are fixed "external" points) connected by single lines. Thus the mass operator $K_1^{(1)}\{1;\mu_1\}$ is represented by all connected 1-irreducible 1 diagrams, (i.e., 1 diagrams such that by cutting one point, they cannot be separated into two disconnected parts),

$$K^{(1)}\{1;\mu_1\} =$$



(6.2)

The contributions associated with each 1 diagram are calculated with the set of rule $\mathcal{A}$:

(i) to each heavy black dot j, associate $\mu_1(j)$
(ii) to each line ij, associate $\exp[-\beta v_2(i, j)] - 1$
(iii) keep fixed the argument 1 of the white dot (external point); sum over the arguments j of the heavy black dot j (internal points) with a weight factor s^{-1}, where s is a symmetry number of the diagram.

Eqs. (6.1) and (6.2) were originally constructed, term by term, by Yvon, using a method parallel to the one described by Paul Martin for quantum systems. These equations were subsequently derived by several authors[8,10,28] using different methods.

2. The second reciprocal transformation leads to[29]

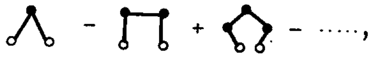
$$\begin{aligned}\beta v_2(1,2) &= -\log[1 + C_2(1,2)] \\ &\quad + N_2\{1,2;\mu_1,C_2\} + K_2^{(2)}\{1,2;\mu_1,C_2\}, \qquad (6.3)\end{aligned}$$

where C_2 is the correlation function related to the two-body distribution function $\mu_2(1, 2)$ by

$$\mu_2(1,2) = \mu_1(1)\mu_1(2)[1 + C_2(1,2)] \qquad (6.4)$$

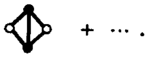
and

$$N_2\{1,2;\mu_1,C_2\} =$$



(6.5)

$$K_2^{(2)}\{1,2;\mu_1,C_2\} =$$



(6.6)

Finally, the entropy[10,11] is given by

$$\begin{aligned}S = \int d1\, \mu_1(1)(1 - \log \mu_1(1)) + \frac{1}{2}\int d1\, d2\, \mu_1(1)\mu_1(2) \\ \times [C_2(1,2) - (1 + C_2(1,2)) \log(1 + C_2(1,2))] \\ + \mathfrak{N}\{\mu_1, C_2\} + \mathfrak{K}^{(2)}\{\mu_1, C_2\}, \qquad (6.7)\end{aligned}$$

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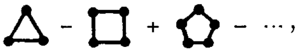
[26] See also J. Yvon, Cours de Mecanique Statistique, Saclay 1950.

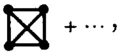
[27] Rather than G_1, to conform with notations of reference 12.

[28] F. Buff and F. Stillinger, J. Chem. Phys. 25, 312 (1956) (where a special system is studied), and to be published.

[29] Variants of Eq. (6.3) may be found in particular, in: J. Van Leuwen, J. Groeneveld, and J. de Boer, Physica 25, 792 (1959); E. Meeron, Phys. Fluids 1, 246 (1958), J. Math. Phys. 1, 192 (1960); M. S. Green, Hughes Aircraft Company Report (1959) (unpublished); T. Morita and K. Hiroike, Progr. Theoret. Phys. (Kyoto) 23, 1003 (1960). L. Verlet, Nuovo Cimento 18, 77 (1960). Early work in that direction may be found in J. Yvon, Rev. Sci. 662, (1939), Nuovo Cimento Suppl. 9, 144 (1958).

with

$\mathcal{N}\{\mu_1, C_2\} =$  (6.8)

$\mathcal{K}^{(2)}\{\mu_1, C_2\} =$  (6.9)

where $\mathfrak{N}$ is the sum of polygonal (also called nodal) diagrams with alternate signs, $\mathcal{K}^{(2)}$ the sum of 2-irreducible diagrams (diagrams which cannot be separated into two disconnected parts by cutting two points, a single line being not considered as a separate part). Such diagrams are calculated with a rule $\mathcal{B}$ differing from $\mathcal{A}$ through

($\mathcal{B}$ii) to each heavy line i, j associate $C_2(i, j)$ The quantities N_2 and $K_2^{(2)}$ occurring in Eq. (6.3) are clearly functional derivatives of $\mathfrak{N}$ and $\mathcal{K}^{(2)}$ respectively,

$$\mu_1(1)N_2(1, 2)\mu_1(2) = 2[\delta/\delta C_2(1, 2)]\mathfrak{N}\{\mu_1, C_2\}, \quad \text{etc} \cdots . \qquad (6.10)$$

Equations (6.3) and (6.4) are in close analogy with (5.2) and (5.6), the analog of the ladder term being contained in the log term of Eq. (5.6). Again self-consistent ladder, ring or hypernetted approximations may be generated by truncating the right-hand side of Eq. (6.3).

The entropy functional is stationary under constraints of constant energy and particle number with respect to changes of μ_1 and C_2, and the quadratic form of the second variations is negative definite. The variation with respect to C_2 leads to (6.1) but, contrary to the quantum-mechanical case, the variation with respect to μ_1 does not reproduce explicitly from the first equation of the Yvon hierarchy (i.e., the equilibrium limit of the B–B–K–Y hierarchy).

It appears plausible that, outside of and not too far from equilibrium, the functional form of S could be used as a generalized Boltzmann H function, a conjecture which becomes obvious for systems infinitesimally displaced from equilibrium. The case is not as clear for the functional derived for quantum systems since its second variation has no definite sign.

VII. CONCLUSION

We have expressed the thermodynamical functions, and the successive potentials in terms of distribution functions. This is carried out in an explicit way for quantum and classical systems, the expansions being given in terms of diagrams, simply characterized by their topological properties. We have carried out only the transformations necessary to eliminate the potentials assumed (v_1, v_2), and the one potential necessary to remove the degeneracies of anomalous systems ($v_{\frac{1}{2}}$). Clearly we could have introduced 3-body (or higher) potentials, allowing them to be eventually vanishing or nonvanishing. The thermodynamical functions would have become functionals of a 3-body distribution function and stationary with respect to changes of that extra function. Although there seems to be no apparent compelling reason to introduce such higher distribution functions, this procedure will probably be useful for treating in a fundamental and consistent way, the formation, dissociation, and interactions of few-particle bound states.

ACKNOWLEDGMENT

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The Master Equation with Special Transition Probabilities

E. VERBOVEN
*Studiecentrum voor Kernenergie, Mol, Belgium**
(Received 22 August 1962)

The Van Hove master equation to general order is solved, making a special ansatz for the function $W_{11'}(kk')$. Approximate solutions are found for strong and weak coupling. For $\lambda = 1$, a comparison is given with the exact numerical solution.

I. INTRODUCTION

THE purpose of this paper is to present a survey of recent work in the investigation of the evolution to quantum statistical equilibrium for special quantum systems, and some preliminary results of numerical work performed on a special model. The survey deals with articles of Van Hove,[1] Janner,[2] Van Hove and Verboven[3] and a forthcoming paper by Janner, Van Hove, and Verboven.[4]

In references 1 and 2, the general formalism is developed. In these papers it has been shown that for special classes of operators, certain quantum mechanical many-body systems reach microcanonical equilibrium. In reference 1 the random-phase assumption for the initial state was used. This assumption is dropped in reference 2 and the proof uses only the special properties of the interaction between the many degrees of freedom in large quantum systems. However, very little is known of how the equilibrium value for special observables is reached in the general coupling case. For weak coupling, the evolution is well known; it is given by the solution of the Pauli master equation and reveals an exponential tendency in the evolution to equilibrium. A first attempt to study this aspect of the problem for general coupling has been made in reference 3, where a highly simplified model was introduced and a rough investigation made of its time evolution for general coupling. In reference 4 a more accurate study of the behavior in time is given, which is valid for large values of the coupling. Because both references 3 and 4 give approximate results, there still remains a region of values for the coupling constant for which neither reference 3 nor 4 give satisfactory results. Therefore, an entirely numerical solution is proposed. Preliminary results of these calculations can be found in this survey. These results are preceded by a sketch of the general formalism and a short discussion of the simple model.

II. GENERAL EXPRESSION FOR THE DIAGONAL AND THE INTERFERENCE TERM

Here we recall briefly the derivation of an expression for the diagonal and the interference term of the probability density.[1,2] The Hamiltonian of the system is supposed to be the sum of two terms

$$H = H_0 + \lambda V, \tag{2.1}$$

with

$$H_0 \,|\alpha\rangle = \epsilon_\alpha \,|\alpha\rangle.$$

In the limit of an infinite system we adopt the normalization

$$\langle \alpha \mid \alpha' \rangle = \delta(\alpha - \alpha'). \tag{2.2}$$

Consider the wavefunction $|\varphi_0\rangle$ of the system at time $t = 0$:

$$|\,\varphi_0\rangle = \int |\,\alpha\rangle\, c(\alpha)\, d\alpha. \tag{2.3}$$

The evolution in time is given by

$$|\,\varphi_t\rangle = U_t \,|\,\varphi_0\rangle, \tag{2.4}$$

$$U_t = \exp\left[-i(H_0 + \lambda V)t\right]. \tag{2.5}$$

For an operator A diagonal in the $|\alpha\rangle$ representation we can consider

$$\langle \varphi_t \mid A \mid \varphi_t \rangle = \int A(\alpha_0) p_t(\alpha_0)\, d\alpha_0, \tag{2.6}$$

which introduces the probability density $p_t(\alpha_0)$ (course-grained because we suppose $A(\alpha)$ to be a smooth function of α). We can also write Eq. (2.6) in the form

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* Present address: Instituut voor theoretische fysica der Katholieke Universitat, Nijmegen, Netherlands.

[1] L. Van Hove, Physica **23**, 441 (1957).

[2] A. Janner, Helv. Phys. Acta. **35**, 47 (1962).

[3] L. Van Hove and E. Verboven, Physica **27**, 418 (1961).

[4] A. Janner, L. Van Hove, and E. Verboven, Physica (to be published).

$$\begin{aligned}\langle \varphi_t \mid A \mid \varphi_t\rangle &= \langle \varphi_0 \mid U_{-t} A U_t \mid \varphi_0\rangle \\ &= \int A(\alpha_0)\, d\alpha_0 \int P_t(\alpha_0\alpha)\, d\alpha\, |c(\alpha)|^2 \\ &\quad + \int A(\alpha_0)\, d\alpha_0 \int I_t(\alpha_0\alpha\alpha')\, d\alpha' c^*(\alpha) c(\alpha'), \qquad (2.7)\end{aligned}$$

where we have separated $U_t A U_t$ in its diagonal and nondiagonal part. Comparing Eqs. (2.7) and (2.6) we have

$$\begin{aligned}p_t(\alpha_0) &= \int P_t(\alpha_0\alpha)\, |c(\alpha)|^2\, d\alpha \\ &\quad + \int I_t(\alpha_0\alpha\alpha')\, d\alpha\, d\alpha' c^*(\alpha) c(\alpha'). \qquad (2.8)\end{aligned}$$

At this stage the "random phase assumption" is usually introduced, reducing Eq. (2.8) to

$$p_t(\alpha_0) = \int P_t(\alpha_0\alpha)\, d\alpha\, |c(\alpha)|^2. \qquad (2.9)$$

In reference 2 it has been shown that this assumption is unnecessary. $P_t(\alpha_0\alpha)$ and $I_t(\alpha_0\alpha\alpha')$ can be written in the form

$$\begin{aligned}P_t(\alpha_0\alpha) &= -\frac{1}{(2\pi)^2} \int_\gamma d\rho \int_{\gamma'} d\rho' \\ &\quad \times \exp\,[i(\rho - \rho')t] X_{\rho\rho'}(\alpha_0\alpha), \qquad (2.10)\end{aligned}$$

$$\begin{aligned}I_t(\alpha_0\alpha\alpha') &= -\frac{1}{(2\pi)^2} \int_\gamma d\rho \int_{\gamma'} d\rho' \\ &\quad \times \exp\,[i(\rho - \rho')t] Y_{\rho\rho'}(\alpha_0\alpha\alpha'), \qquad (2.11)\end{aligned}$$

γ being a counterclockwise contour around the real axis. $Y_{\rho\rho'}(\alpha_0\alpha)$ can be expressed by $X_{\rho\rho'}(\alpha_0\alpha)$ and another function $V_{\rho\rho'}(\alpha_0\alpha\alpha')$:

$$Y_{\rho\rho'}(\alpha_0\alpha\alpha') = \int d\alpha_1\, X_{\rho\rho'}(\alpha_0\alpha_1) V_{\rho\rho'}(\alpha_1\alpha\alpha'), \qquad (2.12)$$

where $V_{\rho\rho'}(\alpha_0\alpha\alpha')$ is defined from

$$\begin{aligned}&\langle \alpha \mid \{(1 - \lambda D_\rho V + \lambda^2 D_\rho V D_\rho V \cdots) \\ &\quad \times A(1 - \lambda V D_{\rho'} + \lambda^2 V D_{\rho'} V D_{\rho'} - \cdots)\}_{ind} \mid \alpha'\rangle \\ &= \int d\alpha_0\, A(\alpha_0) V_{\rho\rho'}(\alpha_0\alpha\alpha').\end{aligned}$$

From now on, we restrict our investigation to $P_t(\alpha_0\alpha)$. The extension to $I_t(\alpha_0\alpha\alpha')$ can be found in reference 4. $X_{\rho\rho'}(\alpha_0\alpha)$ can be expressed by irreducible diagonal parts, giving

$$\begin{aligned}X_{\rho\rho'}(\alpha_0\alpha) &= D_\rho(\alpha_0) D_{\rho'}(\alpha_0) \delta(\alpha_0 - \alpha) + \lambda^2 D_\rho(\alpha_0) D_{\rho'}(\alpha_0) \\ &\quad \times \Big[W_{\rho\rho'}(\alpha_0\alpha) + \lambda^2 \int d\alpha_1\, W_{\rho\rho'}(\alpha_0\alpha_1) D_\rho(\alpha_1) \\ &\quad \times D_{\rho'}(\alpha_1) W_{\rho\rho'}(\alpha_1\alpha) + \cdots \Big] D_\rho(\alpha) D_{\rho'}(\alpha). \qquad (2.13)\end{aligned}$$

The function $W_{\rho\rho'}(\alpha_0\alpha)$ occurring in Eq. (2.12), is defined by

$$\begin{aligned}&\{(V - \lambda V D_\rho V + \cdots) A (V - \lambda V D_{\rho'} V + \cdots)\}_{id} \mid \alpha\rangle \\ &\qquad = \mid \alpha\rangle \int d\alpha_0\, A(\alpha_0) W_{\rho\rho'}(\alpha_0\alpha), \qquad (2.14)\end{aligned}$$

and D_ρ is the diagonal part of the resolvent operator $R_\rho = [H_0 + \lambda V - \rho]^{-1}$. D_ρ is usually written in terms of another function,

$$D_\rho = (H_0 - \rho - \lambda^2 G_\rho)^{-1}; \qquad (2.15)$$

G_ρ obeys the equation

$$G_\rho = \{V D_\rho V - \lambda V D_\rho V D_\rho V + \cdots\}_{id}. \qquad (2.16)$$

Relation (2.10) can also be written

$$P_t(\alpha_0\alpha) = \int_{-\infty}^{\infty} dE\, P_{E,t}(\alpha_0\alpha);$$

$$P_{E,t}(\alpha_0\alpha) = \frac{s(t)}{2\pi^2} \int_\gamma d\rho\, \exp\,(2i\rho t) X_{E+\rho,E-\rho}(\alpha_0\alpha) \qquad (2.17)$$

$$[s(t) = |t|\, t^{-1}].$$

In reference 1, a generalized master equation for $P_{E,t}(\alpha_0\alpha)$ has been derived. In reference 2 the same has been done for the interference term, using essentially Eq. (2.12).

An important relation between $G_\rho(\alpha)$ and $W_{\rho\rho'}(\alpha_0\alpha)$ is given by

$$\begin{aligned}&\lambda^2 G_\rho(\alpha) - \lambda^2 G_{\rho'}(\alpha) \\ &\quad = \lambda^2 \int d\alpha_0\, [D_\rho(\alpha_0) - D_{\rho'}(\alpha_0)] W_{\rho\rho'}(\alpha_0\alpha), \qquad (2.18)\end{aligned}$$

which is easily obtained from Eq. (2.15).

III. SIMPLE MODEL

In this section we apply the general theory to a simple situation: an electron in a system of randomly distributed, static, elastic scattering centers. The quantum numbers α are simply given by the three components of the wave vector $\mathbf{k}$ of the electron (the spin is neglected).

We make for the basic function $W_{\rho\rho'}(\mathbf{k}_0\mathbf{k})$ a very simple ansatz

$$W_{\rho\rho'}(\mathbf{k}_0\mathbf{k}) = \begin{cases} W & \text{for } |\mathbf{k}_0| \text{ and } |\mathbf{k}| \le a \\ 0 & \text{for } |\mathbf{k}_0| \text{ or } |\mathbf{k}| > a, \end{cases} \qquad (3.1)$$

with a and W given positive constants. This ansatz simplifies $X_{\rho\rho'}(\mathbf{k}_0\mathbf{k})$ extensively. Indeed, the series (2.12) can be summed giving

$$X_{\rho\rho'}(\mathbf{k}_0\mathbf{k}) = D_\rho(\mathbf{k}_0)D_{\rho'}(\mathbf{k})\,\delta(\mathbf{k}_0 - \mathbf{k}) + \lambda^2 W D_\rho(\mathbf{k}_0)D_{\rho'}(\mathbf{k}_0)D_\rho(\mathbf{k})D_{\rho'}(\mathbf{k}) \times \left[1 - \lambda^2 W \int dk_1\, D_\rho(k_1)D_{\rho'}(k_1)\right]^{-1}. \quad (3.2)$$

We remark that from now on all vectors are restricted to a sphere of radius a, which is also the integration range.

Using Eq. (2.17) and the ansatz (3.1) we obtain

$$G_\rho(\mathbf{k}) - G_{\rho'}(\mathbf{k}) = W\int d\mathbf{k}_0\,[D_\rho(\mathbf{k}_0) - D_{\rho'}(\mathbf{k}_0)]. \quad (3.3)$$

In the limit $\rho' \to \infty$ we find

$$G_\rho(\mathbf{k}) = W\int d\mathbf{k}_0\, D_\rho(\mathbf{k}_0) = g_\rho \quad (3.4)$$

such that $D_\rho(\mathbf{k})$ becomes in our model

$$D_\rho(\mathbf{k}) = (\epsilon_k - \rho - \lambda^2 g_\rho)^{-1}, \quad (3.5)$$

ϵ_k being the unperturbed electron energy (we put $2m = 1$, m being the electron mass). Substitution of Eq. (3.5) in Eq. (3.4) gives a transcendental equation for g_ρ:

$$g_\rho = 4\pi N\int_0^a d\mathbf{k}_0\, k_0^2(\epsilon_{k_0} - \rho - \lambda^2 g_\rho)^{-1}. \quad (3.6)$$

Using the relation

$$D_\rho(\mathbf{k}_0)D_{\rho'}(\mathbf{k}_0) = (\rho + \lambda^2 g_\rho - \rho' - \lambda^2 g_{\rho'})^{-1} \times [D_\rho(\mathbf{k}_0) - D_{\rho'}(\mathbf{k}_0)], \quad (3.7)$$

we obtain for $X_{\rho\rho'}(\mathbf{k}_0\mathbf{k})$ the simple expression

$$X_{\rho\rho'}(\mathbf{k}_0\mathbf{k}) = D_\rho(\mathbf{k}_0)D_{\rho'}(\mathbf{k}_0) \times \{\delta(\mathbf{k}_0 - \mathbf{k}) + [\lambda^2 W/(\rho - \rho')][D_\rho(\mathbf{k}) - D_{\rho'}(\mathbf{k})]\}. \quad (3.8)$$

Applying Eq. (2.16) we obtain the partial transition probability $P_{E,t}(\mathbf{k}_0\mathbf{k})$ to general order. For $t > 0$, this formula becomes

$$P_{E,t}(\mathbf{k}_0\mathbf{k}) = \frac{1}{2\pi^2}\int_\gamma d\rho \exp(2i\rho t)D_{E+\rho}(\mathbf{k}_0)D_{E-\rho}(\mathbf{k}_0) \times \left\{\delta(\mathbf{k}_0 - \mathbf{k}) + \frac{\lambda^2 W}{2\rho}[D_{E+\rho}(\mathbf{k}_1) - D_{E-\rho}(\mathbf{k}_0)]\right\}. \quad (3.9)$$

The asymptotic value of this expression at $t = +\infty$ is immediately obtained as the residue of the pole at $\rho = 0$. It is

$$P_{E,\infty}(\mathbf{k}_0\mathbf{k}) = \frac{iW}{2\pi}\,\frac{D_{E-i0}(\mathbf{k}_0) - D_{E+i0}(\mathbf{k}_0)}{g_{E-i0} - g_{E+i0}} \times [D_{E-i0}(\mathbf{k}) - D_{E+i0}(\mathbf{k})]. \quad (3.10)$$

Using Eq. (3.3) and the definition

$$\Delta_E(\mathbf{k}) = \frac{1}{2\pi i}[D_{E+i0}(\mathbf{k}) - D_{E-i0}(\mathbf{k})],$$

this expression can be written

$$P_{E,\infty}(\mathbf{k}_0\mathbf{k}) = \left[\int \Delta_E(\mathbf{k}')\,d\mathbf{k}'\right]^{-1}\Delta_E(\mathbf{k}_0)\Delta_E(\mathbf{k}), \quad (3.11)$$

in agreement with the corresponding result of the general theory [Eqs. (7.6) and (7.7) of reference 1].

IV. TIME VARIATION OF $P_t(\mathbf{k}_0\mathbf{k})$

To study the behavior of $P_{E,t}(\mathbf{k}_0\mathbf{k})$ and $P_t(\mathbf{k}_0\mathbf{k})$ for all times, one needs an explicit expression of g_ρ which would require solving the transcendental equation (3.6).

In reference 3 this was avoided and replaced by an (incomplete) investigation of the general behavior of g_ρ in the complex ρ plane. By so doing it was found that $D_\rho(\mathbf{k})$ has a pole in its analytic continuation in the second sheet of the complex ρ plane. The pole is given by

$$p_k = k^2 - 4\pi W\lambda^2 a + 2\pi\lambda^2 Wk \ln[(a + k)/(a - k)] + 2\pi^2 i\lambda^2 Wk \quad (4.1)$$
$$= \bar{\epsilon}_k + i\gamma_k,$$

where $\bar{\epsilon}_k$ is the real part and γ_k the imaginary part of $p_k (\gamma_k > 0)$. $P_{E,t}(\mathbf{k}_0\mathbf{k})$ is then evaluated by contour deformation. Taking only the contribution of the pole, and simplifying the residue to one, the following result for $P_{E,t}(\mathbf{k}_0\mathbf{k})$ has been obtained in reference 3:

$$P_{E,t}(\mathbf{k}_0\mathbf{k}) - P_{E,\infty}(\mathbf{k}_0\mathbf{k}) = -\frac{i}{\pi}\,\frac{\exp[2it(\bar{\epsilon}_{k_0} - E + i\gamma_{k_0})]}{2(\bar{\epsilon}_{k_0} - E)}$$
$$\times \{\delta(\mathbf{k}_0 - \mathbf{k}) + \lambda^2 W[2(\bar{\epsilon}_{k_0} - E + i\gamma_{k_0})]^{-1}[\bar{\epsilon}_k - \bar{\epsilon}_{k_0} - i\gamma_{k_0} + i\gamma_k)^{-1} - (\bar{\epsilon}_k + \bar{\epsilon}_{k_0} - 2E + i\gamma_{k_0} - i\gamma_k)^{-1}]\}$$
$$+ i/\pi \exp[2it(E - \bar{\epsilon}_{k_0} + i\gamma_{k_0})][2(\bar{\epsilon}_{k_0} - E)]^{-1}$$

$$\times\ \{\delta(\mathbf{k}_0-\mathbf{k})+\lambda^2W[2(E-\epsilon_{k_0}+i\gamma_{k_0})]^{-1}[(\bar{\epsilon}_k+\bar{\epsilon}_{k_0}-2E-i\gamma_{k_0}+i\gamma_k)^{-1}-(\bar{\epsilon}_k-\bar{\epsilon}_{k_0}+i\gamma_{k_0}-i\gamma_k)^{-1}]\}$$
$$-(i\lambda^2W/2\pi)\exp[2it(\bar{\epsilon}_k-E+i\gamma_k)][(\bar{\epsilon}_{k_0}-\bar{\epsilon}_k-i\gamma_k+i\gamma_k)(\bar{\epsilon}_{k_0}+\bar{\epsilon}_k-2E+i\gamma_k-i\gamma_{k_0})(\epsilon_k-E+i\gamma_k)]^{-1}$$
$$-(i\lambda^2W/2\pi)\exp[2it(E-\bar{\epsilon}_k+i\gamma_k)]$$
$$\times\ [\bar{\epsilon}_{k_0}+\bar{\epsilon}_k-2E-i\gamma_k+i\gamma_{k_0})(\bar{\epsilon}_{k_0}-\bar{\epsilon}_k+i\gamma_k-i\gamma_{k_0})(E-\bar{\epsilon}_k+i\gamma_k)]^{-1}. \tag{4.2}$$

The integration over E may be carried out, giving for $P_t(\mathbf{k}_0\mathbf{k})$:

$$P_t(\mathbf{k}_0\mathbf{k})-P_\infty(\mathbf{k}_0\mathbf{k})=\exp(-2\gamma_kt)\delta(\mathbf{k}_0-\mathbf{k})$$
$$-2\lambda^2W\exp[-(\gamma_{k_0}+\gamma_k)t]\{[(\bar{\epsilon}_{k_0}-\bar{\epsilon}_k)^2+(\gamma_{k_0}-\gamma_k)^2][(\bar{\epsilon}_{k_0}-\bar{\epsilon}_k)^2+(\gamma_{k_0}+\gamma_k)^2]\}^{-1}$$
$$\times\ \{[(\bar{\epsilon}_{k_0}-\bar{\epsilon}_k)^2+(\gamma_{k_0}^2-\gamma_k^2)]\cos[(\bar{\epsilon}_{k_0}-\epsilon_k)t]+2\gamma_k(\bar{\epsilon}_{k_0}-\bar{\epsilon}_k)\sin[(\bar{\epsilon}_{k_0}-\bar{\epsilon}_k)t]\}$$
$$+(\lambda^2W/\gamma_{k_0})\exp(-2\gamma_{k_0}t)(\gamma_{k_0}-\gamma_k)[(\bar{\epsilon}_{k_0}-\bar{\epsilon}_k)^2+(\gamma_{k_0}-\gamma_k)^2]^{-1}. \tag{4.3}$$

In the limit of weak coupling for t of order λ^{-2}, Eq. (4.3) becomes

$$P_t(\mathbf{k}_0\mathbf{k})-P_\infty(\mathbf{k}_0\mathbf{k})=\exp(-2\gamma_{k_0}t)\delta(\mathbf{k}_0-\mathbf{k})$$
$$-(\pi\lambda^2W/\gamma_k)\exp(-2\gamma_{k_0}t)\delta(\epsilon_{k_0}-\epsilon_k), \tag{4.4}$$

which is a solution of the Pauli master equation in the simple situation treated here.

From the value of the residue

$$N_k^{-1}=[1+\lambda^2(dg\rho/d\rho)]_{\rho=p_k}, \tag{4.5}$$

it is seen that the coupling may not become too large for the validity of the approximation.

Therefore in reference 4 another approximation was proposed, valid for large values of λ. If λ is very large it is shown in reference 4 that g_ρ for ρ real, takes the form

$$g_\rho=(1/2\lambda^2)g\rho$$

$$\gamma_\rho=\begin{cases}-\rho+i(A^2-\rho^2)^{\frac{1}{2}}\text{ for }\rho=\operatorname{Re}\rho+i0,\\ \qquad\qquad -A\leq\operatorname{Re}\rho\leq A\\ -\rho-i(A^2-\rho^2)^{\frac{1}{2}}\text{ for }\rho=\operatorname{Re}\rho-i0,\\ \qquad\qquad -A\leq\operatorname{Re}\rho\leq A,\end{cases} \tag{4.6a}$$

and

$$\gamma_\rho=\begin{cases}-\rho+(\rho^2-A^2)^{\frac{1}{2}}\text{ for }\rho=\operatorname{Re}\rho\pm i0\\ \qquad\qquad \operatorname{Re}\rho\geq A\\ -\rho-(\rho^2-A^2)^{\frac{1}{2}}\text{ for }\rho=\operatorname{Re}\rho\pm i0\\ \qquad\qquad \operatorname{Re}\rho\geq A,\end{cases} \tag{4.6b}$$

$$A=(16\pi Wa^3\lambda^2/3)^{\frac{1}{2}}. \tag{4.7}$$

The strong coupling condition is given by

$$\lambda^2\gg 3a/4\pi W. \tag{4.8}$$

Under this condition D_ρ becomes independent of $\mathbf{k}$ and hence

$$D_\rho=(4\lambda^2/A^2)g_\rho=(2/A^2)\gamma_\rho. \tag{4.9}$$

In this approximation we may evaluate the coefficient of the $\delta(\mathbf{k}_0-\mathbf{k})$ function in $P_{E,t}(\mathbf{k}_0\mathbf{k})$ for $E=0$. It is

$$(2/\pi A)J_1(2tA)+(2/\pi A)J_3(2tA), \tag{4.10}$$

showing, as found before, an oscillatory behavior in time. The decrease with time is however much

TABLE I. ρ integrations.

$\tau=2At$	$P(t)$	Precision
0	1.000000	10^{-8}
0.5	0.984474	10^{-8}
1	0.939105	10^{-7}
1.5	0.967349	10^{-8}
2	0.774577	10^{-8}
2.5	0.667485	10^{-8}
3	0.553409	10^{-8}
3.5	0.439616	10^{-8}
4	0.332611	10^{-8}
4.5	0.237604	10^{-8}
5	0.158146	10^{-7}
5.5	0.095974	10^{-8}
6	0.051093	10^{-8}
6.5	0.022017	10^{-8}
7	0.006162	10^{-8}
7.5	0.000314	10^{-8}
8	0.001090	10^{-8}
8.5	0.005358	10^{-8}
9	0.010546	10^{-8}
9.5	0.014826	10^{-5}
10	0.017169	10^{-8}
10.5	0.017274	10^{-8}
11	0.015415	10^{-8}
11.5	0.012230	10^{-7}
12	0.008505	10^{-8}
12.5	0.004988	10^{-8}
13	0.002240	10^{-8}
13.5	0.000566	10^{-8}
14	0.000001	10^{-8}
14.5	0.000357	10^{-8}
15	0.001300	10^{-8}
15.5	0.002444	10^{-8}

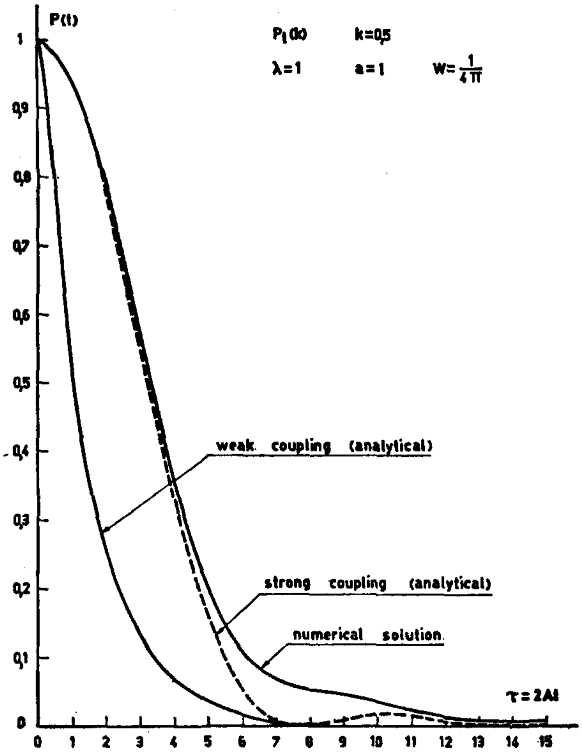

FIG. 1

slower than was found in the previous treatment; the function (4.10) decays as $t^{-\frac{1}{2}}$, whereas in the pole treatment we found an exponential decay. The strong coupling limit of $P_t(\mathbf{k}_0\mathbf{k})$ may be written as

$$P_t(\mathbf{k}_0\mathbf{k}) = \delta(\mathbf{k}_0 - \mathbf{k})P(t) + P_1(t), \tag{4.11}$$

with

$$P(t) = \frac{s(t)}{2\pi^2} \int_{-\infty}^{\infty} dE \int_\gamma d\rho \exp(2i\rho t) D_{E+\rho} D_{E-\rho}, \tag{4.12}$$

$$P_1(t) = \frac{s(t)}{2\pi^2} \lambda^2 W \int_{-\infty}^{\infty} dE \int_\gamma d\rho$$
$$\times \exp(2i\rho t) \frac{1}{\rho} D^2_{E+\rho} D_{E-\rho}. \tag{4.13}$$

The unitarity condition

$$\int d\mathbf{k}_0 \, P_t(\mathbf{k}_0\mathbf{k}) = 1 \tag{4.14}$$

requires

$$(4\pi a^3/3)[P_1(t)] + P(t) = 1. \tag{4.15}$$

This implies that $P_t(\mathbf{k}_0\mathbf{k})$ can be expressed by $P(t)$:

$$P_t(\mathbf{k}_0\mathbf{k}) = 3/4\pi a^3 + \{\delta(\mathbf{k}_0 - \mathbf{k}) - 3/4\pi a^3\}P(t). \tag{4.16}$$

In reference 4, the following expression was found for $P(t)$:

$$\begin{aligned} P(t) = -\frac{32}{3\pi^2} \Big\{ &\int_0^1 d\rho \sin 2A\rho t[(\rho^2 - 1)K(\rho) \\ &+ (\rho^2 + 1)E(\rho) - \tfrac{3}{4}\pi\rho] \\ &+ \int_1^\infty d\rho \sin 2A\rho t - \rho\Big[(1 - \rho^2)K\Big(\frac{1}{\rho}\Big) \\ &+ (1 + \rho^2)E\Big(\frac{1}{\rho}\Big) - \tfrac{3}{4}\pi\Big] \\ &+ \int_0^1 d\rho \cos 2A\rho t(1 + \rho)\Big[2\rho K\Big(\frac{1-\rho}{1+\rho}\Big) \\ &- (1 + \rho^2)E\Big(\frac{1-\rho}{1+\rho}\Big)\Big]\Big\}. \end{aligned} \tag{4.17}$$

In this formula $K(\rho)$ and $E(\rho)$ are the Legendre complete elliptic integrals of first and second kind defined by

$$\begin{aligned} K(k) &= \int_0^1 \frac{dx}{[(1 - x^2)(1 - k^2x^2)]^{\frac{1}{2}}} \\ &= \int_0^{\pi/2} \frac{d\rho}{[1 - k^2 \sin^2 \rho]^{\frac{1}{2}}}, \end{aligned} \tag{4.18}$$

$$\begin{aligned} E(k) &= \int_0^1 dx \left[\frac{1 - k^2x^2}{1 - x^2}\right]^{\frac{1}{2}} \\ &= \int_0^{\pi/2} d\varphi\, [1 - k^2 \sin^2 \rho]^{\frac{1}{2}}. \end{aligned} \tag{4.19}$$

In the evaluation of $P(t)$, use has been made of Gröbner and Hofreiter.[5]

The ρ integrations in Eq. (4.17) have been performed by computer. The results are collected in Table I.

In Fig. 1 we plot the results for the coefficient of the delta function in $P_t(\mathbf{k}_0\mathbf{k})$.

The lowest curve gives this coefficient for $k = 0.5$ $\lambda = 1$, $a = 1$, $W = 1/4\pi$ in the pole approximation, and, one observes a rapid exponential decay. The dashed curve is the strong coupling approximation $P(t)$, which coincides for small time values with the exact numerical solution. For larger time values, the strong coupling approximation exhibits small oscillations not present in the analytical solution.

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[5] W. Gröbner and N. Hofreiter, *Integraltafeln.* II (Springer-Verlag, Wien, 1950), p. 223, (5a), (5c), (5g), (6a), (6c), and (6g).

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Asymptotic Form of the Structure Function for Real Systems

P. MAZUR AND J. VAN DER LINDEN
Lorentz Institute of Theoretical Physics, University of Leiden, Leiden, Netherlands
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It is shown that the asymptotic formula for the structure function obtained by Khinchin for the case of a system of n noninteracting components, also holds for a classical system of N interacting particles. It is essential for the derivation that the interactions be such that the system behaves in the limit as N tends to infinity, as a thermodynamic system.

I. INTRODUCTION

In his monograph on the mathematical foundations of statistical mechanics, Khinchin[1] has shown that the structure function for a system consisting of a large number of noninteracting components has asymptotically a very simple form: it becomes proportional to the product of an exponential and a Gaussian. With the help of this asymptotic form it is possible to demonstrate the equivalence of the canonical and the microcanonical ensemble. Although Khinchin states specifically that the components of a system considered by him are only approximately energetically isolated components, and "that it is precisely their presence (of interaction terms) that assures the possibility of an exchange of energy between the particles on which is based the whole method of the statistical mechanics", he entirely neglects these interactions in the mathematical analysis leading to the asymptotic formula for the structure function, on the grounds that such interaction terms in the expression for the energy are, in the great majority of points in phase space, negligible as compared with the energy of the components. It is however well known that "small" interaction terms may give rise to large effects (e.g. phase transitions). In this paper we wish to establish the asymptotic form of the structure function of a real system without neglecting the interactions between its constituting particles.

II. FORMAL PROPERTIES OF THE STRUCTURE FUNCTION AND THE GENERATING FUNCTION

We consider a classical system consisting of N identical particles of mass m, confined in a volume V and having coordinates $\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N$ and momenta $\mathbf{p}_1, \mathbf{p}_2, \cdots, \mathbf{p}_N$. The Hamiltonian of the system is given by

$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}^N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j=1}^{N} u(|\mathbf{r}_i - \mathbf{r}_j|). \tag{1}$$

Here $\mathbf{r}^N$ and $\mathbf{p}^N$ denote the sets of all coordinates and momenta respectively, $U(\mathbf{r}^N)$ is the total potential energy of interaction and $u(|\mathbf{r}_i - \mathbf{r}_j|)$ the pair interaction energy between particles i and j.

The structure function of the system (or normalizing factor of the microcanonical ensemble) is defined as

$$\Omega_N(E) = \frac{1}{h^{3N} N!} \iint d\mathbf{r}^N \, d\mathbf{p}^N \, \delta[H(\mathbf{r}^N, \mathbf{p}^N) - E], \tag{2}$$

where h is Planck's constant. The integration over coordinates is confined to the volume V of the system. The physical systems under consideration are such that the potential energy $U(\mathbf{r}^N)$ has a finite minimum $E_N^{(0)}$. It then follows from (1) and (2) that

$$\Omega_N(E) \begin{cases} = 0 & \text{if } E \leq E_N^{(0)}, \\ > 0 & \text{if } E > E_N^{(0)}. \end{cases} \tag{3}$$

Let us now define the Laplace transform $\Phi_N(\alpha)$ of the structure function, or generating function of the system

$$\Phi_N(\alpha) = \int_{-\infty}^{+\infty} e^{-\alpha E} \Omega_N(E) \, dE. \tag{4}$$

We require this integral to converge for any α such that $0 < \alpha < \infty$. [In other words we require that $\Omega_N(E)$ does not increase too fast as $E \to \infty$.] Therefore also in view of conditions (3),

$$0 < \Phi_N(\alpha) < \infty \quad \text{for} \quad 0 < \alpha < \infty. \tag{5}$$

This condition is satisfied in all actual physical systems. With the definition (2) the integral (4) may

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[1] A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (Dover Publications, Inc., New York, 1949).

also be written as

$$\Phi_N(\alpha) = \frac{1}{h^{3N}N!}\iint d\mathbf{r}^N\, d\mathbf{p}^N \exp\,[-\alpha H(\mathbf{r}^N, \mathbf{p}^N)]. \tag{6}$$

(The function $\Phi_N(\alpha)$ is identical with the partition function of the system if α is replaced by $1/kT$, where k is Boltzmann's constant and T the absolute temperature). Let us also consider the first and second logarithmic derivatives of $\Phi_N(\alpha)$. We have [cf. Eq. (4)],

$$\frac{d \log \Phi_N(\alpha)}{d\alpha} = -\frac{1}{\Phi_N(\alpha)}\int_{-\infty}^{+\infty} Ee^{-\alpha E}\,\Omega_N(E)\,dE \equiv -A_N(\alpha), \tag{7}$$

$$\frac{d^2 \log \Phi_N(\alpha)}{d\alpha^2} = \frac{1}{\Phi_N(\alpha)} \times \int_{-\infty}^{+\infty} \{E - A_N(\alpha)\}^2 e^{-\alpha E}\,\Omega_N(E)\,dE \equiv B_N(\alpha). \tag{8}$$

In view of conditions (3) and (5),

$$\left.\begin{aligned} E_N^{(0)} < A_N(\alpha) < \infty \\ 0 < B_N(\alpha) < \infty \end{aligned}\right\} \text{ for } 0 < \alpha < \infty. \tag{9}$$

In fact it can be shown[1] that the generating function $\Phi_N(\alpha)$ has logarithmic derivatives of all orders.

Let us now extend the definition of $\Phi_N(\alpha)$ to complex values s of the argument,

$$\Phi_N(s) = \int_{-\infty}^{+\infty} e^{-sE}\,\Omega_N(E)\,dE, \tag{10}$$

or, with (2),

$$\Phi_N(s) = \frac{1}{h^{3N}N!}\iint d\mathbf{r}^N\, d\mathbf{p}^N \exp\,[-sH(\mathbf{r}^N, \mathbf{p}^N)]. \tag{11}$$

It follows from (10) or (11) that

$$|\Phi_N(s)| \leq \Phi_N\,(\mathrm{Re}\, s), \tag{12}$$

and thus together with condition (5), that

$$|\Phi_N(s)| < \infty \quad \text{for} \quad 0 < \mathrm{Re}\, s < \infty. \tag{13}$$

The integrals (10) and (11) therefore converge for $0 < \mathrm{Re}\ s < \infty$. On the other hand one finds from expressions (11) and (1) that

$$\Phi_N(s) = \left(\frac{2\pi m}{h^2 s}\right)^{\frac{3}{2}N} Q_N(s), \tag{14}$$

with

$$Q_N(s) = \frac{1}{N!}\int d\mathbf{r}^N \exp\,[-sU(\mathbf{r}^N)]. \tag{15}$$

(For real values $\alpha = 1/kT$ of the argument the function $Q_N(s)$ is identical with the configurational integral of the system). Again it follows from (15) that

$$|Q_N(s)| \leq Q_N\,(\mathrm{Re}\, s), \tag{16}$$

and in combination with (14),

$$|\Phi_N(s)| \leq \left|\frac{\mathrm{Re}\, s}{s}\right| \tfrac{3}{2}N\ \Phi_N\,(\mathrm{Re}\, s), \tag{17}$$

which is stronger than the previously obtained condition (12).

III. ASYMPTOTIC PROPERTIES OF THE GENERATING FUNCTION

Let us now consider the function

$$\varphi_N(s) = \frac{1}{N}\log \Phi_N(s). \tag{18}$$

According to expression (14) one has

$$\varphi_N(s) = \tfrac{3}{2}\log\,(h^2 s/2\pi m) + f_N(s), \tag{19}$$

where

$$f_N(s) = \frac{1}{N}\log Q_N(s). \tag{20}$$

Now Van Hove[2] has shown that for particles with a hard-core and short-range interaction and for $s = \alpha$ (real and positive), the function (20) has a finite limit as $N \to \infty$, $V \to \infty$ and $V/N = v$ is kept constant,

$$\lim_{N\to\infty} f_N(\alpha) = f(\alpha), \qquad 0 < \alpha < \infty. \tag{21}$$

[In Eq. (21), $f_N(\alpha)$, and $f(\alpha)$ are considered as functions of α and of the specific volume v.] As a consequence of (21) and (19), the function $\varphi_N(\alpha)$ also possesses a finite limit as N tends to infinity and V/N is kept constant. (The existence of this limit implies, according to statistical thermodynamics, the existence of a free energy per particle in an infinitely large real system.)

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[2] L. Van Hove, Physica 15, 951 (1949). A proof of (21), under very general conditions has recently been given by D. Ruelle and independently by M. E. Fisher (to be published). This proof does not seem to suffer from the difficulties encountered in Van Hove's demonstration.

In the remainder of this section we shall investigate whether all derivatives of the function $f_N(\alpha)$, and thus of $\varphi_N(\alpha)$, also have finite limits as N tends to infinity. To this end we shall consider a system with the following potential of pair interaction $u(r)$, r being the distance between a pair of particles:

$$u(r)\begin{cases} = \infty & \text{if } 0 \leq r < a, \\ = -\epsilon,\ (\epsilon > 0), & \text{if } a \leq r < b, \\ = 0 & \text{if } b \leq r < \infty. \end{cases} \tag{22}$$

This so-called Herzfeld potential, is of course highly unrealistic. The discussion in this section may however be generalized in a straightforward way to potentials $u(r)$ such that $u(r) = \infty$ for $r \leq a$ and $u(r) = 0$ for $r > b$, while for $a < r \leq b$, the curve of $u(r)$ consists of a finite number of upward or downward steps of height ϵ and may be either positive or negative. One can thus obtain a fairly good model to a realistic pair potential, approximating the true potential curve by a large enough number of these finite steps. Note however that the potential function (22) has all the characteristic properties of any realistic potential function $u(r)$: it becomes infinite (strongly repulsive) as r tends to zero, it has a negative (attractive) tail, and it tends to zero "sufficiently fast" (short range) as r tends to infinity.

With (22), the function (15) for $s = \alpha$ (real and positive) becomes

$$Q_N(\alpha) = \frac{1}{N!}\int d\mathbf{r}^N \prod_{i<j=1}^{N} \sigma[|\mathbf{r}_i - \mathbf{r}_j| - a] \times \exp\,[n(\mathbf{r}^N)\alpha\epsilon]. \tag{23}$$

Here $\sigma(r)$ is the unit stepfunction; due to the occurrence of the product of these in the integral (23), the contributions of configurations, with one or more interparticle distances smaller than a, vanish, and $n(\mathbf{r}^N)$ is the number of pairs of particles which, in a given configuration with nonvanishing contribution to the integral (23), have distances lying between a and b. Due to the hard cores of the particles, [the presence of the σ functions in (23)], the integral (23) will vanish whenever more than a finite number m of particles lie within the range of attraction of any particular particle. We therefore obtain the following upper bound to the maximum M_N of $n(\mathbf{r}^N)$,

$$n(\mathbf{r}^N) \leq M_N < \tfrac{1}{2}Nm. \tag{24}$$

We now introduce the new variable defined by

$$x = e^{\alpha\epsilon}. \tag{25}$$

The integral (23), (in fact a sum of exponential terms), then becomes a polynomial in x;

$$Q_N^*(x) = \sum_{n=0}^{M_N} \omega_{n,N} x^n, \tag{26}$$

with coefficients

$$\omega_{n,N} = \frac{1}{N!}\int_{n(\mathbf{r}^N)=n} d\mathbf{r}^N \prod_{i<j=1}^{N} \sigma[|\mathbf{r}_i - \mathbf{r}_j| - a]. \tag{27}$$

The integration at the right-hand side must be performed over that part of phase space for which $n(\mathbf{r}^N)$ is equal to the integer n. Since the coefficients $\omega_{n,N}$ are positive, the zeros $z_\nu(N)$ of the polynomial (26), for complex values z of the argument

$$Q_N^*(z) = \sum_{n=0}^{M_N} \omega_{n,N} z^n = \omega_{0,N} \prod_{\nu=1}^{M_N}\left(1 - \frac{z}{z_\nu(N)}\right), \tag{28}$$

do not lie on the positive real axis: they are either situated on the negative real axis or occur for complex values of z (in complex conjugated pairs). We shall assume that as N tends to infinity (V/N being kept constant), these zeros may get arbitrarily close to the real axis for $x > 1$ ($\alpha > 0$) only in a finite number L of distinct points, say $x_1, x_2, \cdots, x_L$. An attempt to justify this assumption by analyzing Eq. (28) lies outside the scope of this paper. [However, it should be noted that the asymptotic distribution of zeros must be such that the limit (21) exists.] We shall return later to the physical significance of this behavior of (26). [We remark here that the behavior of (26) near the real axis for $0 < x < 1$ concerns a system of which the pair potential $u(r)$ satisfies condition (20) with $\epsilon < 0$, and is therefore purely repulsive.]

We now expand the function

$$f_N^*(z) = (1/N)\log Q_N^*(z) \tag{29}$$

into a Taylor series around a point $x_0 > 1$ of the real axis and situated at a finite distance from any of the points x_λ ($\lambda = 1, 2, \cdots, L$), i.e. with the property that there exists a $\rho(x_0) > 0$ such that

$$|z_\nu(N) - x_0| > \rho(x_0) \tag{30}$$

for all ν *and all* N. We then obtain

$$f_N^*(z) = f_N^*(x_0) + \sum_{l=1}^{\infty} b_{l,N}(x_0)(z - x_0)^l, \qquad |z - x_0| < \rho(x_0), \tag{31}$$

where

$$b_{l,N}(x_0) = \frac{1}{l!N}\left(\frac{d^l \log Q_N^*(z)}{dz^l}\right)_{x_0}, \tag{32}$$

or, with Eq. (28),

$$b_{l,N}(x_0) = -\frac{1}{lN}\sum_{\nu=1}^{M_N}\frac{1}{(z_\nu(N) - x_0)^l}. \tag{33}$$

With (30) and (24) it then follows that

$$|b_{l,N}(x_0)| < \frac{M_N}{lN}\frac{1}{[\rho(x_0)]^l} < \frac{m}{[\rho(x_0)]^l}. \tag{34}$$

Using this result and the expansion (31), one obtains the following inequality:

$$|f_N^*(z) - f_N^*(x_0)| \leq m\left[\frac{|z - x_0|}{\rho(x_0)}\Big/ 1 - \frac{|z - x_0|}{\rho(x_0)}\right],$$
$$|z - x_0| < \rho(x_0), \tag{35}$$

which establishes the fact that the sequence of functions $f_N^*(z) - f_N^*(x_0)$ is uniformly bounded for $|z - x_0| \leq \rho(x_0) - \delta$, $(\delta > 0)$, that is to say, in the interior $R_0(\delta)$ of the circle $|z - x_0| \leq \rho(x_0)$. On the other hand we also know that $f_N^*(z) - f_N^*(x_0)$ has a finite limit as N tends to infinity (V/N constant) on the positive real axis for $x > 1$, [cf. Eqs. (21) and (25)]. According to the Vitali convergence theorem (used in a similar case by Lewis and Siegert[3]), we may then conclude that $f_N^*(z) - f_N^*(x_0)$, and $f_N(z)$ itself, tend to a finite limit, as $N \to \infty$ (V/N constant), everywhere within the region $R_0(\delta)$:

$$\lim_{N\to\infty} f_N^*(z) = f^*(z), \tag{36}$$

with $f^*(z)$ an analytic function of z in $R_0(\delta)$. As a consequence we also have

$$\lim_{N\to\infty}\frac{d^p f_N^*(x_0)}{dx_0^p} = \frac{d^p f^*(x_0)}{dx_0^p} \qquad p \geq 1, \tag{37}$$

for all $x_0 > 1$ unequal to x_λ ($\lambda = 1, 2, \cdots, L$), and [cf. Eqs. (19) and (25)],

$$\lim_{N\to\infty}\frac{d^p\varphi_N(\alpha)}{d\alpha^p} = \frac{d^p\varphi(\alpha)}{d\alpha^p} \qquad p \geq 1, \tag{38}$$

for all $\alpha > 0$ unequal to $\alpha_\lambda = \epsilon^{-1}\log x_\lambda$ ($\lambda = 1, 2, \cdots, L$). Here the function $\varphi(\alpha)$ is given by

$$\varphi(\alpha) = \tfrac{3}{2}\log\frac{h^2\alpha}{2\pi m} + f(\alpha). \tag{39}$$

Equation (38) contains the result we set out to prove in this section. At a point α_λ the derivatives of (39) do not exist for $p \geq P_\lambda$: according to statistical thermodynamics, this corresponds to a phase transition of order $P_{\lambda+1}$ occurring at a temperature $T_\lambda = 1k\alpha_\lambda$. Our assumption concerning the location of the zeros $z_\nu(N)$ of the polynomial (28) as $N \to \infty$, therefore physically implies that "phase transitions" (of any order) occur at most at a finite number of temperatures T_λ in every finite temperature interval.

We wish to remark that the analysis leading to the result (38) is similar to Yang and Lee's analysis dealing with the grand partition function.[4]

In the next section we shall use (38) to obtain the asymptotical expression as N tends to infinity for the structure function (2).

IV. THE ASYMPTOTIC FORM OF THE STRUCTURE FUNCTION

Consider the function

$$U_N^{(\alpha)}(\xi) = N^{\frac{1}{2}}\exp\left[-\alpha(A_N(\alpha) + N^{\frac{1}{2}}\xi)\right]$$
$$\times\ \Omega_N(A_N(\alpha) + N^{\frac{1}{2}}\xi)/\Phi_N(\alpha), \tag{40}$$

where ξ is defined as

$$\xi = [E - A_N(\alpha)]/N^{\frac{1}{2}}, \tag{41}$$

with $A_N(\alpha)$ given by (7). Since the function (40) is positive, [cf. (3) and (5)], and has, according to (4), the property that

$$\int_{-\infty}^{+\infty} U_N^{(\alpha)}(\xi)\,d\xi = 1, \tag{42}$$

it may be interpreted as the frequency function of the random variable ξ. Its characteristic function is given by

$$\psi_N^{(\alpha)}(t) = \int_{-\infty}^{+\infty} U_N^{(\alpha)}(\xi)e^{it\xi}\,d\xi, \tag{43}$$

which has the inversion

$$U_N^{(\alpha)}(\xi) = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\psi_N^{(\alpha)}(t)e^{-it\xi}\,dt. \tag{44}$$

From (10), (40) and (41), we find the following relation between the characteristic function $\psi_N^{(\alpha)}(t)$ and the generating function $\Phi_N(s)$:

$$\psi_N^{(\alpha)}(t) = \exp\left[-\frac{itA_N(\alpha)}{N^{\frac{1}{2}}}\right]\frac{\Phi_N(\alpha - it/N^{\frac{1}{2}})}{\Phi_N(\alpha)}. \tag{45}$$

The moments of the frequency function (40) are given by

$$\mu_{r,N}^{(\alpha)} = \left[\frac{d^r\psi_N^{(\alpha)}(t)}{d(it)^r}\right]_{t=0}$$
$$= \int_{-\infty}^{+\infty}\xi^r U_N^{(\alpha)}(\xi)\,d\xi, \qquad r \geq 1. \tag{46}$$

The first two are, according to (7), (8), (40), and (41),

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[3] M. B. Lewis, and A. J. F. Siegert, Phys. Rev. **101**, 1227 (1956). For the Vitali convergence theorem, see, e.g., E. C. Titchmarsh, *Theory of Functions* (Clarendon Press, Oxford, England, 1939).

[4] C. N. Yang, and T. D. Lee, Phys. Rev. **87**, 404 (1952).

$$\mu_{1,N}^{(\alpha)} = 0, \tag{47}$$

$$\mu_{2,N}^{(\alpha)} = N^{-1}B_N(\alpha). \tag{48}$$

They are related to the cumulants

$$\kappa_{p,N}^{(\alpha)} = [d^p \log \psi_N^{(\alpha)}(t)/d(it)^p]_{t=0}, \qquad p \geq 1, \tag{49}$$

by the set of relations[5]

$$\begin{aligned}
\mu_{1,N} &= \kappa_{1,N} = 0,\\
\mu_{2,N} &= \kappa_{2,N},\\
\mu_{3,N} &= \kappa_{3,N},\\
\mu_{4,N} &= \kappa_{4,N} + 3\kappa_{2,N}^2,\\
\mu_{5,N} &= \kappa_{5,N} + 10\kappa_{3,N}\kappa_{2,N},\\
\mu_{6,N} &= \kappa_{6,N} + 15\kappa_{4,N}\kappa_{2,N} + 10\kappa_{3,N}^2 + 15\kappa_{2,N}^3, \text{ etc.}
\end{aligned} \tag{50}$$

Now from (45) it follows that

$$\begin{aligned}
\kappa_{p,N}^{(\alpha)} &= N^{-\frac{1}{2}p}(-1)^p(d^p \log \Phi_N(\alpha)/d\alpha^p)\\
&= N^{1-\frac{1}{2}p}(-1)^p(d^p\varphi_N(\alpha)/d\alpha^p), \qquad p \geq 2,
\end{aligned} \tag{51}$$

where we have also used the definition (18).

At this point we shall explicitly make use of the results of the previous section. With Eq. (38), we obtain

$$\lim_{N\to\infty} N^{\frac{1}{2}p-1}\kappa_{p,N}^{(\alpha)} = (-1)^p \frac{d^p\varphi(\alpha)}{d\alpha^p}, \qquad p \geq 2, \tag{52}$$

and, in particular,

$$\begin{aligned}
\lim_{N\to\infty} \kappa_{2,N}^{(\alpha)} &= \lim_{N\to\infty} \mu_{2,N}^{(\alpha)}\\
&= \lim_{N\to\infty} N^{-1}B_N(\alpha) = \frac{d^2\varphi(\alpha)}{d\alpha^2} \equiv g(\alpha),
\end{aligned} \tag{53}$$

$$\lim_{N\to\infty} \kappa_{p,N}^{(\alpha)} = 0, \qquad p \geq 3. \tag{54}$$

According to the relation (50), these conditions imply, for the moments $\mu_{r,N}^{(\alpha)}$, that

$$\left.\begin{aligned}
\lim_{N\to\infty} \mu_{p,N}^{(\alpha)} &= 1\cdot3\cdot5 \cdots (p-1)g^{\frac{1}{2}p} && \text{for } p \text{ even},\\
\lim_{N\to\infty} \mu_{p,N}^{(\alpha)} &= 0 && \text{for } p \text{ odd},
\end{aligned}\right\} \tag{55}$$

i.e. they become asymptotically the moments of a normal (Gaussian) distribution function with variance $g(\alpha)$. By combining the first and second limit theorem[5] of probability theory, we have

$$\lim_{N\to\infty} \psi_N^{(\alpha)}(t) = \exp[-\tfrac{1}{2}gt^2], \tag{56}$$

uniformly in any finite t-interval. This formula expresses the fact that the sequence of characteristic functions $\psi_N^{(\alpha)}(t)$ tends, in the limit as $N \to \infty$ (V/N constant), to the characteristic function of the normal distribution function with variance $g(\alpha)$.

In order to investigate whether also the frequency function $U_N^{(\alpha)}(\xi)$ is asymptotically equal to the frequency function of the normal distribution function with variance $g(\alpha)$, we consider the function

$$\begin{aligned}
&2\pi\left\{U_N^{(\alpha)}(\xi) - \frac{1}{(2\pi g)^{\frac{1}{2}}}\exp[-\tfrac{1}{2}g^{-1}\xi^2]\right\}\\
&= \int_{-\infty}^{+\infty}\{\psi_N^{(\alpha)}(t) - \exp[-\tfrac{1}{2}gt^2]\}\exp[-it\xi]\,dt\\
&= \int_{-T}^{T}\{\psi_N^{(\alpha)}(t) - \exp[-\tfrac{1}{2}gt^2]\}\exp[-it\xi]\,dt\\
&\qquad + \int_{|t|\geq T}\psi_N^{(\alpha)}(t)\exp[-it\xi]\,dt\\
&\qquad - \int_{|t|\geq T}\exp[-\tfrac{1}{2}gt^2 - it\xi]\,dt,
\end{aligned} \tag{57}$$

where T is an arbitrary positive constant. In the second member of (57) we have used formula (44). From (57) we obtain

$$\begin{aligned}
&2\pi\left|U_N^{(\alpha)}(\xi) - \frac{1}{(2\pi g)^{\frac{1}{2}}}\exp[-\tfrac{1}{2}g^{-1}\xi^2]\right|\\
&\leq \int_{-T}^{T}|\psi_N^{(\alpha)}(t) - \exp[-\tfrac{1}{2}gt^2]|\,dt\\
&\qquad + \int_{|t|\geq T}|\psi_N(t)|\,dt + \int_{|t|\geq T}\exp[-\tfrac{1}{2}gt^2]\,dt.
\end{aligned} \tag{58}$$

Using (45) and (17) we get for the second integral at the right-hand side of the inequality (58)

$$\begin{aligned}
\int_{|t|\geq T}|\psi_N^{(\alpha)}(t)|\,dt &\leq \int_{|t|\geq T}\left|\frac{\alpha}{\alpha - itN^{-\frac{1}{2}}}\right|^{\frac{3}{4}N} dt\\
&= \int_{|t|\geq T}\frac{dt}{(1 + N^{-1}\alpha^{-2}t^2)^{\frac{3}{8}N}}.
\end{aligned} \tag{59}$$

But if $N \geq 2$, then

$$\begin{aligned}
&(1 + N^{-1}\alpha^{-2}t^2)^{\frac{3}{8}N} \geq (1 + N^{-1}\alpha^{-2}t^2)^{[\frac{3}{4}N]}\\
&\geq 1 + N^{-1}[\tfrac{3}{4}N]\alpha^{-2}t^2 \geq 1 + \tfrac{1}{2}\alpha^{-2}t^2 > \tfrac{1}{2}\alpha^{-2}t^2,
\end{aligned} \tag{60}$$

where $[\frac{3}{4}N]$ is the integral part of the number $\frac{3}{4}N$. We therefore have, for all N,

$$\int_{|t|\geq T}|\psi_N^{(\alpha)}(t)|\,dt < 2\int_{|t|\geq T}\alpha^2t^{-2}\,dt, \tag{61}$$

and consequently [*cf.* (58)],

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[5] See e.g. M. G. Kendall, *The Advanced Theory of Statistics I*, (Griffin and Company, Ltd., London, England, 1952).

$$2\pi\left|U_N^{(\alpha)}(\xi)-\frac{1}{(2\pi g)^{\frac{1}{2}}}\exp\left[-\tfrac{1}{2}g^{-1}\xi^2\right]\right|$$
$$\leq\int_{-T}^{T}\left|\psi_N^{(\alpha)}(t)-\exp\left[-\tfrac{1}{2}gt^2\right]\right|dt$$
$$+\int_{|t|\geq T}\left(\exp\left[-\tfrac{1}{2}gt^2\right]+2\alpha^2t^{-2}\right)dt, \tag{62}$$

or using the result (56),

$$\lim_{N\to\infty}2\pi\left|U_N^{(\alpha)}(\xi)-\frac{1}{(2\pi g)^{\frac{1}{2}}}\exp\left[-\tfrac{1}{2}g^{-1}\xi^2\right]\right|$$
$$<\int_{|t|\geq T}\left(\exp\left[-\tfrac{1}{2}gt^2\right]+2\alpha^2t^{-2}\right)dt. \tag{63}$$

Now since T is arbitrary, the integral at the right-hand side can be made as small as one wishes, so that the limit of $U_N^{(\alpha)}(\xi)$ for N going to infinity is indeed equal to the Gaussian frequency function with variance $g(\alpha)$. By substituting into this result (40), (41), and (53), we obtain for $N\to\infty$

$$\Omega_N(E)\sim\Phi_N(\alpha)e^{\alpha E}\frac{1}{[2\pi B_N(\alpha)]^{\frac{1}{2}}}$$
$$\times\exp\left\{-\frac{[E-A_N(\alpha)]^2}{2B_N(\alpha)}\right\}. \tag{64}$$

This is the desired asymptotic form of the structure function derived for all $\alpha>0$ unequal to α_λ ($\lambda=1, 2, \cdots, L$). It has been obtained by Khinchin for a system consisting of a large number of *non-interacting components* by making use of the central limit theorem of probability theory. The systems considered by Khinchin correspond to the case that the functions $\log\Phi_N(\alpha)$ are additive for all N (e.g. the ideal gas represented by Eq. (14) with $Q_N(s)=V^N$ for all s) and not to the more general case considered here, that these functions are asymptotically additive. (Yamamoto and Matsuda's[6] attempt to justify Khinchin's procedure for the case of interacting components cannot be considered to be satisfactory.)

V. CONCLUSIONS

The derivation of (64) given above, shows that due to the short range of the interactions, the system behaves, for almost all values of α, as if it consists of a large number of noninteracting components. One might think of subsystems consisting of large numbers of particles; the interaction between these subsystems is then a surface effect and very small compared to the energy content of the subsystems themselves. The result (64) expresses the fact that for all α unequal to α_λ ($\lambda=1, 2, \cdots, L$) the energies of these subsystems behave as "almost independent random variables" so that a central limit theorem still applies. We see however, that for $\alpha=\alpha_\lambda$ ($\lambda=1, 2, \cdots, L$), this is no longer the case: even though the interaction energies between the subsystems may be negligibly small, their effect may become important. Physically this simply means that a system of interacting components may undergo a phase transition, which implies a strong dependency and not an almost statistical independency between the components. (Obviously the systems considered by Khinchin can never undergo a phase transition).

In all our previous considerations the parameter α is completely arbitrary, having as yet no physical meaning. We shall, on Khinchin's footsteps, choose α in such a way that in (64),

$$E-A_N(\alpha)=0, \tag{65}$$

which equation has one single positive solution $\alpha=\beta$.[1] One then obtains from Eq. (64), in the limit as $N\to\infty$, $E\to\infty$, $V\to\infty$ ($V/N=v$ constant, $E/N=e$ constant),

$$\eta(e,v)=\varphi(\beta,v)+\beta e, \tag{66}$$

and consequently

$$\partial\eta(e,v)/\partial e=\beta, \tag{67}$$

where

$$\eta(e,v)=\lim_{N\to\infty}\frac{1}{N}\log\Omega_N(E,V),$$
$$\left(\frac{E}{N}=e,\frac{V}{N}=v\right). \tag{68}$$

The following conclusions can be drawn from the relations (66) and (67):

1. The existence of the function $\varphi(\beta,v)$ [cf. (21) *et seq.*] implies the existence of the function $\eta(e,v)$; no separate proof, analogous to Van Hove's proof of the existence of $\varphi(\beta,v)$, is needed to establish this result. The fact that relation (66) is not obtained for $\beta=\alpha_\lambda$ ($\lambda=1, 2, \cdots, L$) does not constitute a restriction on this statement since $\varphi(\beta,v)$ is a continuous function of β.

2. If the validity of thermodynamics has been established in the microcanonical ensemble, that is, if $\eta(e,v)$ (or rather $h^{-1}\eta(e,v)$) is to be interpreted as the entropy per particle of the system, we may conclude from (66) and (67) that β (or rather $k\beta$) is the reciprocal absolute temperature, and $\beta^{-1}\varphi(\beta,v)$

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[6] T. Yamamoto, and H. Matsuda, Progr. Theoret. Phys. 16, 269 (1956).

represents the free energy per particle. This however justifies the use of the canonical ensemble, since all the thermodynamic quantities of the system can also be obtained from the function $\Phi_N(\beta, V)$ defined by (4). The singularities α_λ ($\lambda = 1, 2, \cdots, L$) of $\varphi(\beta, v)$ are indeed to be interpreted as singularities of the free energy and thus correspond truly to phase transitions.

Finally we wish to stress the fact that all our results are based on the assumption (30) concerning the asymptotic distribution of zeros of the polynomial $Q_N^*(z)$. [This assumption has also been made in the related cases considered by Yang and Lee[4] and Lewis and Siegert.[3]] If this distribution were, for instance, such that these zeros are asymptotically everywhere dense on some segment of the real axis, our results would break down for that segment. This point, therefore, also requires further analysis. Another question to be answered is whether it is possible to reformulate the present classical derivation of Eq. (64) for the quantumstatistical case, as we did on basis of Khinchin's method in a previous paper.[7]

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[7] J. Van der Linden and P. Mazur, Physica **27**, 609 (1961).

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Lattice Statistics—A Review and an Exact Isotherm for a Plane Lattice Gas

MICHAEL E. FISHER
Wheatstone Physics Laboratory, King's College, London, England

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Progress in the theory of lattice statistics is reviewed with emphasis on the use of series expansions to study the critical behavior and on the exact results obtained by transformation theory. Recent work is reported which indicates that the magnetization of the three-dimensional Ising model vanishes as $(T_c - T)^\beta$ with $\beta \simeq \frac{5}{16}$, while the low-temperature susceptibility diverges as $(T_c - T)^{-\gamma}$ with $\gamma = \frac{5}{4}$ ($\gamma = \frac{7}{4}$ in two dimensions). An Appendix is devoted to a detailed tabulation of the exact numerical values and best estimates for the critical temperatures, energies, specific heats, entropies, magnetizations, and the ferro- and antiferromagnetic susceptibilities of four plane lattices and the simple, body-centered, and face-centered cubic lattices.

A square lattice gas with infinite nearest-neighbor repulsions and weak second-neighbor attractions (across alternate squares) is solved exactly for one particular temperature by transformation. The gas undergoes a transition at a density $\rho_t = \frac{1}{4}\sqrt{2}$, the corresponding form of the isotherm being

$$\frac{p - p_t}{kT} = \frac{\alpha(\rho_t - \rho)}{\ln \alpha\,|\rho_t - \rho|},$$

where $\alpha = \pi(1 + \frac{3}{4}\sqrt{2})$, so that the isothermal compressibility becomes logarithmically infinite.

1. INTRODUCTION

IN this paper, I would like to review briefly some recent progress in lattice statistics and to describe, in particular, a two-dimensional lattice gas of hard squares for which an isotherm can be calculated exactly. Present day interest in lattice statistics, centers of course, on the behavior in the transition regions. The Ising model is one of the most fundamental examples of a system exhibiting a phase transition and although it is not a realistic model in all of the many physical situations to which it can be applied, I believe there is still much to be learned about phase transitions by its study.

To determine the true properties of the model there are basically two approaches. On the one hand, one can attempt to obtain exact, rigorous analytic results; the major landmark in this direction is, of course, Onsager's closed expression for the partition function of the plane square lattice in zero magnetic field which was published over eighteen years ago, in 1944.[1] One should also remember that in 1936 Peierls[2] had shown generally why a transition should take place and that Kramers and Wannier[3] had located the exact critical point in 1941.

The alternative approach to the problem is to employ *systematic, successive* approximations which may be studied numerically. I have stressed the adjectives "systematic" and "successive" since I believe that the day of the "one-shot" approximation, however elaborate or ingenious, is past. Simple approximations like the mean-field and Bethe approximations[4] are useful general guides, especially in correlating experimental data, although the rigorous results have shown them to be seriously misleading in the transition region. Recently, however, some rather lengthy and complicated approximate treatments of the Ising model have appeared the results of which are no better than those of the Bethe approximation. While such treatments are probably useful in throwing light on the deficiencies of methods which are also applicable to other problems, they do not add to our knowledge of the true nature of the Ising model transitions. Successive approximations, on the other hand, enable one, by studying their trend, to obtain numerical information of known reliability.

Such approximation methods may be roughly grouped into two classes: those which yield closed formulas and those based on power-series expansions. Of the former, one should mention, in particular, the method of Kikuchi,[4,5] which has been developed by Hijmans and de Boer[6] and Kruseman, Aretz, and Cohen,[7] and the method of Yvon and Fournet.[4,8] The first Kikuchi approximation is usually rather

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[1] L. Onsager, Phys. Rev. 65, 117 (1944).

[2] R. Peierls, Proc. Cambridge Phil. Soc. 32, 477 (1936).

[3] H. A. Kramers and G. H. Wannier, Phys. Rev. 60, 252, 263 (1941).

[4] For a discussion of the approximations and general review of the field, see C. Domb, Advan. Phys. 9, Nos. 34, 35 (1960).

[5] R. Kikuchi, Phys. Rev. 81, 988 (1951).

[6] J. Hijmans and J. de Boer, Physica 21, 471, 485, 499 (1955).

[7] F. E. J. Kruseman Aretz and E. G. D. Cohen, Physica 26, 967, 981 (1960).

[8] J. Yvon, Cahiers phys. No. 28 (1945), Nos. 31, 32 (1948).

accurate except near the transition point, but unfortunately, higher approximations are very much harder to compute and the rate of convergence seems disappointingly slow. Direct series expansions are relatively easier to calculate and the labor of obtaining higher terms does not, in practice, increase as rapidly. Furthermore, the trends of successive approximations are more regular. The use of extended series to derive information about the transition region has been developed particularly by Domb and Sykes and their collaborators[9–12] and has proved rather fruitful. Since it is not always realized how much accurate information is obtainable in this way, especially in the light of recent developments, I would like, before going on to discuss some progress on the exact analytic approach, to outline the present state of numerical knowledge of the Ising model. A table summarizing the information for one-, two-, and three-dimensional lattices is presented in Appendix A.

2. THE SERIES APPROACH

By expanding the partition function at high temperatures, low temperatures, or high fields one obtains[4] the specific heat, the reduced susceptibility, etc. as power series,

$$A(w) = \sum_{n=0} a_n w^n. \qquad (1)$$

In practice, one can normally calculate from eight to twenty-four exact coefficients a_n. To analyze such a power series numerically, there are now two techniques available: the ratio method of Domb and Sykes[12] and the Padé approximant procedure, more recently developed by Baker and Gammel.[13,14] (This latter is, effectively, a generalization of Park's method.[15])

The ratio method is applicable when the series of coefficients a_n (or those of some transformed series such as the logarithmic derivative) are of one sign, in which case the dominant singularity of $A(w)$ lies on the real axis and corresponds (normally) to the transition point. It is found, in many cases, that the ratios

$$\mu_n = a_n/a_{n-1}$$

rapidly approach linear behavior with $1/n$. The gradient of the corresponding line then determines the nature of the dominant singularity (pole or branch point) and the intercept with the $1/n = 0$ axis yields the transition point.[12] Application of this method to the high-temperature susceptibility series has lead to estimates of the critical temperatures accurate to 0.1% or better (see below) and has shown[11,12] that the susceptibility diverges at $T = T_c$ as

$$\chi(T) \approx (Nm^2/kT_c)C_T^+/[1 - (T_c/T)]^\gamma \quad (T > T_c), \qquad (2)$$

where $\gamma = \frac{7}{4}$ in two dimensions and $\gamma = \frac{5}{4}$ in three dimensions. The former result has since been confirmed by analytic arguments[16] based on the exact results of Onsager and Kaufman for the correlations.[17] (Values of the amplitudes C_T^+ are given in the Appendix.)

It has proved possible in some cases to remove the dominant singularity in a function in order to study the behavior at other singularities. In this way, for examples, Sykes and Fisher[18] have examined the analytic behavior of the *anti*ferromagnetic susceptibilities at T_c and obtained values of χ_{anti} accurate to 0.5% or better, even in the critical region. (Some of these results are presented in the Appendix.)

The second technique, the Padé approximant procedure, is basically a method of analytically continuing a power series. The $[L, M]$ Padé approximant to a function $A(w)$ whose power series expansion is known, is the ratio of two polynomials $P(w)$ and $Q(w)$ of degrees L and M, with coefficients chosen so that the expansion of $P(w)/Q(w)$ agrees with the exact expansion of $A(w)$ up to the term in w^{L+M}. (The calculations for the coefficients involve the solution of M simultaneous linear equations.) The distribution of zeros and poles of successive approximants reveals the analytic behavior of $A(w)$ and evaluation of the approximants yields accurate estimates of $A(w)$ well beyond the radius of convergence of the original series. The Padé approximants may be regarded as closed-form approximations derived from the series; since they agree with a greater number of the exact terms than do the usual closed-form approximations they may be expected to be correspondingly more accurate.

Using this technique to investigate $\chi(v)$, $(d/dv)\cdot \ln \chi(v)$, and $[\chi(v)]^\gamma$, Baker[14] confirmed Domb and Sykes' estimates for T_c and for the behavior (2) of the susceptibility at T_c. The two methods, in fact, yield estimates for T_c agreeing with one another (and with the exact results in two dimensions) to within

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1 or 2 parts in 10^4, so that for most practical purposes the critical points of the three-dimensional lattices may be regarded as known exactly. (The values are tabulated in the Appendix.)

The real power of the Padé approximant procedure, however, has revealed itself in its ability to deal with series, such as the spontaneous magnetization of the body-centered and face-centered cubic lattices, in which the signs and magnitudes of the coefficients are so irregular that all direct analysis seemed hopeless! Baker[14] showed, in this way, that the magnetization of the three-dimensional lattices vanishes as

$$I(T) \approx D_T[1 - (T/T_c)]^\beta, \quad (T < T_c), \tag{3}$$

where $\beta \simeq 0.30$. More recently, this problem has been re-examined using longer series and we have concluded[19] that β is probably exactly equal to $\frac{5}{16} = 0.312500$ for all three-dimensional lattices (compared with $\beta = \frac{1}{8}$ in two dimensions). For a simple lattice gas with nearest-neighbor attractions, (3) should give the shape of the liquid–vapor coexistence curve near the critical point. Consequently, it is interesting to note that the coexistence curves for the classical rare gases can be fitted with $\beta = 0.33$.[20]

Among other results derived from the series expansions, one may mention the *low*-temperature susceptibilities (evaluated in the limit of zero field) which, for a lattice gas, correspond to the (reciprocal) slope of the isotherms at the condensation point. As at high temperatures, the behavior is found to be

$$\chi_0(T) \approx (Nm^2/kT_c)C_T^-/[1 - (T/T_c)]^\gamma, \quad (T < T_c), \tag{4}$$

where $\gamma = \frac{7}{4}$ in two dimensions and $\frac{5}{4}$ in three dimensions. The amplitudes C_T^- are, however, much smaller than above T_c (see Appendix).

The specific heats of the three-dimensional lattices exhibit weaker singularities than the susceptibilities and it is more difficult to draw accurate conclusions. Above T_c, the specific heats are relatively much smaller than in two dimensions (where they are symmetric about T_c) and the evidence suggests[4,10] that

$$C(T) \approx A/[1 - (T_c/T)]^{1/5}, \quad (T > T_c). \tag{5}$$

The series can, however, be fitted quite well by a logarithmic singularity which suffices to yield reasonably accurate estimates for the critical energies and entropies. These differ characteristically from the two-dimensional results[4,18] (see Appendix). Below T_c, the specific heat is much greater in magnitude and recent work on the diamond lattice as well as on the cubic lattices indicates that the logarithmic singularity, originally assumed somewhat arbitrarily by Wakefield,[21] is probably correct.

3. TRANSFORMATIONS

Onsager's work gave us the exact partition function of the plane square Ising lattice in zero magnetic field. Similar relatively complicated calculations soon afterwards yielded the partition function for the plane triangular lattice.[22] The partition function of the honeycomb lattice could then be derived in a few lines by using the "star–triangle" transformation discovered by Onsager.[1,22,23] This transformation which replaces a "star," consisting of a central spin connected by bonds to three outer spins, by a "triangle," made of direct bonds between the three outer spins, admits of considerable generalization.[24] As we will indicate, solutions can be obtained in this way for many other types of Ising model, some of which are of considerable physical interest.

The basic idea of the transformation is to replace a function $\psi(s_1, s_2, \cdots s_n)$ of n discrete spin variables $s_i = \pm 1$, by a function $\psi^*(s_1, s_2, \cdots s_n)$ of different functional form chosen, however, in such a way that $\psi \equiv \psi^*$ for the 2^n distinct values of the arguments. The mathematics is then essentially unchanged, but the different functional forms lead to different physical interpretations. In practice, one also uses the fact that the variables s_i commute, so that the summations in the partition function

$$Q_N(K, L) = \sum_{s_i=\pm1} \exp\,[K \sum_{(ij)} s_i s_j + L \sum_i s_i]; \tag{6}$$

$$K = J/kT, \qquad L = mH/kT \tag{7}$$

can be performed in any order.

The simplest example of this principle is found in Van de Waerden's[25] method of expanding the partition function in zero field. To avoid the appearance of "repeated bonds" in the graphical expansion, one must linearize the Boltzmann factor $\psi(s_1, s_2) = \exp Ks_1s_2$. If we write

$$\psi(s_1, s_2) = \exp Ks_1s_2 = \alpha + \beta s_1 s_2 \tag{8}$$

and impose the identity for the values $s_1, s_2 = \pm 1$, we obtain the equations

$$\psi(1, 1) = e^K = \alpha + \beta, \quad \psi(1, -1) = e^{-K} = \alpha - \beta, \tag{9}$$

which are immediately solved to yield the well-

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known result

$$\alpha = \cosh K, \qquad \beta = \sinh K. \tag{10}$$

(By an obvious generalization for the case of spin one, when $s_i = 1, 0, -1$, it is only necessary to consider single bonds and double bonds.)

To extend this bond transformation, consider a lattice in which each bond is "decorated" with an arbitrary physical system which interacts only with the spins at the ends of the bond and with external fields. We aim to show, by summing over the states of the decorating systems, that the partition function of the decorated lattice can be reduced to that of the underlying simple Ising lattice. For each bond of the decorated lattice, the partition function has, in virtue of the commutation, a factor

$$\begin{aligned}\psi(s_1, s_2) &= \mathrm{Tr}\,\{\exp\,[-\mathcal{H}(s_1, s_2)/kT]\}\\ &= \sum_n \exp\,[-E_n(s_1, s_2)/kT],\end{aligned} \tag{11}$$

where $\mathcal{H}(s_1, s_2)$ is the Hamiltonian and $E_n(s_1, s_2)$ the energy levels of the decorating system for a fixed spin configuration. We now attempt to satisfy the identity

$$\psi(s_1, s_2) = g \exp\,[K's_1s_2 + \delta L_1s_1 + \delta L_2s_2], \tag{12}$$

where the exponential factor corresponds to a direct (undecorated) bond of the underlying lattice with additional magnetic fields acting at the vertices. Imposing the identity for the four possibilities s_1, $s_2 = \pm 1$ leads to four equations for the four parameters g, K', δL_1, and δL_2. These are readily solved to yield

$$e^{4K'} = \psi_{++}\psi_{--}/\psi_{+-}\psi_{-+}, \tag{13}$$

$$\begin{aligned}e^{4\delta L_1} &= \psi_{++}\psi_{+-}/\psi_{--}\psi_{-+},\\ e^{4\delta L_2} &= \psi_{++}\psi_{-+}/\psi_{--}\psi_{+-},\end{aligned} \tag{14}$$

and

$$g^4 = \psi_{++}\psi_{--}\psi_{+-}\psi_{-+}, \tag{15}$$

where $\psi_{\pm\pm} = \psi(\pm 1, \pm 1)$. With these results the partition function of the decorated lattice may be written

$$Z_M(T, L) = g^M Q_N(K', L') \tag{16}$$

where M is the number of decorated bonds and $Q_N(K', L')$ is the partition function of the underlying lattice of N sites, with bond parameter K', and field parameters L', that include the increments δL_i.

As an example of this transformation, consider a decorated square lattice in which each bond carries a quantum-mechanical spin ($S = \frac{1}{2}$) which is acted on by parallel and perpendicular magnetic fields, H_z and H_x, and which is coupled anisotropically to *non*magnetic vertex spins. The bond partition function is then

$$\begin{aligned}\psi(s_1, s_2) &= \mathrm{Tr}\,\{\exp\,[K\sigma_0^z(s_1 + s_2) + L_z\sigma_0^z + L_x\sigma_0^x]\}\\ &= 2\cosh\,[(Ks_1 + Ks_2 + L_z)^2 + L_x^2]^{1/2}.\end{aligned} \tag{17}$$

(Similar expressions could obviously be written down for arbitrary higher values of the spin on the bond.) If we now suppose that the spins on the vertical bonds are coupled ferromagnetically to the vertex spins, whereas those on the horizontal bonds are coupled antiferromagnetically (i.e., $K \to -K$) we obtain a "super-exchange" antiferromagnet. (The bond spins form a square lattice which orders antiferromagnetically, in virtue of the indirect coupling through the vertex spins.) Now the operation $K \to -K$ induces the changes $\psi_{++} \to \psi_{--}$ and $\psi_{--} \to \psi_{++}$, so that by (14), $\delta L \to -\delta L$. This means that when all the decorating bonds are removed, the additions to the magnetic parameter L_i at each vertex cancel one another. Consequently, the partition function of the superexchange lattice in an arbitrary magnetic field is obtainable from Onsager's solution in *zero* field. The explicit relationship is

$$Z_{2N}(K, L_x, L_z) = g^{2N}Q_N(K', 0), \tag{18}$$

where K' and g are given in terms of K, L_x, and L_z by (13), (15), and (17).

The thermodynamic and magnetic properties of the model follow from the partition function (18) in the standard way, and have been investigated in detail for parallel fields.[26] The correlation functions for the model may be related to those for the standard square lattice by extending the arguments.[27] As might be expected, the specific heat in zero field for the superexchange lattice becomes logarithmically infinite at T_c. The transition temperature is lowered in a field and goes to zero at the critical parallel field $H_z = 2J/m$. The specific heat in a field still exhibits a logarithmic singularity, but its strength falls with increasing field.

The most interesting results concern the magnetization and the susceptibility since these are only known approximately for the normal Ising lattice. The zero-field parallel susceptibility has a vertical tangent at T_c and passes through a maximum about 40% above T_c. The critical behavior is

$$\chi_\parallel(T) \approx (Nm^2/kT)\{\xi_c + B(T - T_c)\ \ln\,|T - T_c|\}, \tag{19}$$

where

$$\xi_c = 1 - \tfrac{1}{2}\sqrt{2}. \tag{20}$$

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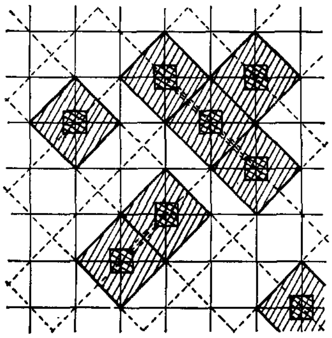

FIG. 1. Hard-square lattice gas with attractions across alternate squares (indicated by broken lines).

The more modern experimental work[28] with antiferromagnetic crystals confirms that $\partial\chi_{\parallel}/\partial T$ becomes infinite at T_c and that the maximum in $\chi_{\parallel}$ lies above T_c.

One can show,[16] by expressing the antiferromagnetic parallel susceptibility in terms of the correlation functions and using the results of Onsager and Kaufman,[17] that the critical behavior (19) is also valid for the standard plane Ising models in zero field. The constants ξ_c and B have not been determined exactly in these cases but quite accurate estimates can be obtained from the series[18] (see the Appendix).

The *perpendicular* susceptibilities of the plane square and honeycomb lattice can be calculated in closed form (in zero field) by an extension of the transformation technique.[29,30] The partition function of a lattice with a single magnetic spin in a perpendicular field is replaced by the zero-field partition function and a set of near-neighbor-pair and higher order correlation functions.[30] The resulting formula for the honeycomb lattice is relatively simple, but that for the square lattice is lengthy and involves sums and products of elliptic integrals. In the critical region the behavior is similar to (19). (Numerical values of the corresponding constants are given in the Appendix).

For the exactly soluble superexchange model, the magnetization *in a field* is continuous at the transition but its gradient in the (H, T) plane becomes infinite as $\ln|H - H_c|$ or $\ln|T - T_c|$. It seems likely that, as for the zero-field properties, this result is also true for the standard plane Ising models in a field. If this is so, it has some interesting consequences for the behavior of the corresponding plane lattice gases with repulsive interactions (see Sec. 4).

4. HARD-SQUARE LATTICE GAS

One of the simplest models with which one might hope to study the steric effects arising from the finite "hard core" radius of the atoms and molecules in real gases, is a plane lattice gas of hard squares. The grand partition function for this model is equivalent to the canonical partition function of the corresponding antiferromagnetic Ising lattice in a finite magnetic field evaluated in the limit $T \to 0$.[31–33] Because of the repulsive interactions, Yang and Lee's powerful theorem on the zeros of the grand partition function[31] no longer applies, and the location and nature of the transition from ordered to disordered state is not known. Approximate treatments by Burley[33] using the Bethe and related approximations indicate a second-order transition with a discontinuous gradient in the isotherm. Temperley,[32] on the other hand, has suggested that the transition might be first order.

An obvious extension of the model is the introduction of attractive forces between squares which touch along a side. (This is equivalent to introducing second-neighbor interactions in the Ising lattice.) One might expect this model to exhibit a gas–liquid condensation as well as solid–gas (sublimation) and solid–liquid (melting) transitions. If we modify this model slightly, it turns out that we can calculate an exact isotherm for one particular temperature. The modification is to weaken the attractive forces so that they only come into play across *alternate* squares of the underlying square lattice, as indicated in Fig. 1. (This is equivalent to deleting the diagonal second-neighbor interactions in every other square of the lattice.)

The first few terms of the Mayer expansion of the grand partition function in powers of the fugacity

$$z = e^{-\phi} \tag{21}$$

are easily derived for this model and yield

$$\Gamma(z, f) = p/kT = z - (\tfrac{5}{2} - f)z^2 + (10\tfrac{1}{3} - 8f + f^2)z^3 + \cdots, \tag{22}$$

where, as usual, if V_0 is the depth of the attractive part of the potential,

$$f = e^{4C} - 1, \qquad 4C = V_0/kT. \tag{23}$$

[For simple hard squares $f = 0$ and (22) reduces to the known expansion.[32,33]] The density is given by

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$$\rho = n/2N = (z\,\partial/\partial z)\Gamma$$
$$= z - (5-2f)z^2 + (31 - 24f + 3f^2)z^3 + \cdots, \quad (24)$$

where n is the mean number of atoms on the lattice of $2N$ sites. Hence, the virial expansion is

$$p/kT = \rho + (\tfrac{5}{2} - f)\rho^2 + (4\tfrac{1}{3} - 4f + 2f^2)\rho^3 + \cdots. \quad (25)$$

Expansions can also be obtained at high densities by considering holes in the close-packed configuration at $\rho = \rho_{\max} = \frac{1}{2}$.

To derive an analytic expression for the grand partition function

$$\Xi(z, f) = \Xi(\phi, C) = \exp 2N\Gamma(z, f), \quad (26)$$

we may write

$$\Xi(\phi, C) = \lim_{G\to\infty} \Xi^{\dagger}(\phi, C, G, G^*), \quad (27)$$

where $\Xi^{\dagger}$ is the grand partition function of a gas with soft repulsive cores, of strength $V_1 = 4GkT$, and an additional "four-body" repulsive interaction, of strength $V^* = 4G^*kT$ which comes into play between adjacent atoms when the remaining two sites in the alternate squares are unoccupied. This last interaction is merely introduced as a device which enables us to transform the problem into the superexchange model discussed in the previous section.

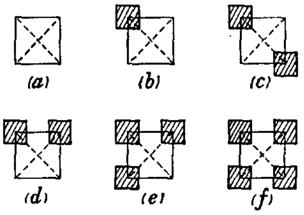

FIG. 2. Distinct configurations of atoms around a square in the soft-square gas.

The corresponding Boltzmann factors for the six possible distinct configurations of atoms around a square, as shown in Fig. 2 are:

(a) 1, (b) 1, (c) e^{4C},

(d) e^{-4G-4G^*}, (e) e^{-8G+4C}, (f) $e^{-16G+8C}$.

Introducing the spin variables $s_i = \pm 1$ and associating $s_i = +1$ with an occupied site and $s_i = -1$ with a vacant site, we can write

$$\Xi^{\dagger}(\phi, C, G, G^*) = \sum_{s_i=\pm 1} \prod_{k=1}^{N} \Psi(s_{k1}, s_{k2}, s_{k3}, s_{k4}), \quad (28)$$

where the product is taken over the N alternate squares across which the attraction takes place, and where

$$\Psi(s_1, s_2, s_3, s_4) = \exp\left[-\tfrac{1}{2}\phi \sum_{i=1}^{4} \tfrac{1}{2}(1+s_i)\right]$$
$$\times \exp\{C[(1+s_1)(1+s_3) + (1+s_2)(1+s_4)]\} \exp\{-G[(1+s_1)(1+s_2) + (1+s_2)(1+s_3)$$
$$+ (1+s_3)(1+s_4) + (1+s_4)(1+s_1)]\} \exp\{-G^*(1-s_1s_3)(1-s_2s_4)\}, \quad (29)$$

which can be rewritten as

$$\Psi = \exp[-\phi + 2C - 4G - G^*] \exp\left[-(\tfrac{1}{4}\phi - C + 2G) \sum_{i=1}^{4} s_i\right]$$
$$\times \exp[(C + G^*)(s_1s_3 + s_2s_4) - G(s_1s_2 + s_2s_3 + s_2s_4 + s_4s_1) - G^*s_1s_2s_3s_4]. \quad (30)$$

Now, by performing the summations over the *vertex* spins, the partition function for the superexchange lattice in a parallel field ($L_x = 0$) can be written

$$Z_{2N}(K, L) = \sum_{s_i=\pm 1} \prod_{k=1}^{N} \psi(s_{k1}, s_{k2}, s_{k3}, s_{k4}), \quad (31)$$

where the summation is over the configurations of the $2N$ bond spins, the product is over the N vertices, and where

$$\psi(s_1, s_2, s_3, s_4) = 2\exp\left[\tfrac{1}{2}L \sum_{i=1}^{4} s_i\right] \times \cosh K(s_1 - s_2 + s_3 - s_4). \quad (32)$$

As in the previous section, we next attempt to satisfy the identity

$$\Psi(\phi, C, G, G^*) = h\psi(K, L) \quad (33)$$

for the 16 possible combinations of $s_{1-4} = \pm 1$. Since Ψ involves four parameters but ψ only contains two, we cannot satisfy (33) in general. It is easily found, however, that the necessary and sufficient conditions for the identity to be valid are

$$G = \tfrac{1}{8} \ln \cosh 4K, \quad (34)$$

$$G^* = \tfrac{1}{2} \ln \cosh 2K - \tfrac{1}{8} \ln \cosh 4K, \quad (35)$$

$$C = G - G^*$$
$$= -\tfrac{1}{2} \ln \cosh 2K + \tfrac{1}{4} \ln \cosh 4K, \quad (36)$$

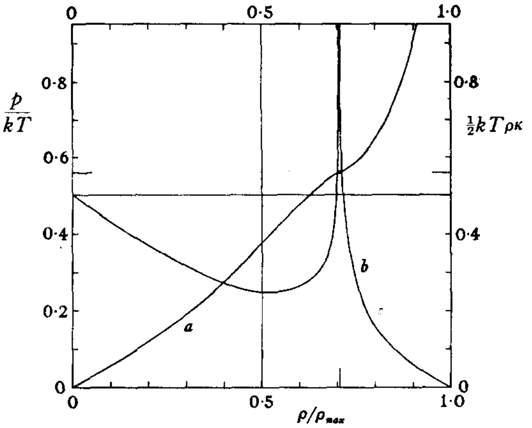

FIG. 3. Variation with density of the pressure (a) and isothermal compressibility (b) of the lattice gas at a fixed temperature $T = V_0/k \ln 2$.

$$L = -\tfrac{1}{2}\phi - \ln\cosh 2K, \tag{37}$$

$$\ln h = -\phi - 2\ln\cosh 2K - \ln 2. \tag{38}$$

To obtain the hard-square gas we have to take the limit $G \to \infty$, so that by (34) we must consider $|K| \to \infty$. For large $K > 0$ one finds

$$G = \tfrac{1}{2}K - \tfrac{1}{8}\ln 2 + O(e^{-8K}), \tag{39}$$

$$G^* = \tfrac{1}{2}K - \tfrac{3}{8}\ln 2 + O(e^{-4K}), \tag{40}$$

$$L = -\tfrac{1}{2}\phi - 2K + \ln 2 + O(e^{-4K}), \tag{41}$$

$$\ln h = -\phi - 4K + \ln 2 + O(e^{-4K}), \tag{42}$$

and finally

$$C = \tfrac{1}{4}\ln 2 + O(e^{-4K}). \tag{43}$$

This last relation restricts our solution to the single temperature $T = V_0/k \ln 2$, for which

$$f = 1. \tag{44}$$

It does not seem possible to avoid this limitation. For this case we find, by comparing (28) and (31) and substituting in (27),

$$\Xi(\phi, \tfrac{1}{4}\ln 2) = \lim_{K\to\infty} 2^N e^{-N\phi-4NK} Z_{2N}(K, -\tfrac{1}{2}\phi - 2K + \ln 2). \tag{45}$$

But, by the analysis of the previous section, Z_{2N} can be re-expressed in terms of the partition function of the standard square lattice. Thus,

$$Z_{2N}(K, L) = g^{2N} Q_N(K'), \tag{46}$$

where by (13), (15), and (17) with $L_z = L$ and $L_x = 0$ we have

$$e^{4K'} = \cosh(2K + L)\cosh(2K - L)/\cosh^2 L, \tag{47}$$

and

$$g^4 = 2^4 \cosh(2K + L)\cosh(2K - L)\cosh^2 L. \tag{48}$$

Substituting $L = -\tfrac{1}{2}\phi - 2K + \ln 2$ and taking the limit $K \to \infty$, yields

$$e^{4K'} = 1 + 4e^{-\phi} = 1 + 4z, \tag{49}$$

and finally

$$\Xi(\phi, \tfrac{1}{4}\ln 2) = 2^{-N}(1 + 4z)^{N/2} Q_N[\tfrac{1}{4}\ln(1 + 4z)], \tag{50}$$

which expresses the grand partition function of the gas in terms of the partition function of the plane square lattice in zero field as calculated by Onsager.[1]

By expanding the logarithm of the left-hand side of (50) in powers of z, one easily checks (22) for $f = 1$. The exact results for the model follow by using Onsager's formulas. The pressure and the density are conveniently expressed as

$$\Gamma(z, 1) = p/kT = K' + \int_0^{K'} \omega_1(K)\,dK, \tag{51}$$

and

$$\rho(z) = \tfrac{1}{4}(1 - e^{-4K'})[1 + \omega_1(K')], \tag{52}$$

where K' is given by (49) and where $\omega_1(K)$ is the reduced energy (or first-neighbor correlation function) of the plane square lattice. Thus,[1]

$$\omega_1(K) = \tfrac{1}{2}\coth 2K(1 + (2/\pi)k_1''K(k_1)], \tag{53}$$

where

$$k_1 = 2\tanh 2K/\cosh 2K, \qquad k_1'' = 2\tanh^2 2K - 1, \tag{54}$$

and $K(k_1)$ is the complete elliptic integral of modulus k_1.

It follows that the gas undergoes a transition to an ordered state when the fugacity is

$$z_t = \tfrac{1}{2}(1 + \sqrt{2}) = 1.207107. \tag{55}$$

The Mayer expansion in z, however, diverges owing to a closer singularity on the negative real axis at

$$z_0 = \tfrac{1}{2}(1 - \sqrt{2}) = -0.207107, \tag{56}$$

(A similar situation prevails when $f = 0$.) The other critical parameters are

$$\Gamma_t = p_t/kT = \tfrac{1}{4}\ln(\tfrac{3}{2} + \sqrt{2}) + G/\pi = 0.558961, \tag{57}$$

and

$$\rho_t = \tfrac{1}{4}\sqrt{2} = 0.353553. \tag{58}$$

The equation of state is obtained formally by eliminating the fugacity z (or K') between the relations (51) and (52). It does not seem possible to express the result in closed form, but it is easily seen that the pressure is a smooth continuous function of the density as shown in Fig. 3. In the transition region we find

$$\frac{p}{kT} \approx \frac{p_t}{kT} + \frac{\alpha(\rho_t - \rho)}{\ln \alpha\,|\rho_t - \rho|}, \tag{59}$$

with

$$\alpha = \pi(1 + \tfrac{3}{4}\sqrt{2}), \tag{60}$$

so that the isotherm levels out and has a horizontal tangent at the transition. Correspondingly, the isothermal compressibility

$$\kappa = \rho^{-1}\,\partial\rho/\partial p = 1/kT\rho(\partial\Gamma/\partial\rho) \tag{61}$$

becomes logarithmically infinite at $\rho=\rho_t$ (see Fig. 3).

The "second-order" transition revealed here is evidently a "fluid–solid" transition, but whether the "fluid" is "gas" or "liquid" we cannot say, since only the isotherm for $f = 1$ is known. It seems likely, however, that $f = 1$ corresponds to a temperature above the gas–liquid critical point (if it exists) rather than to one below the triple point (if it exists). Thus, unless $f = 1$ is some other kind of singular point, the nature of the transition should remain essentially unchanged as f is reduced to zero. We conclude that the transition for the simple hard square lattice gas (with no attractions) is probably rather similar. (This is in agreement with a suggestion of Burley.[33])

It is difficult to judge whether these results have any relevance to continuum gases of hard circles and spheres. Indeed, there are indications that the situation is somewhat different even for a gas of hard hexagons on the triangular lattice, which should be a better approximation to a gas of hard circles. On the other hand, the possibility that the transition in a gas of hard spheres is of similar type should be borne in mind since, if so, it might be rather difficult to detect it by Monte Carlo studies or by approximate theoretical calculations.

By extending the analysis along the lines used to calculate the correlation properties of the super-exchange model,[27] it is also possible to determine the energy and long-range order of the gas as a function of density for the case $f = 1$.

Finally, we note that when $f = -1$, so that the atoms exert infinite *repulsive* forces across alternate squares of the lattice, the model reduces to the dimer problem[34] (on the underlying lattice). This has recently been solved rigorously for the case of maximum density ($\rho = \frac{1}{4}$) by the use of Pfaffians.[35–37] It is also possible to calculate certain correlation properties for this case with the aid of perturbation techniques but the problem of dimers at intermediate densities has so far resisted attack.

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ACKNOWLEDGMENTS

It is a pleasure to thank Professor C. Domb, Dr. M. F. Sykes, and Dr. H. N. V. Temperley for many stimulating discussions.

APPENDIX A—EXACT AND ESTIMATED NUMERICAL PARAMETERS FOR THE ISING MODEL

The exact results in the table below, derived from the work of Onsager,[38] Yang,[39] Houtappel,[40] Syozi,[41] and others,[42–46] are given in most cases to six or more decimal places. The estimates for the three-dimensional lattices (and for the parallel susceptibilities in two dimensions) are based on the series obtained by Domb and Sykes[47,48] and extended more recently by Essam and Sykes.[49] Critical point parameters have been obtained by numerical analysis based on the behavior of the ratios[48–50] and the sequences of Padé approximants.[51,52] The errors in the estimates are generally confined to the last one or two decimal places. (Many of the entries in the table are reproduced from a similar table in reference 49.)

The lattice types considered are: linear chain (c), plane honeycomb (h), plane square (sq), kagomé (k), triangular (t), simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc). Definitions of symbols used in the table are given below. A blank entry indicates that the numerical value has not been computed, three dots that the category is inapplicable.

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[38] L. Onsager, Phys. Rev. **65**, 117 (1944) [*zero-field properties of the plane square lattice*].

[39] C. N. Yang, Phys. Rev. **85**, 808 (1952) [*magnetization of the plane square lattice*].

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[50] M. F. Sykes and M. E. Fisher, Physica **28**, 919, 939 (1962) [*antiferromagnetic susceptibilities, energies, etc.*].

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Table I. Table of exact and estimated numerical parameters for the Ising model

	Lattice							
	c	h	sq	k	t	sc	bcc	fcc
q	2	3	4	4	6	6	8	12
$1/v_c$	1	1.7320508	2.4142136	2.296630	3.7320508	4.5840	6.4032	9.8280
v_c	1	0.5773503	0.4142136	0.4354206	0.2679492	0.21815	0.15617	0.10175
z_c	0	0.2679492	0.4142136	0.3933198	0.5773503	0.64183	0.72985	0.81529
K_c	∞	0.6584788	0.4406868	0.4665661	0.2746531	0.22171	0.15746	0.10208
θ_c	0	0.5062173	0.5672963	0.5358297	0.6068256	0.75172	0.79385	0.81617
α	···	0.7603459	0.8813734	0.8683772	0.9514269	0.96797	0.98366	0.99308
Energy								
U_c/U_0	1	0.7698003	0.7071068	0.7440169	0.6666667	0.328	0.270	0.244
A_+	0	0.6366198	0.6366198	0.5924414	0.6366198	0.343	0.343	0.345
A_-	0	0.6366198	0.6366198	0.5924414	0.6366198	$\simeq$1.0	$\simeq$1.0	$\simeq$1.0
Entropy								
S_c	0	0.26471	0.306470	0.28052	0.33028	0.541	0.586	0.597
$S_\infty - S_c$	0.6931472	0.42844	0.386677	0.41263	0.36287	0.152	0.107	0.096
S_0	0	0	0	0.50183	0.32306	0	0	0
Magnetization								
β	···	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\simeq$0.3125	$\simeq$0.3125	$\simeq$0.3125
D_T	···	1.264904	1.2224099	1.2·····	1.2032700	1.570	1.491	1.488
Ferromagnetic Susceptibility								
γ	1	$\frac{7}{4}$	$\frac{7}{4}$	$\frac{7}{4}$	$\frac{7}{4}$	1.250	1.250	1.250
C_+	···	0.6480	0.77184	0.7962	0.8473	1.0181	0.9727	0.967
$C_T{}^+$	···	1.0466	0.96272	1.0176	0.9244	1.0604	0.9929	0.975
$C_T{}^-$	···	0.0280	0.0261		0.0249	0.196	0.190	0.189
Antiferromagnetic Susceptibility (Parallel)								
ξ_c	0	0.1214	0.1570	(0.18943)	(0.1389)	0.3397	0.3692	(0.000)
χ_c/χ_0	0	0.2398	0.2768	(∞)	(∞)	0.4519	0.4651	(0.000)
B_+	···	0.332	0.3174	···	···	0.115	0.111	···
B_-	···	$\leq$0.33	$\leq$0.317	···	···	0.301	0.316	···
$\theta_{\max}$	1.000000	0.8544	0.8720	···	···	0.8255	0.8457	0.14
$T_{\max}/T_c$	···	1.6877	1.5371	···	···	1.0981	1.0653	···
$\chi_{\max}/\chi_0$	0.183939	0.41628	0.42957	···	···	0.46444	0.47310	0.73
$\chi_{\max}/\chi_c$	···	1.736	1.552	···	···	1.0277	1.017	···
Perpendicular Susceptibility								
$\chi_{\perp c}/\chi_0$	···	1.154701	1.136951					
b_T	···	0.4840··	0.4701715					
$\theta_{\max}$	0.416779	0.558···	0.617625					
$T_{\max}/T_c$	···	1.104···	1.08872··					
$\chi_{\perp\max}/\chi_0$	1.199678	1.2126··	1.183144					

NOTATION

q is the coordination number,

$$v = \tanh K = \tanh (J/kT), \qquad z = (1-v)/(1+v) = \exp(-2K),$$

$$K = J/kT, \qquad \theta = kT/qJ,$$

$$\alpha = \lim_{T\to T_c} [1-(v/v_c)]/[1-(T_c/T)],$$

Energy:

$$U_0 = \lim_{T\to 0} U(T) = \lim_{v\to 1} U(v),$$

$$A_\pm = \lim_{v_c - v\to 0\pm} [U(v)-U_c]/U_0[1-(v/v_c)] \ln|1-(v/v_c)|. \text{ [a]}$$

Entropy:

$$S^0 = \lim_{v\to -1} S(v) = \lim_{T\to 0} S(T) \quad (J<0).$$

Magnetization:

$$\beta = \lim_{v\to v_c} \ln I(v)/\ln[1-(v_c/v)] = -\lim_{T\to T_c} \ln I(T)/\ln[1-(T/T_c)],$$

$$D_T = \lim_{T\to T_c} I(T)/[1-(T/T_c)]^\beta.$$

Susceptibility:

$$\xi = (kT/Nm^2)\chi, \qquad \chi_0 = Nm^2/qJ = \chi_\perp(0),$$

$$\gamma = -\lim_{v\to v_c} \ln \xi(v)/\ln[1-(v/v_c)] = -\lim_{T\to T_c} \ln\chi(T)/\ln[1-(T_c/T)],$$

$$C_\pm = \lim_{v_c-v\to 0\pm} \xi(v)\,|1-(v/v_c)|^\gamma, \qquad C_T{}^\pm = \lim_{T-T_c\to 0\pm} \xi(T)\,|1-(T_c/T)|^\gamma,$$

$$B_\pm = \lim_{v_c-v\to 0\pm} [\xi(v)-\xi_c]/[1-(v/v_c)]\ln|1-(v/v_c)|, \text{ [a]}$$

$$b_T = \lim_{T\to T_c} [\chi_\perp(T)-\chi_{\perp c}]/\chi_\perp(0)[(T/T_c)-1]\ln|(T/T_c)-1|. \text{ [a]}$$

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[a] This may not be the exact form of the singularity in three dimensions.

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Dimer Statistics and Phase Transitions

P. W. Kasteleyn

Koninklijke/Shell-Laboratorium, Amsterdam, Netherlands, (Shell Internationale Research Maatschappij N.V.)

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After the introduction of the concept of lattice graph and a brief discussion of its role in the theory of the Ising model, a related combinatorial problem is discussed, namely that of the statistics of non-overlapping dimers, each occupying two neighboring sites of a lattice graph. It is shown that the configurational partition function of this system can be expressed in terms of a Pfaffian, and hence calculated explicitly, if the lattice graph is planar and if the dimers occupy all lattice sites. By the examples of the quadratic and the hexagonal lattice, it is found that the dimer system may show a phase transition similar to that of a two-dimensional Ising model, or one of a different nature, or no transition at all, depending on the activities of various classes of bonds. The Ising problem is then shown to be equivalent to a generalized dimer problem, and a rederivation, of Onsager's expression for the Ising partition function of a rectangular lattice graph is sketched on the basis of this equivalence.

I. INTRODUCTION

MANY aspects of the Ising model have been investigated by exact methods[1] since the publication of Onsager's solution of the two-dimensional problem.[2] In addition to their direct significance for the theory of phase transitions, the results thus obtained were important as a test for the various approximation methods which have been developed for the study of cooperative systems. It was found that approximate theories, though describing the overall properties of the model in a rather satisfactory way, fail to yield an adequate description of its most characteristic behavior, viz. that in the neighborhood of the transition temperature. This knowledge has, in turn, led to an increased interest in exact solutions of other combinatorial problems on crystal lattices. By studying a variety of problems one might hope to get some insight into such questions as: (a) Why, by the methods developed thus far, can the Ising problem be exactly solved for a one-dimensional lattice in an arbitrary magnetic field and for two-dimensional lattices with nearest neighbor interaction in the absence of a magnetic field, but not for any other system? (b) What determines the mathematical form of the singularities in the properties of the Ising model, and can the behavior at the singular point be predicted if the lattice and the interactions are known?

(a) The first question has been answered only partially thus far. It is easy to see that the applicability of the existing methods depends not only on the geometrical arrangement of the lattice sites (and thus, e.g., the dimensionality, in the usual, geometrical sense), but also on the way in which the sites combine to interacting pairs. On the other hand, it is obvious that when we represent the resulting structure by a *graph*, connecting any two interacting sites by a line, only the topological and not the metrical properties of this *lattice graph* are relevant.[3] We now know the determining property, at least for the success of the determinantal approach to the Ising problem introduced by Kac and Ward[4]: the partition function of a system can be expressed in terms of a single determinant only if its lattice graph is *planar*, i.e. can be imbedded (drawn without intersecting lines) in a plane. For lattice graphs which can be imbedded in a torus but not in a plane, one needs four determinants to express the partition function; more generally, for a graph which can be drawn on a surface of genus g,[5] but not on one of genus $g - 1$ (and which is, therefore, called[6] a *graph of genus* g), one needs 4^g determinants. In the limit $g \to \infty$, application of the method is impossible even in principle. It can easily be seen that the lattice graphs for which the Ising problem could not be solved are all of infinite genus. We thus see that the genus of the lattice graph

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[1] For a general review, see C. Domb, Advan. Phys. 9, 149 (1960).

[2] L. Onsager, Phys. Rev. 65, 117 (1944).

[3] A system in a magnetic field is equivalent to a system with a more complicated lattice graph in zero field; it is this graph which will then be called the lattice graph of the original system.

[4] M. Kac and J. C. Ward, Phys. Rev. 88, 1332 (1952); R. B. Potts and J. C. Ward, Progr. Theoret. Phys. (Kyoto) 13, 38 (1955); S. Sherman, J. Math. Phys. 1, 202 (1960).

[5] The *genus g of a surface* is the maximum number of nonintersecting closed curves which one can draw on the surface without disconnecting it. A plane and a sphere have $g = 0$, a torus $g = 1$, etc.

[6] D. König, *Theorie der endlichen und unendlichen Graphen* (Chelsea Publishing Company, New York, 1936, and 1950), p. 198.

plays a dominant role in the solubility of the Ising problem.

On the other hand, it is well known that several other combinatorial problems defined with respect to a lattice graph can be solved for *arbitrary graphs*, both planar and nonplanar. Among these we mention the problems of random walks on a lattice,[7] the distribution of electric current and potential in an infinite resistance network,[8] and the enumeration of trees, or branched polymers, in a lattice graph.[9]

It might be a real step forward if we understood clearly *why* in the Ising model the genus of the lattice graph plays such an important part, whereas in other problems it does not.

(b) There are various reasons for conjecturing that the behavior in the critical region is primarily determined by the dimensionality of the lattice graph.[1] The dimensionality dim L of an infinite lattice graph L can be defined with the aid of the asymptotic behavior, for $n \to \infty$, of the number N_n of lattice sites whose shortest path to a fixed site consists of n bonds of L: $\dim \mathrm{L} = 1 + \lim_{n\to\infty} (\ln N_n/\ln n)$. It is not necessarily equal to the geometrical dimensionality of the underlying point lattice. Thus, if in a two-dimensional, quadratic point lattice only horizontal neighbors are connected by a bond, the resulting (nonconnected) lattice graph has dimensionality 1. In those cases where exact solutions are available, they generally bear out the conjecture; numerical calculations seem to support its validity for three-dimensional lattices, and a comparison with other combinatorial problems shows that analogous quantities have singularities of the same mathematical form. However, no general relations between dimensionality and critical behavior of the Ising model have been rigorously established thus far.

In order to contribute to the discussion on these two points, we consider in this paper a cooperative problem which has recently been solved for a certain class of systems. It concerns the statistics of dimers on a crystal lattice, when each dimer occupies two neighboring lattice sites, and no dimers overlap. This "dimer problem" arises in the theory of liquids consisting of molecules of different size,[10] in the cell-cluster theory of the liquid state,[11] and in the theory of adsorption of diatomic molecules.[12] We concentrate mainly on the case of the dimers completely filling the lattice. A method for solving this problem for a rather general class of lattice graphs is developed in Sec. 2; as no use is made of the regular structure (periodicity) of a lattice graph, the terms "graph" and "lattice graph" are interchangeable in this section. In Secs. 3 and 4, two applications to particular lattices are given, and the phase transitions occurring there are discussed. A connection between the dimer problem and the Ising problem is derived in Sec. 5. The case of a quadratic lattice has been dealt with in detail in an earlier paper;[13] an alternative approach, leading to results identical to ours, has been independently developed by Temperley and Fisher.[14]

II. DIMER CONFIGURATIONS AND PFAFFIANS

Consider a *lattice graph* L consisting of N *sites* (points, vertices), connected by R *bonds* (lines, edges), which are divided into several classes, $\mathrm{C}_1, \mathrm{C}_2, \cdots, \mathrm{C}_h$ (e.g. the "horizontal" and "vertical" bonds in a simple quadratic lattice). *Dimers* (figures consisting of two points linked by a line) can be placed on L so as to occupy two sites connected by a bond. A (*close-packed*) *dimer configuration* on L is an arrangement of dimers on L such that all sites are singly occupied. Obviously no such arrangement is possible if the number of sites is odd; therefore let N be even, $N = 2M$. Let $g_{\mathrm{L}}(N_1, N_2, \cdots, N_h)$ be the number of dimer configurations occupying N_1 bonds from the class C_1, N_2 from $\mathrm{C}_2, \cdots, N_h$ from C_h $(N_1 + \cdots + N_h = \frac{1}{2} N = M)$. We want to derive an expression for *the generating function for dimer configurations on* L,

$$Z_{\mathrm{L}}(z_1, z_2, \cdots, z_h) = \sum_{N_1,\cdots,N_h} g_{\mathrm{L}}(N_1, \cdots, N_h) z_1^{N_1} \cdots z_h^{N_h}. \qquad (1)$$

The variables z_α $(\alpha = 1, \cdots, h)$ may be consider as activities, and Z_{L} as the *configurational partition function* of the dimer system. If all z_α are set equal to 1, Z_{L} reduces to the number of ways in which L can be filled with dimers.

It is not difficult to find a certain analogy with the Ising problem. There the determinantal method of Kac and Ward[4] was based on the fact that, by their cyclic character, configurations of polygons on a lattice are reminiscent of the terms in the

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[7] E. W. Montroll, J. Soc. Ind. Appl. Math. **4**, 241 (1956).

[8] H. Davies, Quart. J. Math. (Oxford) **6**, 232 (1955).

[9] H. N. V. Temperley, Discussions Faraday Soc. **25**, 92 (1958).

[10] E. A. Guggenheim, *Mixtures* (Clarendon Press, Oxford, England, 1952) Chap. X.

[11] E. G. D. Cohen, J. de Boer, and Z. W. Salsburg, Physica **21**, 137 (1955).

[12] T. S. Chang, Proc. Roy. Soc. (London) **A169**, 512 (1939).

[13] P. W. Kasteleyn, Physica **27**, 1209 (1961).

[14] H. N. V. Temperley and M. E. Fisher, Phil. Mag. **6**, 1061 (1961); M. E. Fisher, Phys. Rev. **124**, 1664 (1961).

expansion of a determinant. Here, the pairwise connection of lattice sites in a dimer configuration reminds one of the terms of another mathematical form, the Pfaffian.[15] The Pfaffian of a skew-symmetric $n \times n$ matrix $\mathbf{A}$ with elements $a(k, k')$ (n even $= 2m$) is defined by[16]

$$\mathrm{Pf}\,\mathbf{A} = \sum_{\mathrm{P}}{}' \epsilon_{\mathrm{P}}\, a(k_1, k_2)a(k_3, k_4) \cdots a(k_{n-1}, k_n) \qquad (2a)$$

$$= [m!\,2^m]^{-1} \sum_{\mathrm{P}} \epsilon_{\mathrm{P}}\, a(k_1, k_2) \cdots a(k_{n-1}, k_n). \qquad (2b)$$

The first sum runs over those permutations $\mathrm{P} = k_1k_2 \cdots k_n$ which satisfy $k_1 < k_2$; $k_3 < k_4$; $\cdots$, $k_{n-1} < k_n$, and $k_1 < k_3 < \cdots < k_{n-1}$; the second sum runs freely over all permutations, and ϵ_{P} is the signature of the permutation P ($\epsilon_{\mathrm{P}} = +1$ or -1 according as P is even or odd). The equivalence of Eqs. (2a) and (2b) follows from the skew symmetry of $\mathbf{A}$. An important property of Pfaffians is their relation to determinants:

$$[\mathrm{Pf}\,\mathbf{A}]^2 = \det \mathbf{A}. \qquad (3)$$

By analogy with the Kac–Ward method we shall now try to construct a skew-symmetric $N \times N$ matrix $\mathbf{D}$ with elements $d(k, k')$ such that Pf $\mathbf{D}$ is, in absolute value, equal to the generating function for close-packed dimer configurations on L:

$$|\mathrm{Pf}\,\mathbf{D}| = Z_{\mathrm{L}}(z_1, \cdots, z_h). \qquad (4)$$

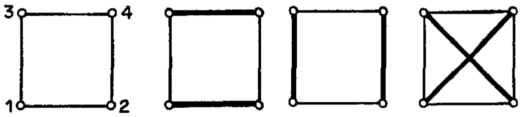
This will have been achieved if (a) there is a one-to-one correspondence between the nonvanishing different terms of Pf $\mathbf{D}$ and the dimer configurations on L; (b) to a dimer configuration occupying N_1 bonds from C_1, N_2 bonds from C_2, etc., there corresponds a term in Eq. (2a) of absolute magnitude $z_1^{N_1}z_2^{N_2} \cdots z_h^{N_h}$; (c) all terms have the same sign (either $+$ or $-$).

To satisfy condition (a), let the row and column indices of $\mathbf{D}$ correspond to the sites of L (numbered *in an arbitrary way*), and let

$$\left.\begin{array}{l} d(k, k') = 0 \text{ if the sites } k \text{ and } k' \text{ are not} \\ \text{connected by a bond.} \end{array}\right\} \qquad (5a)$$

Condition (b) can be fulfilled by defining

$$\left.\begin{array}{l} d(k, k') = -d(k', k) = \pm z_\alpha \text{ if } k \text{ and } k' \text{ are} \\ \text{connected by a bond of the class } \mathrm{C}_\alpha. \end{array}\right\} \qquad (5b)$$



(a) (b) (c) (d)

FIG. 1. (a) Example of a lattice graph; (b) and (c) Close-packed dimer configurations on this graph; (d) Representation of the vanishing term in the corresponding Pfaffian.

From Eqs. (5a) and (5b),

$$\mathrm{Pf}\,\mathbf{D} = \sum_{N_1, \cdots, N_h} \sum_{\mathrm{C}}^{(N_\alpha)} (\pm)\, z_1^{N_1} \cdots z_h^{N_h}, \qquad (6)$$

where the second sum runs over all configurations C with given values of N_α ($\alpha = 1, \cdots, h$). If, e.g., L is the lattice graph of Fig. 1a, and

$$\mathbf{D} = \begin{bmatrix} 0 & z_1 & z_2 & 0 \\ -z_1 & 0 & 0 & z_2 \\ -z_2 & 0 & 0 & z_1 \\ 0 & -z_2 & -z_1 & 0 \end{bmatrix},$$

then

$$\mathrm{Pf}\,\mathbf{D} = \epsilon_{1234}\, d(1, 2)\, d(3, 4) + \epsilon_{1324}\, d(1, 3)\, d(2, 4)$$
$$+ \epsilon_{1423}\, d(1, 4)\, d(2, 3) = +z_1^2 - z_2^2 + 0;$$

the three terms correspond successively to Figs. 1b and 1c (representing dimer configurations on L) and 1d (not representing a dimer configuration on L).

The crux of the problem lies in condition (c). For an arbitrary choice of signs in Eq. (5b), the terms in Eq. (6) will not have equal signs, owing to the occurrence of the signature ϵ_{P} in Eq. (2) and the skew symmetry of $\mathbf{D}$. It is formally possible, of course, to avoid all minus signs by working with a symmetric matrix, and its hafnian and permanent[17] (in whose definitions ϵ_{P} does not occur). However, this is of no use if we want to evaluate the partition function for a large periodic lattice, since we do not have a "permanent calculus" by which to calculate permanents of cyclic matrices. Therefore it has to be investigated whether it is possible to choose the signs in Eq. (5b) such as to satisfy condition (c). To facilitate the discussion, we represent the signs of the matrix elements by arrows along the bonds of L: an arrow pointing from site k to site k' will indicate that $d(k, k') > 0$, and hence $d(k', k) < 0$. To each choice of signs in Eq. (5b), then, corresponds an *orientation* of the lattice graph L.

Consider two configurations, C and C′, and further the graph consisting of the sites of L, the bonds of L occupied by C, and the bonds occupied by C′ (Fig. 2); it is made up of *double bonds* and *cycles* (closed paths without double points). Clearly, C′ can be obtained from C (and vice versa) by shifting,

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[15] For earlier references to this connection, cf. G. Brunel, Mém. Soc. Sci. Bordeaux (4) **5**, 165 (1895); W. T. Tutte, J. London Math. Soc. **22**, 107 (1947).

[16] T. Muir, *A Treatise on the Theory of Determinants* (Cambridge University Press, New York, 1904), p. 92.

[17] E. R. Caianiello, Nuovo Cimento **10**, 1634 (1953).

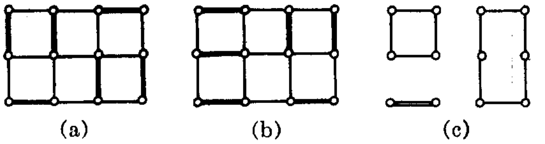

FIG. 2. (c) Transition graph of two close-packed dimer configurations (a) and (b).

in each of these cycles, all dimers by one step in either direction; therefore we call this graph the *transition graph* of C and C′, and its cycles *transition cycles*. As each cycle contains an *even* number of sites, the transition from C to C′ involves as many *odd* permutations of lattice sites as there are cycles in the transition graph. Now the sign of a term in Pf **D** is the product of the signature of a permutation and the signs of M matrix elements. From this, one readily sees that the terms representing C and C′ have equal signs if *in all cycles of the transition graph the number of bonds oriented in either direction is odd.* If, for a cycle of even length (*even cycle*), the parity of the number of bonds oriented in either direction is called the *orientation parity*, we thus have the following theorem:

(A) If the orientation of L which corresponds to **D** is such that the orientation parity of all transition cycles is odd, then $|\text{Pf } \mathbf{D}| = Z_L$.

From now on, the discussion will be restricted to *planar* lattice graphs, although for the next theorem a more general formulation can be given which holds for nonplanar graphs as well. A plane representation of a planar graph L is a *net* whose *meshes* are bounded by cycles (*mesh cycles*). The following theorems can easily be proved:

(B) A planar graph can be oriented in such a way that for all even mesh cycles the orientation parity is odd.

(C) If in an oriented planar graph the orientation parity of all even mesh cycles is odd, then the orientation parity of an arbitrary even cycle enclosing an even (odd) number of sites is odd (even).

(D) In a planar graph all transition cycles enclose an even number of sites.

From (A), (B), (C) and (D) we conclude that for planar lattice graphs, a matrix **D** can be defined such that $|\text{Pf } \mathbf{D}| = Z_L$. It is only in the proof of (C) and (D) that the planarity of the graph plays an essential role: if a nonplanar graph is represented in a plane (*with* intersecting lines, of course), neither (C) nor (D) is true.

When the dimers do not completely fill the lattice, i.e. when vacancies or monomers are present, the theory also ceases to be true. It is not difficult to construct a matrix whose Pfaffian generates all monomer–dimer configurations on a lattice graph. However, except for graphs such as that of Fig. 1(a), which have no "interior points," it is impossible to get all configurations correctly counted. The reason is that in this case a transition cycle may enclose an *odd* number of sites, e.g. one site occupied by a monomer, contrary to Theorem (D).

As in the case of the Ising model, the above method can be extended formally to cover nonplanar lattice graphs as well. For a toroidal graph, however, the partition function is a linear combination of *four* Pfaffians, etc., and for lattice graphs of infinite genus the method fails completely. The only use of this extension lies in the application to two-dimensional lattice graphs with periodic boundary conditions.[13]

III. THE QUADRATIC LATTICE

For a quadratic $m \times n$ lattice graph with $N = mn$ even, (suppose: m is even), the orientation sketched in Fig. 3 satisfies the condition of Theorem (A). According to (3), the evaluation of Pf **D** can be reduced to that of det **D**. If the class C_1 contains all "horizontal" and C_2 all "vertical" bonds, the matrix **D** has a periodic structure, so that it can be diagonalized, and its determinant evaluated. For the total partition function (generation function) $Z_{mn}(z_1, z_2)$ and the partition function per site for the infinite quadratic lattice, $Z(z_1, z_2)$, we then find

$$Z_{mn}(z_1, z_2) = \prod_{k=1}^{\frac{1}{2}m} \prod_{l=1}^{n} 2\left[z_1^2 \cos^2 \frac{k\pi}{m+1} + z_2^2 \cos^2 \frac{l\pi}{n+1}\right]^{\frac{1}{2}}, \quad (7)$$

$$\begin{aligned} Z(z_1, z_2) &= \lim_{\substack{m\to\infty \\ n\to\infty}} [Z_{mn}(z_1, z_2)]^{1/mn} \\ &= \exp\left\{(2\pi)^{-2} \int_0^{\pi} d\omega_1 \int_0^{\pi} d\omega_2 \ln 2[z_1^2 + z_2^2 \right. \\ &\qquad \left. + z_1^2 \cos\omega_1 + z_2^2 \cos\omega_2]\right\}. \quad (8) \end{aligned}$$

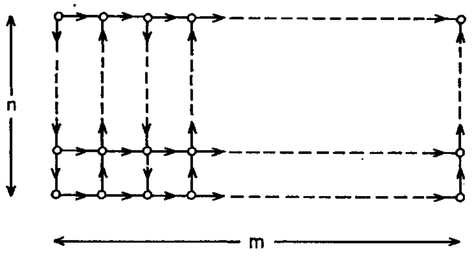

FIG. 3. Orientation of the $m \times n$ quadratic lattice graph, (m even).

The *molecular freedom* φ_2 of dimers in an infinite lattice defined as *the number of arrangements per dimer,* is given by

$$\varphi_2 = Z^2(1, 1) = \exp(2G/\pi) = 1.791\,622\,812 \cdots, \tag{9}$$

where $G = 1^{-2} - 3^{-2} + 5^{-2} - 7^{-2} + \cdots = 0.915\,965\,594 \cdots$ (Catalan's constant).

The expression (8) has a remarkable resemblance to Onsager's expression for the Ising partition function per site for an infinite rectangular lattice.[2] In fact, when z_1 and z_2 are replaced by sinh $(2J/kT)$ and sinh $(2J'/kT)$, where J and J' are the horizontal and vertical Ising coupling constants, Eq. (8) reduces, apart from uninteresting factors, to the Ising partition function *at the critical point* (which varies with J and J'). This is consistent with the fact that for no values of z_1/z_2 has Eq. (8) a singular point.[14]

It is possible to extend the dimer problem on a quadratic lattice so that a correspondence to the Ising problem *at all temperatures* is established. To achieve this, make a further distinction between various types of horizontal and vertical bonds, e.g. by introducing four activities, z_1, z_2, z_3 and z_4, as indicated in Fig. 4. The dimer partition has then, for real values of the activities, a singularity at $z_1 = z_2$, $z_3 = z_4$. The mathematical form of the singularity is the same as in the Ising partition function. If $z_1/z_2 = z_3/z_4 = u$, and if u is increased from 0 to ∞, a "phase transition" takes place at $u = 1$. We are used to relate such a transition to the appearance or disappearance of a certain ordering. It is not immediately evident, however, in which respect the phase with $u > 1$ or that with $u < 1$ is ordered. What is more, the symmetry of the system with respect to the transformation $u \rightarrow u^{-1}$ seems to exclude the possibility that one phase is ordered, and the other disordered. The solution to this dilemma is simple. It is possible to find *two order criteria* such that the phase with $u > 1$ is *ordered* with respect to the first criterion, but *disordered* with respect to the second, whereas the phase with $u < 1$ is *disordered* with respect to the first criterion, but *ordered* with respect to the second. A full discussion of these two kinds of order would take us too far, but it is intended to publish the details elsewhere.

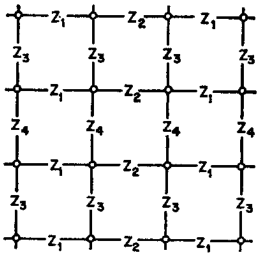

FIG. 4. Generalized quadratic lattice exhibiting a phase transition.

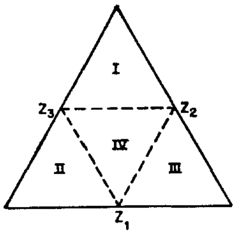

FIG. 5. The four phases of a close-packed system of dimers on a hexagonal lattice.

IV. THE HEXAGONAL LATTICE

When in the infinite hexagonal lattice graph three classes of bonds are distinguished, each one containing all bonds parallel to one of the three principal directions, a close-packed system of dimers on this lattice shows an interesting behavior.[18] The partition function per site, $Z(z_1, z_2, z_3)$, is a smoothly varying function of the activities z_1, z_2 and z_3 if these are in a "triangle relation", i.e. if $z_1 < z_2 + z_3$, $z_2 < z_3 + z_1$, $z_3 < z_1 + z_2$. If, on the other hand, one of the activities is larger than the sum of the other two, Z is identically equal to the square root of the largest activity, e.g., for $z_1 > z_2 + z_3$ we find $Z(z_1, z_2, z_3) \equiv z_1^{\frac{1}{2}}$, independent of z_2 and z_3. In words, when "z_1 bonds" are favored strongly enough, only one dimer configuration, viz. that with dimers only on z_1 bonds is realized. This is related to the fact that all transition cycles connecting this ordered configuration with other configurations have infinite length, i.e. that no configurations exist which deviate from it in the position of only a finite number of dimers. Obviously, a phase transition takes place when $z_1 = z_2 + z_3$; it can be shown that at the transition point $Z(z_1, z_2, z_3)$ behaves as $z_1^{\frac{1}{2}}[1+a(z_2+z_3-z_1)^{\frac{3}{2}}]$. Likewise we find a phase transition when $z_2 = z_3 + z_1$ and when $z_3 = z_1 + z_2$. The four phases of this system of dimers are best represented in a triangular diagram where the distances of a point to the three axes are proportional to z_1, z_2 and z_3. In Fig. 5, the regions I, II and III represent successively the

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[18] A similar behavior is found for a dimer system on a quadratic lattice graph if a suitable, but somewhat more artificial classification of bonds is introduced. This is not surprising, as the hexagonal lattice graph can be considered as a quadratic lattice graph with certain bonds removed (or having zero activity). On the other hand, there is also an (again less "natural") classification of the bonds of the hexagonal lattice graph for which the partition function shows the analytical behavior sketched in the previous section.

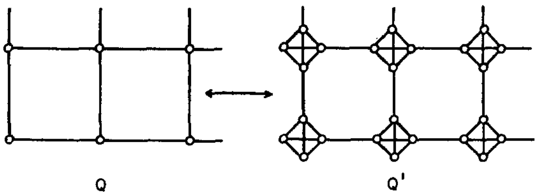

FIG. 6. Part of a finite simple quadratic lattice graph Q and the corresponding part of the cluster lattice graph Q′

ordered phases in which Z is identically equal to $z_1^{\frac{1}{2}}$, $z_2^{\frac{1}{2}}$ and $z_3^{\frac{1}{2}}$; region IV represents the disordered phase, in which Z is a more complicated, continuous function of all three activities. It is interesting to compare this behavior of a system of dimers on a hexagonal lattice with the peculiar properties of the Ising antiferromagnetic triangular lattice.[19]

A system like this will be realized when diatomic molecules with an electric dipole moment p fixed to the axis are adsorbed on a hexagonal surface (leaving no vacancies) in the presence of an electric field E. This system exhibits a phase transition at a temperature T_c given by $pE/kT_c = 2 \ln [\frac{1}{2}(1 + 3^{\frac{1}{2}} + 2^{\frac{1}{2}}3^{\frac{1}{4}})]$. A remarkable feature of this phase transition is that *at the transition point the system shows a perfect (directional) ordering*; when the temperature is lowered from $T = T_c$ to $T = 0$, this ordering exhibits no further change.

V. THE ISING PROBLEM

In Sec. II, we have seen that the dimer problem is analogous to the Ising problem in that it admits of a combinatorial solution involving one single determinant for planar lattices only. The relation between the two problems is much clarified by the fact that *the Ising problem can be formulated as a dimer problem*. This was implied already in the recent approach to the Ising problem by Hurst and Green.[20] Whereas these authors arrived at a Pfaffian by an algebraic method,[21] and did not introduce dimers at all, we shall reduce the Ising problem directly to a (generalized) dimer problem, which can then be solved by the method developed in Sec. II. In this way another purely combinatorial solution of the Ising problem is obtained.

It is well known[1] that the solution of the Ising problem for a simple quadratic lattice graph Q can be reduced to the determination of the number of ways in which a given number of horizontal and of vertical bonds can be selected so as to form closed polygons, i.e. configurations in which the number of selected bonds incident with any site is even (0, 2 or 4).

Now associate with Q another lattice graph Q′ in the following way: replace each site of Q by a cluster containing four sites, and each bond between two sites of Q by a bond between the opposite sites of two corresponding clusters; within the cluster, connect any site with any other (Fig. 6).

Consider a dimer configuration on the "cluster lattice" Q′. Since each cluster contains an even number of sites, the total number of dimers connecting it to neighboring clusters is even (0, 2 or 4). The analogy of these dimer configurations with the polygon configurations on Q, and therefore the possibility of translating them into each other, is obvious. More precisely, we have the following correspondence: (1) *With each dimer configuration on* Q′, *we can uniquely associate a polygon configuration on* Q. (2) *With each polygon configuration on* Q *we can associate a dimer configuration on* Q′; *this association, however, is not unique.* For a site of Q, where four or two bonds of a polygon meet, there is only one way of translating this local configuration with the aid of dimers, placed on the corresponding cluster of sites of Q′ (cf. Fig. 7(a), 7(b); in the latter case an extra dimer has to be introduced to connect the two sites which are not connected by a dimer to the sites of neighboring clusters. For a site of Q that does not lie on any polygon, on the other hand, there are three ways of translating, i.e. of connecting the four corresponding sites of Q′ [Fig. 7(c)].

If this correspondence had been purely one-to-one or purely one-to-three, we should have been able to enumerate polygon configurations on Q by

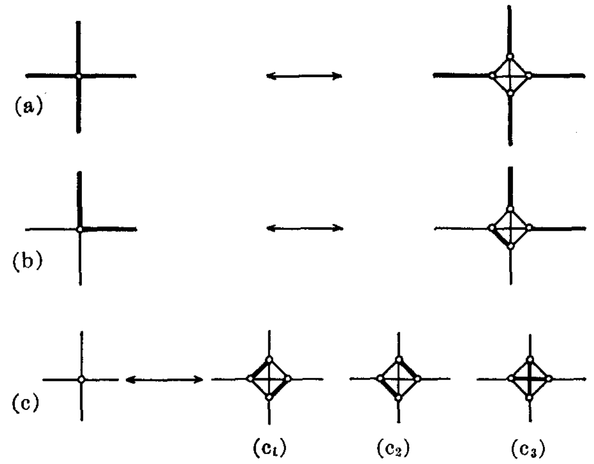

FIG. 7. Correspondence between local polygon configurations on Q and local dimer configurations on Q′.

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[19] R. M. F. Houtappel, Physica 16, 425 (1950).

[20] C. A. Hurst and H. S. Green, J. Chem. Phys. 33, 1059 (1960).

[21] Essentially the same method has been used by Fisher[14] in his solution of the dimer problem.

enumerating dimer configurations on Q′. Still, the mixed character of the correspondence is an advantage rather than a disadvantage. This becomes evident when we try to apply the method developed in Sec. II to the lattice graph Q′. It turns out that we cannot find the proper generating function for dimer configurations on Q′. Q′ is nonplanar (unless it is a $2 \times n$ lattice, but this restriction is not essential to what follows), and no orientation satisfying the condition of theorem (A) can be found. We can, however, easily orient the bonds of Q′ in such a way that the orientation parity of all even cycles *without self-intersections* is odd (Fig. 8). Then, the orientation parity of the transition cycles connecting the local dimer configurations (c_1) and (c_3), and (c_2) and (c_3), of Fig. 7 is even. This implies that the configuration (c_3) is counted with a different sign from that of (c_1) and (c_2). If then we put $z_\alpha = 1$ for all bonds connecting sites of the same cluster, the three local configurations on Q′ corresponding to a single isolated site in the polygon configuration on Q, are counted as $1 + 1 - 1 = 1$. So the nonplanarity of Q′ just compensates for the one-to-three correspondence between isolated sites on Q and isolated clusters on Q′. Apart from this effect, all dimer configurations on Q′ are correctly counted.

Therefore, if we let $|d(k, k')|$ be equal to x, y, 1 or 0, accordingly as k and k' are connected by a horizontal intercluster bond, a vertical intercluster bond, an intracluster bond, or no bond, and we choose the signs of the $d(k, k')$ in accordance with the orientation of Fig. 8, |Pf **D**| *is the generating function for polygon configurations on* Q. **D** is then equivalent to the matrix introduced by Hurst and Green.[20] The Pfaffian, and hence the Ising partition function, can, in principle, be calculated in the standard way. However, there is no simple way of diagonalizing **D** when the lattice graph has edges, i.e., is planar. For a toroidal lattice graph (lattice with periodic boundary conditions), on the other hand, the calculation is easy, although, of course, four Pfaffians (i.e., four matrices) must be introduced. Instead of carrying out the calculations, one may equally well prove that the four corresponding determinants are equal to those introduced by Potts and Ward[4] in their analysis of the Ising model.

The generalization of the above to arbitrary planar (toroidal) graphs is straightforward. The only care to be taken is that a site where an *odd* number of bonds, say p, meet, is replaced by a cluster of $p + 1$ sites in order that the number of dimers connecting the cluster to neighboring clusters be even. The addition of *two* extra sites has no effect.

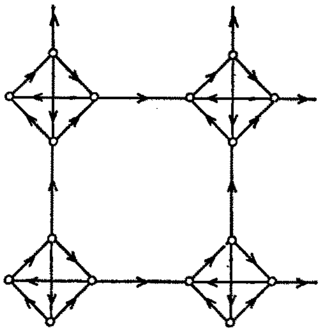

FIG. 8. An orientation of the cluster lattice graph Q′.

Finally, the Ising partition function of a lattice graph L *in the presence of a magnetic field* involves the enumeration of configurations of polygons *and open chains* on L. This is equivalent to the enumeration of configurations of dimers *and monomers* on the cluster lattice L′, for which the present method is not adequate. Only if the ends of the open chains are fixed to certain lattice sites of L, can the above method be used; the clusters of L′ corresponding to these sites should then consist of an odd number of sites. This is important for the calculation of the correlations and the spontaneous magnetization of an infinite lattice.

VI. CONCLUDING REMARKS

It has been shown that the dimer problem has many features in common with the Ising problem. Like the latter, it can only be solved for planar (or toroidal) lattices, under a restrictive condition (no monomers present). It should be added that, here too, the partition function for a one-dimensional lattice can be exactly calculated even if this condition is not fulfilled.[11,14] Morevover, it has been shown that the Ising problem is a special case of a generalized dimer problem (where dimer configurations are not counted as different when they differ within a "cluster"). This approach to the Ising problem has the advantage of making more natural the appearance of square roots of determinants as the fundamental quantities (e.g. in the analysis of toroidal lattices, where linear combinations of Pfaffians rather than of determinants occur).

The question of why the genus plays a part in these problems and not in others, has not been answered. The form of the singularity in the partition function, however, has been found to be of the well-known type again, although in particular cases (e.g. the hexagonal lattice), the specific form of the problem may lead to the appearance of additional singularities of a different mathematical form.

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Time-Dependent Statistics of the Ising Model*

Roy J. Glauber
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts

The individual spins of the Ising model are assumed to interact with an external agency (e.g., a heat reservoir) which causes them to change their states randomly with time. Coupling between the spins is introduced through the assumption that the transition probabilities for any one spin depend on the values of the neighboring spins. This dependence is determined, in part, by the detailed balancing condition obeyed by the equilibrium state of the model. The Markoff process which describes the spin functions is analyzed in detail for the case of a closed N-member chain. The expectation values of the individual spins and of the products of pairs of spins, each of the pair evaluated at a different time, are found explicitly. The influence of a uniform, time-varying magnetic field upon the model is discussed, and the frequency-dependent magnetic susceptibility is found in the weak-field limit. Some fluctuation-dissipation theorems are derived which relate the susceptibility to the Fourier transform of the time-dependent correlation function of the magnetization at equilibrium.

INTRODUCTION

THE statistical study of systems of strongly interacting particles is beset by many problems, largely mathematical in nature. These difficulties have motivated theorists to devote a great deal of effort to devising and studying the simplest sorts of model systems which show any resemblance to those occurring in nature. The property most desired in these models is mathematical transparency. The deeper insights offered by the possibility of exact treatment are intended to compensate for any unrealistic simplifications in the formulation. The first, and most successful of these models is one introduced by Ising[1] in an attempt to explain the ferromagnetic phase transition. While many generalizations of this model have been studied, we may note that the first true understanding of a phase transition in an interacting system was reached by Onsager[2] for the case of the two-dimensional Ising model.

If the mathematical problems of equilibrium statistical mechanics are great, they are at least relatively well-defined. The situation is quite otherwise in dealing with systems which undergo large-scale changes with time. The principles of nonequilibrium statistical mechanics remain in largest measure unformulated. While this lack persists, it may be useful to have in hand whatever precise statements can be made about the time-dependent behavior of statistical systems, however simple they may be. We have attempted, therefore, to devise a form of the Ising model whose behavior can be followed exactly, in statistical terms, as a function of time. While certain of the assumptions underlying the model are to a degree arbitrary, it is surely one of the simplest ones involving N coupled particles for which exact time-dependent solutions can be found.

The model we shall discuss is a stochastic one. The spins of N fixed particles are represented as stochastic functions of time $\sigma_j(t)$, ($j = 1, \cdots N$), which are restricted to the values ± 1, and make transitions randomly between these two values. These transitions take place because of the interaction of the spins with an external agency which may be regarded as a heat reservoir. The transition probabilities of the individual spins, however, are assumed to depend on the momentary values of the neighboring spins as well as on the influence of the heat bath. It is for this reason that statistical correlations arise between the values of neighboring spins. The coupling of the spins through their transition probabilities makes it necessary, in mathematical terms, to deal with the entire N-spin system as a unit. The spin functions form a Markoff process of N discrete random variables with a continuous time variable as argument. Fortunately, if the coupling of the spins is not too complicated, the differential equations governing the probabilities may be simplified greatly, making it possible to solve for all of the quantities of immediate physical interest by elementary means.

In the sections that follow, we introduce first the individual spins interacting with the heat bath, then the means by which they are coupled to one another. The description of the behavior of the model

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* A brief account of this work was given at the Washington, D. C. meeting of the American Physical Society, 1960 [R. J. Glauber, Bull. Am. Phys. Soc. 5, 296 (1960)].

[1] E. Ising, Z. Physik 31, 253 (1925).

[2] L. Onsager, Phys. Rev. 65, 117 (1944).

is then formulated as a matter of solving for the expectation values of the spin functions and of their products. We center the subsequent discussion largely upon explicit solutions for the single-spin and two-spin averages, since most of the interesting properties of the system may be constructed in terms of these. In addition we find the time-delayed spin correlation function, i.e. the average product of two spin variables, each evaluated at a different time. We then describe the model in the presence of a uniform, time-varying magnetic field. Two results of this generalization are a derivation of the complex frequency-dependent magnetic susceptibility for weak fields, and a discussion of fluctuation–dissipation relations which hold when the field-induced departures from equilibrium are small. Our efforts, in the present paper, are confined to treating a one-dimensional model which, as already indicated by the treatment of the Ising model at equilibrium,[2] appears to be a great deal simpler than dealing with the model in two or more dimensions.

SINGLE-SPIN SYSTEM

It may be helpful in introducing our model to begin by discussing the most simple of such systems: a single particle whose interaction with a heat reservoir of some sort causes its spin to flip between the values $\sigma = 1$ and $\sigma = -1$ randomly, but at a known rate. We assume that no magnetic field is present so that neither of the states $\sigma = \pm 1$ is preferred. Then, if the rate per unit time at which the particle makes transitions from either state to the opposite one is written as $\alpha/2$, the probability $p(\sigma, t)$ that the spin takes on the value σ at time t obeys the equation

$$(d/dt)p(\sigma, t) = -\tfrac{1}{2}\alpha p(\sigma, t) + \tfrac{1}{2}\alpha p(-\sigma, t). \tag{1}$$

This equation, or more properly, this pair of equations for $\sigma = \pm 1$, preserves the normalization condition

$$p(1, t) + p(-1, t) = 1. \tag{2}$$

The pair of equations is therefore immediately reducible to a single equation for a single unknown function. A convenient choice of the latter function is the difference of the two probabilities

$$\begin{aligned} q(t) &= p(1, t) - p(-1, t) \\ &= \sum_{\sigma=\pm1} \sigma p(\sigma, t), \end{aligned} \tag{3}$$

which is simply the expectation value of the spin as a function of time, i.e. if we think of the time-dependent spin variable as a stochastic function $\sigma(t)$ taking on the values $\sigma = \pm 1$ we have

$$q(t) = \langle \sigma(t) \rangle. \tag{4}$$

The equation obeyed by the mean spin is seen from (1) to be

$$(d/dt)q(t) = -\alpha q(t), \tag{5}$$

so that the mean spin simply decays exponentially with a relaxation time $1/\alpha$ from whatever value it is known to have initially,

$$q(t) = q(0)e^{-\alpha t}. \tag{6}$$

We may regain the individual probabilities $p(\pm 1, t)$ from a knowledge of $q(t)$ by means of the identities (2) and (3) which together yield

$$p(\sigma, t) = \tfrac{1}{2}[1 + \sigma q(t)]. \tag{7}$$

MANY-SPIN SYSTEM

Particles such as the one we have just discussed, each of them responding to a random spin-flipping agency, will form the basic units of the model we wish to describe. We shall assume that these particles are arranged in a regularly spaced linear array which may be closed to form an N-particle ring. The dynamical resemblance between this model and the Ising model rests on the assumption that the individual spins of the ring are not wholly independent stochastic functions. We may, for example, introduce a tendency for a particular spin σ_j $(j = 1 \cdots N)$ to correlate with its neighboring spins by assuming that its transition probabilities between the states $\sigma_j = \pm 1$ depend appropriately on the momentary spin values of the other particles. To treat any such model we must consider the entire ring as a unit and introduce a set of 2^N probability functions $p(\sigma_1, \cdots \sigma_N t)$, one for each complexion, i.e. each set $\sigma_1, \cdots \sigma_N$ for the ring.

If we let $w_j(\sigma_j)$ be the probability per unit time that the jth spin flips from the value σ_j to $-\sigma_j$, while the others remain momentarily fixed, then we may write the time derivative of the function $p(\sigma_1, \cdots \sigma_N t)$ as

$$\begin{aligned} \frac{d}{dt} p(\sigma_1, \cdots \sigma_N t) &= -[\sum_j w_j(\sigma_j)] p(\sigma_1, \cdots \sigma_N t) \\ &\quad + \sum_j w_j(-\sigma_j) p(\sigma_1, \cdots -\sigma_j, \cdots \sigma_N t), \end{aligned} \tag{8}$$

i.e., the complexion $\sigma_1, \cdots \sigma_N$ is destroyed by a flip of any of the spins σ_j, but it may also be created by spin flip from any complexion of the form $\sigma_1, \cdots -\sigma_j, \cdots \sigma_N$. We shall refer to Eq. (8) as the master equation since its solution would contain the most complete description of the system available.

CORRESPONDENCE WITH THE ISING MODEL

We have already mentioned that the transition probabilities $w_j(\sigma_j)$ may be chosen to depend on neighboring spin values as well as on σ_j. If we want, for example, to describe a tendency for each spin to align itself parallel to its nearest neighbors we may choose the probabilities $w_j(\sigma_j)$ to be of the form

$$w_j(\sigma_j) = \tfrac{1}{2}\alpha\{1 - \tfrac{1}{2}\gamma\sigma_j(\sigma_{j-1} + \sigma_{j+1})\}, \tag{9}$$

which may be seen to take on three possible values

$$w_j(\sigma_j) = \tfrac{1}{2}\alpha(1-\gamma), \qquad \tfrac{1}{2}\alpha, \qquad \tfrac{1}{2}\alpha(1+\gamma). \tag{10}$$

The value $\frac{1}{2}\alpha$ corresponds to the case in which the neighboring spins are antiparallel, $\sigma_{j-1} = -\sigma_{j+1}$. When the neighboring spins are parallel to each other the transition probability takes on the value $\frac{1}{2}\alpha(1-\gamma)$ for σ_j parallel to the two of them or $\frac{1}{2}\alpha(1+\gamma)$ for σ_j antiparallel. Clearly as long as γ is positive the parallel configurations will be longer-lived than the antiparallel ones and we shall be dealing with a model having ferromagnetic tendencies. Conversely negative γ will mean a tendency of neighboring spins to remain aligned oppositely, and will describe the antiferromagnetic case. We note, incidently, that $|\gamma|$ may not exceed unity.

The parameter α which occurs in the transition probabilities simply describes the time scale on which all transitions take place. It has, of course, no analog in the familiar discussions of the Ising model at equilibrium. The parameter γ, however, describes the tendency of spins toward alignment and thereby determines the equilibrium state of the present model much as the exchange interaction does in the Ising model. To indicate the quantitative correspondence between the models we write the Hamiltonian for the linear Ising model as

$$\mathcal{H} = -J\sum_l \sigma_l\sigma_{l+1}. \tag{11}$$

When the Ising model has reached equilibrium at temperature T, the probability that the jth spin will take on the value σ_j as opposed to $-\sigma_j$ (for a given set of values of the neighboring spins) is just proportional to the Maxwell–Boltzmann factor $\exp(-\mathcal{H}/kT)$. The ratio of the probabilities $p_j(-\sigma_j)$ and $p_j(\sigma_j)$ corresponding to the two states for the jth spin is therefore

$$\frac{p_j(-\sigma_j)}{p_j(\sigma_j)} = \frac{\exp[-(J/kT)\sigma_j(\sigma_{j-1}+\sigma_{j+1})]}{\exp[(J/kT)\sigma_j(\sigma_{j-1}+\sigma_{j+1})]}. \tag{12}$$

If the spins other than σ_j are considered as fixed, the stochastic model described by (8) and (9) will approach an equilibrium in which

$$\frac{p_j(-\sigma_j)}{p_j(\sigma_j)} = \frac{w_j(\sigma_j)}{w_j(-\sigma_j)} \tag{13}$$

$$= \frac{1 - \frac{1}{2}\gamma\sigma_j(\sigma_{j-1}+\sigma_{j+1})}{1 + \frac{1}{2}\gamma\sigma_j(\sigma_{j-1}+\sigma_{j+1})}. \tag{14}$$

The exponentials which occur in the ratio (12) may be written in the forms

$$\begin{aligned}\exp\,&[\pm(J/kT)\sigma_j(\sigma_{j-1}+\sigma_{j+1})] \\ &= \cosh\left[\frac{J}{kT}(\sigma_{j-1}+\sigma_{j+1})\right] \\ &\quad \pm \sigma_j \sinh\left[\frac{J}{kT}(\sigma_{j-1}+\sigma_{j+1})\right] \qquad (15)\\ &= \cosh\left[\frac{J}{kT}(\sigma_{j-1}+\sigma_{j+1})\right] \\ &\quad \times\left\{1 \pm \tfrac{1}{2}\sigma_j(\sigma_{j-1}+\sigma_{j+1})\tanh\frac{2J}{kT}\right\}, \qquad (16)\end{aligned}$$

the latter of which is readily checked for the three values the function can take on. The correspondence between the ratios of the equilibrium probabilities (12) and (14) may evidently be made precise by identifying the constant γ as

$$\gamma = \tanh(2J/kT). \tag{17}$$

We should mention that the particular choice we have made for the way in which the transition probabilities (9) depend on neighboring spin values is motivated more by the desire for simplicity than for generality. There exist other, but less simple, coupling schemes which also yield the same equilibrium states as the Ising model with nearest-neighbor interactions. Some of these are discussed in the Appendix. There exists, furthermore, the possibility that each spin is coupled through the transition probabilities to some or all of its more distant neighbors. We shall mention this possibility further at a later point. For the present we shall continue to deal with the transition probabilities (9) and discuss the mathematical treatment of the master equation based on them.

REDUCTION OF THE PROBABILITY FUNCTION

The functions $p(\sigma_1, \cdots \sigma_N t)$ which satisfy the master equation (8) furnish, as we have noted earlier, the fullest possible description of the system. While we cannot deny that it would be desirable to know these functions in their entirety we must nevertheless point out that, for N large, they contain vastly more information than we usually require in practice. To answer the most familiar physical questions about the system, in fact, it suffices to know just the probabilities that individual spins or pairs of spins occupy specified states. Alternatively, we need know only the expectation values of spins or the average products of pairs of spins. Most of our attention in the present paper will be devoted to discussing just these functions. However before proceeding to the discussion, it may be helpful to indicate some general relations between the probability functions and the expectation values of products of spin variables.

We define the functions $q_j(t)$ to be the expectation values of the spins $\sigma_j(t)$ regarded as stochastic functions of time:

$$\begin{aligned} q_j(t) &= \langle \sigma_j(t) \rangle \\ &= \sum_{\{\sigma\}} \sigma_j p(\sigma_1, \cdots \sigma_N t). \end{aligned} \tag{18}$$

Here and in future work we designate by a sum over $\{\sigma\}$, a sum carried out over the 2^N values of the set $\sigma_1, \cdots \sigma_N$. The functions $r_{j,k}(t)$ are defined, likewise, as the expectation values of the products $\sigma_j(t)\sigma_k(t)$:

$$\begin{aligned} r_{j,k}(t) &= \langle \sigma_j(t)\sigma_k(t) \rangle \\ &= \sum_{\{\sigma\}} \sigma_j \sigma_k p(\sigma_1, \cdots \sigma_N t). \end{aligned} \tag{19}$$

We note in particular that the "diagonal" expectation values $r_{j,j}$ are identically unity:

$$r_{j,j}(t) = 1. \tag{20}$$

We next construct a general identity relating the probability to the expectation values as follows: Let σ_j and σ_j' be two possibly different values of the jth spin. Then the function $\frac{1}{2}(1+\sigma_j\sigma_j')$ equals unity for $\sigma_j' = \sigma_j$ and zero for $\sigma_j' = -\sigma_j$. We may therefore construct an identity expressing $p(\sigma_1, \cdots \sigma_N t)$ as a sum over all spins by writing

$$\begin{aligned} p(\sigma_1, \cdots \sigma_N t) &= \frac{1}{2^N} \\ \times \sum_{\{\sigma'\}} (1+\sigma_1\sigma_1') &\cdots (1+\sigma_N\sigma_N') p(\sigma_1', \cdots \sigma_N', t). \end{aligned} \tag{21}$$

If we expand the product in the summand of this relation and carry out the indicated summations, we find

$$\begin{aligned} p(\sigma_1, \cdots \sigma_N, t) = \frac{1}{2^N} \{ 1 &+ \sum_j \sigma_j q_j(t) \\ &+ \sum_{j \neq k} \sigma_j \sigma_k r_{j,k}(t) + \cdots \}, \end{aligned} \tag{22}$$

which exhibits a general expansion of the probability functions in terms of the expectation values of the spins and their products taken two at a time, three at a time, etc., i.e. the functions 1 and σ form a complete orthogonal basis for the expansion of any function of σ, and (22) is just such an expansion with N independent variables. The relation (7) for a single spin is a trivial example of the expansion.

The reduced probability functions which furnish the probabilities that individual spins or pairs of spins occupy specified states, whatever may be the states of the remaining spins, are defined by

$$p_j(\sigma_j, t) = \sum_{\{\sigma \neq \sigma_j\}} p(\sigma_1, \cdots \sigma_N, t), \tag{23}$$

$$p_{jk}(\sigma_j, \sigma_k, t) = \sum_{\{\sigma \neq \sigma_j, \sigma_k\}} p(\sigma_1, \cdots \sigma_N, t), \tag{24}$$

where the notation is intended to indicate summation over all the spin variables save σ_j in (23) and σ_j and σ_k in (24). If these summations are carried out upon the form (22) for $p(\sigma_1, \cdots \sigma_N, t)$ we find

$$p_j(\sigma_j, t) = \tfrac{1}{2}\{1 + \sigma_j q_j(t)\}, \tag{25}$$

$$\begin{aligned} p_{jk}(\sigma_j, \sigma_k, t) = \tfrac{1}{4}\{1 &+ \sigma_j q_j(t) \\ &+ \sigma_k q_k(t) + \sigma_j \sigma_k r_{j,k}(t)\}. \end{aligned} \tag{26}$$

It should be clear that by solving for the expectation values of the spins and their products we are beginning a systematic expansion of the probability functions as well as finding the quantities of greatest physical interest.

As a preliminary step to finding the time-dependent equations satisfied by the expectation values, we may write the master equation (8) in the more compact form

$$\begin{aligned} &\frac{d}{dt} p(\sigma_1, \cdots \sigma_N, t) \\ &= -\sum_m \sigma_m \sum_{\sigma_m'} \sigma_m' w_m(\sigma_m') p(\sigma_1, \cdots \sigma_m', \cdots \sigma_N, t). \end{aligned} \tag{27}$$

If we multiply both sides of this relation by σ_k and sum over all values of the σ variables we obtain

$$\begin{aligned} (d/dt) q_k(t) &= -2 \sum \sigma_k w_k(\sigma_k) p(\sigma_1, \cdots \sigma_N, t) \\ &= -2 \langle \sigma_k(t) w_k[\sigma_k(t)] \rangle. \end{aligned} \tag{28}$$

Similarly, if both sides of (27) are multiplied by the product $\sigma_j \sigma_k$ (where $j \neq k$) and summed over the σ variables we obtain

$$\begin{aligned}\frac{d}{dt}r_{j,k}(t) &= -2\sum_{\{\sigma\}}\sigma_j\sigma_k\{w_j(\sigma_j)+w_k(\sigma_k)\}p(\sigma_1,\cdots\sigma_N,t)\\ &= -2\langle\sigma_j(t)\sigma_k(t)\{w_j[\sigma_j(t)]+w_k[\sigma_k(t)]\}\rangle. \qquad (29)\end{aligned}$$

If we substitute the form (9) for the transition probabilities in (28) we obtain a recursive system of differential equations for the expectation values $q_k(t)$:

$$(d/d\alpha t)q_k(t) = -q_k(t) + \tfrac{1}{2}\gamma\{q_{k-1}(t)+q_{k+1}(t)\}. \qquad (30)$$

An analogous system of equations for the expectation values of products of pairs of spins results from the substitution of (9) in (29). For $j \neq k$ we have

$$\begin{aligned}(d/d\alpha t)r_{j,k}(t) = -2r_{j,k}(t) + \tfrac{1}{2}\gamma\{r_{j,k-1}(t)\\ + r_{j,k+1}(t) + r_{j-1,k}(t) + r_{j+1,k}(t)\}, \qquad (31)\end{aligned}$$

while for $j = k$, the functions obey the identity (20).

These equations, as we shall see, may be solved quite readily. It is worth noting, however, that the assumption of forms different from (9) for the transition probabilities leads, in many cases, to systems of equations in which the expectation values of products of differing numbers of spins are coupled in each equation. Such systems are considerably less tractable than the present one.

SOLUTION FOR THE AVERAGE SPINS: INFINITE RING

The coupled differential equations (30) are particularly easy to solve for the case of an infinite ring, $N \rightarrow \infty$. It is convenient, for this case, to alter slightly the scheme for numbering the spins by labeling a particular spin as the zeroth and designating those to one side of it with positive integers and those to the other side with negative ones. We then construct the generating function

$$F(\lambda, t) = \sum_{k=-\infty}^{\infty}\lambda^k q_k(t), \qquad (32)$$

which, according to Eq. (30), satisfies the differential equation

$$(\partial/\partial\alpha t)F(\lambda,t) = -F(\lambda,t) + \tfrac{1}{2}\gamma(\lambda+\lambda^{-1})F(\lambda,t). \qquad (33)$$

The solution for the generating function is evidently

$$F(\lambda,t) = F(\lambda,0)\exp\left[-\alpha t + \tfrac{1}{2}\gamma(\lambda+\lambda^{-1})\alpha t\right], \qquad (34)$$

which furnishes us an implicit solution for the $q_k(t)$ in terms of the initial values $q_k(0)$. To make the solution an explicit one we note that one of the factors in (34) is just the generating function for the Bessel functions of imaginary argument,[3]

$$\exp\left[\tfrac{1}{2}x(\lambda+\lambda^{-1})\right] = \sum_{n=-\infty}^{\infty}\lambda^n I_n(x), \qquad (35)$$

where

$$I_n(x) = i^{-n}J_n(ix). \qquad (36)$$

Hence the time-dependent generating function is given by

$$F(\lambda,t) = F(\lambda,0)e^{-\alpha t}\sum_{k=-\infty}^{\infty}\lambda^k I_k(\gamma\alpha t). \qquad (37)$$

We consider first the case in which all of the spin expectations q_k vanish initially except for one, which we may choose to be the one at the origin

$$q_k(0) = \delta_{k,0}. \qquad (38)$$

Then the initial value of the generating function is just unity, and at later times it is

$$F(\lambda,t) = e^{-\alpha t}\sum_{k=-\infty}^{\infty}\lambda^k I_k(\gamma\alpha t), \qquad (39)$$

from which we conclude, by comparing with (32), that the spin expectations are given by

$$q_k(t) = e^{-\alpha t}I_k(\gamma\alpha t). \qquad (40)$$

An examination of the functions I_k shows that q_0 decreases steadily to zero as time increases, while the neighboring spin expectations rise from zero to positive values for a while as a form of transient polarization induced by the positive spin at the origin. The functions q_k for spins neighboring the origin rise for times $t \ll k/\gamma\alpha$ as

$$q_k(t) \approx (1/|k|!)(\tfrac{1}{2}\gamma\alpha t)^{|k|}e^{-\alpha t}. \qquad (41)$$

They then reach a maximum[4] at a time given, for $k \gg 1$, by $\alpha t \approx k(1-\gamma^2)^{-\frac{1}{2}}$, and, for much larger times, decrease as

$$q_k(t) \sim (2\pi\gamma\alpha t)^{-\frac{1}{2}}e^{-\alpha(1-\gamma)t}. \qquad (42)$$

The most general solution for the spin expectation values, corresponding to an arbitrary set of initial values $q_k(0)$, may clearly be obtained from (40) by linear superposition,

$$q_k(t) = e^{-\alpha t}\sum_{m=-\infty}^{\infty}q_m(0)I_{k-m}(\gamma\alpha t), \qquad (43)$$

where we note that the functions I_n for negative

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[3] See, for example, G. N. Watson, *Bessel Functions* (Cambridge University Press, Cambridge, England, 1958), pp. 14 and 77.

[4] The locations of the maxima and various other properties of the functions $e^{-ax}I_n(x)$ for $a \geq 1$ are discussed by E. W. Montroll, J. Math and Phys. **25**, 37 (1946).

order are the same as those for positive order, $I_n = I_{-n}$.

AVERAGE SPINS: FINITE RING

A somewhat more general means of treating the set of equations (30) for arbitrary N may be based on a system of normal modes for the spin expectation values q_k. If we seek solutions to Eqs. (30) in the form

$$q_k(t) = A\zeta^k e^{-\nu t}, \tag{44}$$

where A is a constant, then we have

$$\nu = \alpha\{1 - \tfrac{1}{2}\gamma(\zeta^{-1} + \zeta)\}. \tag{45}$$

The closure of the N-spin ring requires that the solution (44) be periodic in k with period N, i.e., that $\zeta^N = 1$. Hence there are N roots for ζ of the form

$$\zeta_m = \exp(2\pi i m/N), \quad m = 0, 1, \cdots N - 1, \tag{46}$$

and for these the eigenvalues ν_m are

$$\nu_m = \alpha\{1 - \gamma \cos(2\pi m/N)\}. \tag{47}$$

The system of mode functions $q_k^{(m)} = \exp(2\pi i m k/N)$ forms a complete orthogonal basis on the ring. Hence any solution to (30) may be written in the form

$$q_k(t) = \sum_{m=0}^{N-1} A_m e^{(2\pi i m k/N) - \nu_m t}, \tag{48}$$

where the constants A_m may be solved for in terms of the $q_k(0)$ by using the orthogonality theorem. These constants are

$$A_m = \frac{1}{N} \sum_{l=1}^{N} q_l(0) e^{-2\pi i m l/N}. \tag{49}$$

The solution for the spin expectation values in terms of their initial values is thus

$$\begin{aligned} q_k(t) &= \frac{1}{N} \sum_{l,m} q_l(0) e^{(2\pi i m/N)(k-l) - \nu_m t} \\ &= e^{-\alpha t} \sum_{l=1}^{N} \sum_{j=-\infty}^{\infty} q_l(0) I_{k-l+jN}(\gamma\alpha t). \end{aligned} \tag{50}$$

The latter form of the solution is obtained from the former by carrying out the summation over m explicitly. That the solutions may be expressed in this way is obvious from the fact that the problem for a finite ring may be solved by inserting periodic initial values in (43).

A particular consequence of the solution (50) is the fact that the total magnetization always decreases exponentially,

$$\sum_k q_k(t) = e^{-\alpha(1-\gamma)t} \sum_l q_l(0), \tag{51}$$

a result which corresponds to the known absence of permanent magnetization in the linear Ising model (with interactions restricted to a finite number of neighbors). The net effect of the spin interactions is to reduce the coefficient in the exponent from the α of Eq. (6) to $\alpha(1 - \gamma)$.

SOLUTION FOR ONE SPIN FIXED

It is interesting to investigate the behavior of the spin system when one of the spins is assumed somehow to be fixed or frozen. We shall, for simplicity, consider the infinite ring and let the zeroth spin, the one at the origin, take on the fixed value $\sigma_0 = 1$. Then the differential equations derived earlier for the $q_k(t)$ still hold for $k \neq 0$. In particular, for $k = 1$, we have

$$(d/d\alpha t)q_1(t) = -q_1(t) + \tfrac{1}{2}\gamma\{1 + q_2(t)\}, \tag{52}$$

while the equations for $k > 1$ assume precisely the form (30). This sequence of equations for $k \geq 1$ is an inhomogeneous one because of the constant term on the right-hand side of (52). It possesses a nonvanishing equilibrium solution, which satisfies the recursion relation

$$q_k = \tfrac{1}{2}\gamma\{q_{k-1} + q_{k+1}\}, \qquad k \neq 0, \tag{53}$$

where $q_0 = 1$. The solution to such a linear difference equation may be written as

$$q_k = \eta^{|k|}, \tag{54}$$

where η satisfies the quadratic equation

$$\eta^2 - 2\gamma^{-1}\eta + 1 = 0. \tag{55}$$

It is worth noting that the same quadratic equation for η holds for negative values of k as for positive values of k, i.e., the equation is unchanged by the substitution of η^{-1} for η. The roots of (55), which are always real, form a reciprocal pair. One member of the pair, $\gamma^{-1}\{1 + (1 - \gamma^2)^{\frac{1}{2}}\}$, always has absolute value greater than unity for $|\gamma| \leq 1$ and therefore is of no use in solving the problem for an infinite ring. The correct root for η has absolute value less than unity and is given by

$$\eta = \gamma^{-1}\{1 - (1 - \gamma^2)^{\frac{1}{2}}\}. \tag{56}$$

For this value, using the correspondence (17) with the static Ising model, we find

$$\eta = \tanh(J/kT). \tag{57}$$

The solution (54) exhibits clearly the tendency of any spin, in this case a fixed one, to surround itself with a "polarization cloud." (In the antiferromagnetic case, $\gamma < 0$, the signs of the induced spins will alternate.) The value of η given by (57) is just the familiar short-range order parameter of the Ising model.

To complete the solution of the time-dependent equations for the $q_k(t)$, with the zeroth spin fixed, we need only note that (54) constitutes a particular solution of the inhomogeneous system. We may add to it any solution to the homogeneous system of equations obtained by requiring q_0 to vanish at all times. Such a boundary condition may easily be satisfied by using the method of images, since the requirement $q_0 = 0$ separates the system into two halves which do not influence each other. (The infinite ring need not be imagined as closed.) If we seek a solution to the homogeneous system of equations in which the q_k assume a particular set of initial values, say v_k for $k > 0$, we may reach a solution for the positive-k half of the system by using the general solution (43) and imagining that the initial values of the q_k at the negative sites are given by $q_{-k}(0) = -v_k$ for $k > 0$, and that we have $q_0(0) = 0$. Interpreted in this way for $k > 0$, the solution (43) may be made to fit the correct initial conditions and yet, since it remains odd at k at all times, meet the boundary condition $q_0(t) = 0$ as well. An analogous imaging procedure solves the equations for negative k as well.

To find the general solution to the time-dependent equations with the zeroth spin fixed we must add together the particular solution (54) for the inhomogeneous system and the general solution, constructed by the method of images, for the homogeneous system, i.e., we add to the solution η^k the solution to the homogeneous system which corresponds for $k > 0$ to the set of initial values $q_k(0) - \eta^k$. The resulting solution for $k > 0$ is

$$q_k(t) = \eta^k + e^{-\alpha t} \sum_{l=1}^{\infty} (q_l(0) - \eta^l) \times \{I_{k-l}(\gamma\alpha t) - I_{k+l}(\gamma\alpha t)\}. \tag{58}$$

An analogous solution exists for negative k values. For times $t \gg (\gamma\alpha)^{-1}$, the solutions in all cases decay exponentially to the equilibrium form.

SOLUTION FOR THE SPIN CORRELATIONS

We next turn our attention to the average values of products of pairs of spin variables. The functions $r_{j,k}(t)$ which express these averages obey the two-index system of Eqs. (31) for $j \neq k$, and for $j = k$ obey the identity $r_{j,j} = 1$. We can secure a rapid insight into the behavior of these functions by simplifying the problem so that they depend, in effect, on only one index. It often happens, in fact, that our knowledge of the initial state of the system is characterized by translational invariance, i.e., our initial knowledge about all of the spins is the same. Then $r_{j,k}(0)$ can only depend on $j - k$, and no other dependence on j or k can be present at later times. In that case it becomes convenient to introduce the abbreviation

$$r_m = r_{k,k+m} \tag{59}$$

for the spin correlation functions. We shall consider this translationally invariant situation first and then return to the more general one presently.

In the uniform case the functions r_m are seen to obey the relations

$$(d/d\alpha t)r_m(t) = -2r_m(t) + \gamma\{r_{m-1}(t) + r_{m+1}(t)\} \tag{60}$$

for $m \neq 0$, and

$$r_0(t) = 1. \tag{61}$$

Aside from a trivial change of a factor of two in the coefficients, this is precisely the sequence of equations we solved in the preceding section, for the single-spin averages with the zeroth spin fixed. The factor of two in the coefficients affects only the time scale in which the functions change. In particular, the equilibrium solution on the infinite chain is again given by

$$r_m = \eta^{|m|}, \tag{62}$$

where η is the short-range order parameter mentioned earlier. The time-dependent solution for arbitrary initial correlations may be constructed immediately from (58). For $m > 0$ we have

$$r_m(t) = \eta^m + e^{-2\alpha t} \sum_{l=1}^{\infty} [r_l(0) - \eta^l] \times \{I_{m-l}(2\gamma\alpha t) - I_{m+l}(2\gamma\alpha t)\}. \tag{63}$$

As a particular example of the type of problem to which this result is applicable, we may suppose that the spin system is suddenly subjected to a change of temperature; i.e., after coming to equilibrium with a heat reservoir at temperature T_0, it is suddenly placed in contact with another heat bath at a different temperature T. In that case the initial values of the r_l are given by

$$r_l(0) = \eta_0^l = [\tanh (J/kT_0)]^l, \tag{64}$$

and the way these relax into the equilibrium values at temperature T is shown by (63).

We return now to the general problem of solving the two-index system of differential equations (31) without the simplifying assumption of translational invariance. The system is an inhomogeneous one because of the condition $r_{k,k}(t) = 1$, which plays a role similar to that of the fixed spin in the preceding section. The translationally invariant equilibrium solution $r_{k,l} = \eta^{|k-l|}$, which we have just discussed, clearly satisfies the system of equations. It can be used as a particular solution to the inhomogeneous system. To this particular solution, we must add a general solution to the homogeneous system obtained by supplementing (31) with the conditions $r_{k,k}(t) = 0$. The solutions to these equations may be obtained and the boundary conditions met by generalizing the methods of the preceding sections to deal with a two-index array $r_{j,k}(t)$, i.e. a matrix, rather than a linear sequence $q_j(t)$.

If, for the moment, we ignore the boundary condition on $r_{k,k}(t)$ and assume that Eqs. (31) hold even for $j = k$, it becomes a simple matter to solve the equations by using a two-parameter generating function analogous to (39). We then find that if all of the initial values of $r_{j,k}(0)$ vanish except one, which is unity, i.e.,

$$r_{j,k}(0) = \delta_{jl}\delta_{km}, \tag{65}$$

the solution for $r_{j,k}(t)$ is

$$r_{j,k}(t) = e^{-2\alpha t} I_{j-l}(\gamma\alpha t) I_{k-m}(\gamma\alpha t). \tag{66}$$

Such solutions may be superposed to secure the appropriate initial values and to meet the condition $r_{k,k}(t) = 0$. To satisfy the latter condition, we must generalize to a two-index array the method of images used earlier.

The matrix $r_{j,k}(t)$ is, or course, symmetric. However, it is quite convenient to think of it as if it were antisymmetric. What we shall do is fix our attention, for the moment, on the values of $r_{j,k}(t)$ for $j > k$ and only attempt to deal correctly with these. We assume that these matrix elements take on their correct initial values but that the elements $r_{k,j}(0)$ are given by $-r_{j,k}(0)$ for $j > k$, and that $r_{j,j}(0) = 0$. The matrix $r_{j,k}$ which is thus assumed initially antisymmetric, maintains its antisymmetry at later times and, therefore, always meets the condition $r_{j,j}(t) = 0$. In fact, it satisfies the sequence of equations (31) including, in virtue of its antisymmetry, the equation of the same form for $j = k$. We need not be embarrassed, therefore, by our inclusion of the $j = k$ equations in the arguments leading to (66).

The basic set of solutions we seek, which meets the initial condition (65) and the boundary condition $r_{j,j}(t) = 0$, is just the solution (66) antisymmetrized in the two indices l and m, i.e., for $j \geq k$ and $l \geq m$

$$r_{j,k}(t) = e^{-2\alpha t}\{I_{j-l}(\gamma\alpha t) I_{k-m}(\gamma\alpha t) - I_{j-m}(\gamma\alpha t) I_{k-l}(\gamma\alpha t)\}. \tag{67}$$

The general solution to the homogeneous system is obtained by superposing the solutions (67). In order to solve the inhomogeneous system with which we began, we must add the particular solution η^{j-k} to the solutions we have just found. The form which satisfies the correct initial conditions for $j \geq k$ is

$$r_{j,k}(t) = \eta^{j-k} + e^{-2\alpha t} \sum_{l>m} [r_{l,m}(0) - \eta^{l-m}] \times \{I_{j-l}(\gamma\alpha t) I_{k-m}(\gamma\alpha t) - I_{j-m}(\gamma\alpha t) I_{k-l}(\gamma\alpha t)\}, \tag{68}$$

which is the general solution for the expectation values of the spin products. When translational invariance holds, this solution may be seen to reduce to (63) by applying the relation

$$I_k(2x) = \sum_{m=-\infty}^{\infty} I_{k+m}(x) I_m(x), \tag{69}$$

which is a special case of the addition theorem for Bessel functions.[5]

TIME-DELAYED SPIN CORRELATION FUNCTIONS

The functions $r_{j,k}(t)$, which we have discussed up to this point, describe whatever tendency the pairs of spins σ_j and σ_k may have to be correlated in direction, on the average, at a particular instant of time t. Not all of the spin correlations of interest, however, have this instantaneous character. In particular, variation of any one spin at a given instant induces polarizations among its neighbors which only become appreciable after finite intervals of time. To describe correlation effects extending over an interval of length t', we shall discuss the functions $\langle \sigma_j(t) \sigma_k(t + t') \rangle$, i.e. the expectation values of the products of the stochastic spin functions σ_j evaluated at time t, and σ_k evaluated at time $t + t'$.

To evaluate these more general correlation functions we represent the values assumed by the spins at time t as $\sigma_1, \cdots \sigma_N$ and at the later time $t + t'$ as $\sigma_1', \cdots \sigma_N'$. The probability associated with the spin values $\sigma_1, \cdots \sigma_N$ at time t is $p(\sigma_1, \cdots \sigma_N, t)$, i.e., the solution to the master equation which satisfies whatever initial conditions our physical knowledge imposes. In order to carry out the averaging correctly, we must also know the probability associated with the final configuration $\sigma_1', \cdots \sigma_N'$ at time $t + t'$. The question we ask in determining that

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[5] Reference 3, p. 361.

probability is rather different from the one answered by $p(\sigma_1, \cdots \sigma_N, t)$, since we assume that the spins are known to have the values $\sigma_1, \cdots \sigma_N$ at time t. The values $\sigma_1, \cdots \sigma_N$ are thus to be regarded as initial spin values in determining the probability of finding $\sigma_1', \cdots \sigma_N'$ at a time t' later. We shall write this conditional probability for finding $\sigma_1', \cdots \sigma_N'$ as $p(\sigma_1, \cdots \sigma_N \mid \sigma_1', \cdots \sigma_N' t)$. The expectation value we seek for the product of two spins may then be constructed by summing over all possible values of the sets $\sigma_1, \cdots \sigma_N$ and $\sigma_1', \cdots \sigma_N'$ as follows:

$$\langle\sigma_j(t)\sigma_k(t+t')\rangle = \sum_{\{\sigma\}\{\sigma'\}} p(\sigma_1, \cdots \sigma_N t)\sigma_j p(\sigma_1, \cdots \sigma_N \mid \sigma_1', \cdots \sigma_N' t')\sigma_k'. \tag{70}$$

The part of this summation which is to be carried out over the variables $\sigma_1', \cdots \sigma_N'$ may be regarded simply as the expectation value of the kth spin when the spins are initially $\sigma_1, \cdots \sigma_N$. We may then write

$$\sum_{\{\sigma'\}} p(\sigma_1, \cdots \sigma_N \mid \sigma_1', \cdots \sigma_N', t')\sigma_k' = q_k(t'), \tag{71}$$

where it is understood that the initial values of the q_k are given by $q_k(0) = \sigma_k$. For the case of an infinite chain, the functions $q_k(t')$ are given in terms of these initial values by the general solution (43) as

$$q_k(t') = e^{-\alpha t'} \sum_l \sigma_l I_{k-l}(\gamma\alpha t'). \tag{72}$$

By substituting (71) and (72) into (70) we find

$$\langle\sigma_j(t)\sigma_k(t+t')\rangle = e^{-\alpha t'} \sum_{l=-\infty}^{\infty} I_{k-l}(\gamma\alpha t') \sum_{\{\sigma\}} p(\sigma_1, \cdots \sigma_N t)\sigma_j\sigma_l. \tag{73}$$

The summation over $\sigma_1, \cdots \sigma_N$, however, is just the instantaneous correlation $r_{j,k}(t)$ defined by (19). The time-delayed correlation function, therefore, reduces to

$$\langle\sigma_j(t)\sigma_k(t+t')\rangle = e^{-\alpha t'} \sum_{l=-\infty}^{\infty} r_{j,l}(t) I_{k-l}(\gamma\alpha t'), \tag{74}$$

where the functions $r_{j,l}(t)$ are given, in general, by the results of the preceding section.

For the particular case of a system in thermal equilibrium at temperature T, the correlation function depends only on the interval t', i.e.,

$$\langle\sigma_j(t)\sigma_k(t+t')\rangle_T = e^{-\alpha t'} \sum_{l=-\infty}^{\infty} \eta^{|j-k+l|} I_l(\gamma\alpha t'). \tag{75}$$

The term corresponding to $l = k - j$ is the only contribution which would be present if there were no correlations between spins in the initial state, as would be true, for example, for infinite temperature. The remaining terms of the series describe the stabilizing effects upon the kth spin of the polarizations which exist about it in the initial state. For either sign of γ, the addition of the effects of neighboring spins in (75) makes the correlation function decrease in magnitude more slowly with increasing t'.

In all of our work to date, we have assumed that we are in possession of some knowledge about the system at an initial time $t = 0$, and have sought, in a probabilistic sense, to answer questions about the behavior of the system at later times. Of course, the same questions may be asked in a reversed sense. What may we say, on the basis of knowledge at $t = 0$, about the behavior of the system at negative times? Since the dynamical properties of our model are presumably reversible, there is no need to construct or solve a new master equation. The probabilities are simply even functions of time. The time t is to be construed more generally as $|t|$ in all of the probability functions we have calculated thus far. In particular, the time-dependent spin correlation function (75) may be written for $t = 0$ and arbitrary t' as

$$\langle\sigma_j(0)\sigma_k(t')\rangle_T = e^{-\alpha|t'|} \sum_{l=-\infty}^{\infty} \eta^{|j-k+l|} I_l(\gamma\alpha\,|t'|). \tag{76}$$

SINGLE SPIN IN A MAGNETIC FIELD

It is not difficult to formulate the equations which describe the behavior of our model when it is placed in a uniform magnetic field. The influence of the magnetic field H, which we suppose is parallel to the axis of spin quantization, is to introduce a preference of the spins for either the $\sigma = 1$ or the $\sigma = -1$ state. For the most simple case, in which only a single spin is present, the transition probability from σ to $-\sigma$ may be written as

$$w(\sigma) = \tfrac{1}{2}\alpha(1 - \beta\sigma).$$

If we equate the ratios of the equilibrium probabilities calculated according to the stochastic model and according to statistical mechanics, we find

$$\begin{aligned}\frac{p(-\sigma)}{p(\sigma)} = \frac{w(\sigma)}{w(-\sigma)} &= \frac{1-\beta\sigma}{1+\beta\sigma} \\ &= \frac{\exp\,[-(\mu H/kT)\sigma]}{\exp\,[(\mu H/kT)\sigma]} \\ &= \frac{1-\sigma\tanh\,(\mu H/kT)}{1+\sigma\tanh\,(\mu H/kT)},\end{aligned} \tag{77}$$

where μ is the magnetic moment associated with the spins or, more concisely, we find the correspondence

$$\beta = \tanh(\mu H/kT). \tag{78}$$

The equation satisfied by the expectation value of the spin is then

$$(d/d\alpha t)q(t) = \beta - q(t). \tag{79}$$

In the work that follows, it will be interesting to be able to discuss the behavior of the spins in time-dependent magnetic fields. Since the arguments of statistical mechanics used in treating the Ising model deal only with constant magnetic fields, we are free in defining the stochastic model to choose any time-dependence of the parameter β which yields (78) when H is constant. The simplest way of defining a time-dependent β is to retain the relation (78) when H depends on time. The solution for the average spins is then

$$q(t) = q(t_0)e^{-\alpha(t-t_0)} + \int_{t_0}^{t} e^{-\alpha(t-t')}\beta(t')\alpha\, dt', \tag{80}$$

where t_0 is a time at which q is known initially.

SPIN SYSTEM IN A MAGNETIC FIELD

To construct a stochastic analog of the Ising model in a magnetic field, we must first find an appropriate set of transition probabilities. To this end we note that the Hamiltonian of the Ising model is

$$\mathcal{H} = -\mu H \sum_m \sigma_m - J \sum_m \sigma_m\sigma_{m+1}, \tag{81}$$

so that, if the spins other than σ_j are considered as fixed, the ratio of equilibrium probabilities for the states $-\sigma_j$ and σ_j is

$$\begin{aligned}\frac{p_j(-\sigma_j)}{p_j(\sigma_j)} &= \frac{\exp\{-(1/kT)\sigma_j[J(\sigma_{j-1}+\sigma_{j+1})+\mu H]\}}{\exp\{(1/kT)\sigma_j[J(\sigma_{j-1}+\sigma_{j+1})+\mu H]\}}\\ &= \frac{w_j(\sigma_j)\exp[-(\mu H/kT)\sigma_j]}{w_j(-\sigma_j)\exp[(\mu H/kT)\sigma_j]},\end{aligned} \tag{82}$$

where the identities (12) and (13) were used in securing the latter relation. If we write the transition probabilities for the model in a magnetic field as $w_j'(\sigma_j)$, the detailed balancing condition at equilibrium requires

$$\begin{aligned}\frac{w_j'(\sigma_j)}{w_j'(-\sigma_j)} &= \frac{p_j(-\sigma_j)}{p_j(\sigma_j)}\\ &= \frac{w_j(\sigma_j)[1-\sigma_j\tanh(\mu H/kT)]}{w_j(-\sigma_j)[1+\sigma_j\tanh(\mu H/kT)]}.\end{aligned} \tag{83}$$

Hence our model will approach the same equilibrium state as the Ising model if we choose

$$\begin{aligned}w_j'(\sigma_j) &= w_j(\sigma_j)[1-\sigma_j\tanh(\mu H/kT)]\\ &= w_j(\sigma_j)(1-\beta\sigma_j)\\ &= \tfrac{1}{2}\alpha\{1-\beta\sigma_j+\tfrac{1}{2}\gamma(\beta-\sigma_j)(\sigma_{j-1}+\sigma_{j+1})\}.\end{aligned} \tag{84}$$

The difference-differential equations satisfied by the average spins and the average products are easily constructed by means of (28) and (29). For the average spins we find the sequence of equations

$$\begin{aligned}(d/d\alpha t)q_k(t) = {}& -q_k(t) + \beta\\ &+ \tfrac{1}{2}\gamma[q_{k-1}(t) + q_{k+1}(t)]\\ &- \tfrac{1}{2}\beta\gamma[r_{k-1,k}(t) + r_{k,k+1}(t)],\end{aligned} \tag{85}$$

which differs from the sequence (30) considered earlier by the inclusion of the inhomogeneous term β and, more importantly, through the inclusion of the pair-correlation terms $r_{k-1,k}$ and $r_{k,k+1}$. The equations for the pair correlation are likewise found to contain terms proportional to other correlation functions, i.e., the single-spin expectations and the expectation of the product of three spins. Such equations appear, because of their mixed structure, to be essentially more difficult to solve than those treated earlier. It is not difficult, however, to solve them in the limit of weak magnetic fields, $\mu H \ll kT$, and by doing so we are able to discuss the time-dependent magnetic susceptibility of the system.

In the weak-field limit, the parameter β is proportional to the magnetic field, $\beta = \mu H/kT$. The first-order changes of the averages $q_k(t)$ may be found from Eqs. (85) by using as a zeroth approximation for the functions $r_{k-1,k}$ and $r_{k,k+1}$ the solution (68) derived for them in our earlier work. The equations for the $q_k(t)$ become in this way an inhomogeneous sequence, with the inhomogeneous terms proportioned to H. The solution of these equations is simplified considerably if we assume that the model is in thermal equilibrium to zeroth order in H, i.e., that the field induces only small departures from equilibrium. In that case we have

$$r_{k-1,k} = r_{k,k+1} = \eta, \tag{86}$$

which is independent of k, and Eqs. (85) reduce to the sequence

$$\frac{d}{d\alpha t}\, q_k = -q_k + \tfrac{1}{2}\gamma(q_{k-1} + q_{k+1}) + \beta(1 - \gamma\eta). \tag{87}$$

We shall assume, as before, that the definition of β holds for time-dependent magnetic fields as well as stationary ones. The inhomogeneous term in (87) may also be written, by using Eq. (55), as

$$\beta(1-\gamma\eta) = \frac{\mu H(t)}{kT}\,\frac{1-\eta^2}{1+\eta^2}. \tag{88}$$

The sequence of Eqs. (87) differs from the sequence (52), which we solved earlier, only by the inclusion of this inhomogeneous term. Since the term is independent of k, the particular solution required may be chosen independent of k as well. Finding the particular solution is then a matter of treating the simplest of first-order linear differential equations. The general solution to the sequence (87) for an infinite chain is

$$\begin{aligned} q_k(t) &= e^{-\alpha(t-t_0)} \sum_l q_l(t_0) I_{k-l}[\gamma\alpha(t-t_0)] \\ &\quad + \frac{\mu}{kT}\,\frac{1-\eta^2}{1+\eta^2}\int_{t_0}^{t} e^{-\alpha(1-\gamma)(t-t')} H(t')\alpha\, dt', \end{aligned} \tag{89}$$

where again we have let t_0 be the initial time. Since the model is assumed to be in thermal equilibrium before the magnetic field is turned on at time t_0, the initial values of the q_l may be taken to vanish. The spin expectations therefore all have the value given by the integral term of (89).

We now introduce the stochastic magnetization function

$$M(t) = \mu \sum_k \sigma_k(t), \tag{90}$$

whose average value is given by the sum

$$\langle M(t)\rangle = \mu \sum_k q_k(t). \tag{91}$$

If we let the initial time recede into the past, $t_0 \to -\infty$, the average magnetization obtained by summing (89) becomes

$$\langle M(t)\rangle = \frac{\mu^2 N}{kT}\,\frac{1-\eta^2}{1+\eta^2}\int_{-\infty}^{t} e^{-\alpha(1-\gamma)(t-t')} H(t')\alpha\, dt'. \tag{92}$$

For the case of a magnetic field which varies harmonically, $H(t) = H_0 e^{-i\omega t}$, we may define a complex, frequency-dependent magnetic susceptibility $\chi(\omega)$ via the relation

$$\langle M(t)\rangle = \chi(\omega) H_0 e^{-i\omega t}. \tag{93}$$

The susceptibility is then given by

$$\begin{aligned} \chi(\omega) &= \frac{\mu^2 N}{kT}\,\frac{1-\eta^2}{1+\eta^2}\,\frac{\alpha}{\alpha(1-\gamma)-i\omega} \\ &= \frac{\mu^2 N}{kT}\,\frac{1+\eta}{1-\eta}\,\frac{\alpha(1-\gamma)}{\alpha(1-\gamma)-i\omega}. \end{aligned} \tag{94}$$

In particular, in the low-frequency limit $\omega \to 0$, we find the static susceptibility

$$\chi(0) = \frac{\mu^2 N}{kT}\,\frac{1+\eta}{1-\eta} = \frac{\mu^2 N}{kT}\exp\frac{2J}{kT}, \tag{95}$$

which is the familiar result furnished by the Ising model.

FLUCTUATION-DISSIPATION THEOREMS

It is interesting to note that our result (94) for the magnetic susceptibility is closely related to the result (76) for the time-dependent correlation function. If we sum the correlation functions (76) over the indices j and k by means of the generating function (35), and multiply by μ^2, we find the time-dependent correlation function for the magnetization,

$$\langle M(0)M(t')\rangle_T = \mu^2 N\,\frac{1+\eta}{1-\eta}\,e^{-\alpha(1-\gamma)|t'|}. \tag{96}$$

The Fourier transform of this function is

$$\begin{aligned} &\int_{-\infty}^{\infty} \langle M(0)M(t')\rangle_T e^{i\omega t'}\, dt' \\ &\qquad = \mu^2 N\,\frac{1+\eta}{1-\eta}\,\frac{2\alpha(1-\gamma)}{\alpha^2(1-\gamma)^2+\omega^2} \\ &\qquad = \frac{2kT}{\omega}\,\mathrm{Im}\,\chi(\omega), \end{aligned} \tag{97}$$

i.e., the imaginary, or dissipative part of the magnetic susceptibility is proportional to the Fourier transform of the time-dependent magnetization correlation function. We thus have in hand a particularly simple example of a fluctuation–dissipation relation. Although the derivation we have given depends on the explicit evaluation of the functions involved, analogous relations are known to hold for a wide class of mechanical systems. These relations are derived from statistical mechanics by discussing the way in which perturbations of the Liouville equation affect the distribution function or density matrix and the expectation values derived from them. Since the model we are discussing, on the other hand, is a stochastic one, our equations do not follow the dynamics of the spin variables in detail. In place of the quantum-mechanical Liouville equation we have the master equation, which has altogether different properties. Our model, nevertheless, does permit the statement of a number of simple identities analogous to the fluctuation–dissipation theorems of statistical mechanics, but differing from them slightly in form. Since these relations may be of use in finding the effect of a weak field upon the average values of quite general functions of the spin variables, we shall derive them here.

We denote the change of any quantity A induced by the presence of the weak magnetic field by the increment symbol ΔA. The change of the transition probabilities according to (84) is then

$$\begin{aligned}\Delta w_i(\sigma_i) &= w_i'(\sigma_i) - w_i(\sigma_i)\\ &= -(\mu H/kT)\sigma_i w_i(\sigma_i). \qquad (98)\end{aligned}$$

The first-order changes of the quantities involved in the master equation (27) are related by

$$\begin{aligned}&\frac{d}{dt}\Delta p(\sigma_1', \cdots \sigma_N', t)\\ &= -\sum_l \sigma_l' \sum_{\sigma_l''} \sigma_l''\{\Delta w_l(\sigma_l'')p(\sigma_1', \cdots \sigma_l'', \cdots \sigma_N', t)\\ &\qquad + w_l(\sigma_l'')\Delta p(\sigma_1', \cdots \sigma_l'', \cdots \sigma_N', t)\}. \qquad (99)\end{aligned}$$

Now if $p(\sigma_1', \cdots \sigma_N' \mid \sigma_1, \cdots \sigma_N t)$ is a conditioned probability function in the sense described earlier, i.e., it satisfies the unperturbed master equation and reduces to $\prod_j \delta_{\sigma_j \sigma_j'}$ for $t = 0$, then it constitutes a Green's function for the sequence of Eqs. (99). If the initial time is $-\infty$, the solution to (99) may be written as

$$\begin{aligned}&\Delta p(\sigma_1, \cdots \sigma_N, t) = -\sum_{\{\sigma'\}} \sum_l \sigma_l' \sum_{\sigma_l''} \sigma_l''\\ &\quad\times \int_{-\infty}^{t} \Delta w_l(\sigma_l'', t')p(\sigma_1', \cdots \sigma_l'', \cdots \sigma_N', t')\\ &\quad\times p(\sigma_1', \cdots \sigma_N' \mid \sigma_1, \cdots \sigma_N, t - t')\, dt'. \qquad (100)\end{aligned}$$

We next substitute the expression (98) for the increment of the transition probabilities into (100) and sum explicitly over the values of σ'', finding

$$\begin{aligned}&\Delta p(\sigma_1, \cdots \sigma_N, t) = \frac{\mu}{kT}\sum_{\{\sigma'\}} \sum_l \sigma_l'\\ &\times \int_{-\infty}^{t} H(t')\{w_l(\sigma_l', t')p(\sigma_1', \cdots \sigma_l', \cdots \sigma_N', t')\\ &+ w_l(-\sigma_l', t')p(\sigma_1', \cdots -\sigma_l', \cdots \sigma_N, t')\}\\ &\times p(\sigma_1', \cdots \sigma_N' \mid \sigma_1, \cdots \sigma_N, t - t')\, dt'. \qquad (101)\end{aligned}$$

The detailed balancing relation (83) assures us that the two products within the curly brackets of (101) are equal, i.e. that the probability increment may be simplified to the form

$$\begin{aligned}&\Delta p(\sigma_1, \cdots \sigma_N, t)\\ &\quad= \frac{2\mu}{kT}\sum_l \sum_{\{\sigma'\}} \int_{-\infty}^{t} H(t')p(\sigma_1', \cdots \sigma_N', t')\sigma_l' w_l(\sigma', t')\\ &\quad\times p(\sigma_1', \cdots \sigma_N' \mid \sigma_1, \cdots \sigma_N, t - t')\, dt'. \qquad (102)\end{aligned}$$

To evaluate the change induced by the magnetic field in the expectation value of any function of the σ variables, $F(\sigma_1, \cdots \sigma_N)$, we have only to multiply Eq. (102) through by F and sum over spins σ_i. The integrand on the right-hand side may then be recognized as an equilibrium-state average of a product of three stochastic functions. Expressed in this way, the change of the average value of F becomes

$$\begin{aligned}&\Delta\langle F[\sigma_1(t), \cdots \sigma_N(t)]\rangle\\ &= \frac{2\mu}{kT}\int_{-\infty}^{t} \sum_l \langle \sigma_l(t')w_l[\sigma_l(t)]F[\sigma_1(t), \cdots \sigma_N(t)]\rangle_T\\ &\qquad\qquad \times H(t')\, dt'. \qquad (103)\end{aligned}$$

In particular, when the transition probabilities are given by (9) we find more simply

$$\begin{aligned}&\Delta\langle F[\sigma_1(t), \cdots \sigma_N(t)]\rangle\\ &= \frac{\mu}{kT}\alpha(1 - \gamma)\int_{-\infty}^{t} \sum_l \langle \sigma_l(t')F[\sigma_1(t), \cdots \sigma_N(t)]\rangle_T\\ &\qquad\qquad \times H(t')\, dt'. \qquad (104)\end{aligned}$$

If the function F is taken to be the magnetization, we find that it obeys the relation

$$\begin{aligned}&\Delta\langle M(t)\rangle = \langle M(t)\rangle\\ &\quad= \frac{1}{kT}\alpha(1 - \gamma)\int_{-\infty}^{t} \langle M(t')M(t)\rangle_T H(t')\, dt'. \qquad (105)\end{aligned}$$

Since the equilibrium state is stationary, the thermal average in the integrand can only depend on $t - t'$. Hence for the case of a harmonic field $H(t) = H_0 e^{-i\omega t}$, we find

$$\chi(\omega) = \frac{1}{kT}\alpha(1 - \gamma)\int_0^{\infty} \langle M(0)M(t)\rangle_T e^{i\omega t}\, dt. \qquad (106)$$

The foregoing relations are rather similar in structure to the complex forms of the fluctuation–dissipation theorems of statistical mechanics, and furnish us with similar information. They differ from those relations, however, in two respects illustrated by comparing (97) and (106). The former equation relates the imaginary part of the susceptibility to the transform of the correlation function, while the latter relates the real part to it with a different proportionality constant. Although both types of relation hold true for the model at hand, it is interesting to see how the difference between them arises. For this purpose let us consider the stochastic function

$$L(t) = -2\mu \sum_m \sigma_m(t)w_m(\sigma_m, t). \qquad (107)$$

The expectation value of L is the time derivative of the average magnetization. To see this, we use

(28) to write

$$\langle L(t)\rangle = \mu \sum_m \frac{d}{dt} q_m(t) = \frac{d}{dt}\langle M(t)\rangle. \tag{108}$$

The function $L(t)$ itself, however, is not the time derivative of $M(t)$. If it were, the substitution of $\dot{M}(t)$ for it in (103) would lead to precisely the relations furnished by discussions based on the Liouville equation. The relations we find instead are evidently quite similar in content.

ALTERNATIVE METHOD AND GENERALIZATION

It may be of interest to mention briefly another way of studying Markoff processes, one rather different from the preceding discussion. The 2^N values of the probability function $p(\sigma_1, \cdots \sigma_N, t)$ may be regarded as the components of a vector $\mathbf{p}$. Then by suitably defining the elements of a matrix M, we may write the master equation (27) in the form

$$(d/dt)\mathbf{p} = M\mathbf{p}, \tag{109}$$

which suggests that p is a superposition of eigenvectors $\mathbf{p}^{(s)}$ which satisfy

$$M\mathbf{p}^{(s)} = -\nu_s \mathbf{p}^{(s)}. \tag{110}$$

One eigenvector, at least, is quite well-known to us. The probability distribution for the Ising model at equilibrium, the normalized Maxwell–Boltzmann distribution, corresponds to the eigenvalue $\nu = 0$. It is

$$p^{(0)}(\sigma_1, \cdots \sigma_N) = Z^{-1} \exp\left[(J/kT) \sum_l \sigma_l \sigma_{l+1}\right], \tag{111}$$

where Z, the normalizing factor, is the partition function.

Other eigenvectors may be sought by multiplying $\mathbf{p}^{(0)}$ by sums of products of spin variables with undetermined coefficients. For example, if we write

$$p^{(1)}(\sigma_1, \cdots \sigma_N, t) = \sum_j a_j(t)\sigma_j p^{(0)}(\sigma_1, \cdots \sigma_N), \tag{112}$$

we find that the condition that this form satisfy (109) is that the functions $a_j(t)$ satisfy the same sequence of equations (30) as we discussed earlier in connection with $q_j(t)$. The mode functions ζ_m^k, where ζ_m is given by (46) therefore furnish us with N different eigenvectors corresponding to roots ν_m given by (47).

The eigenvectors which are constructed by multiplying $\mathbf{p}^{(0)}$ by higher-order polynomials in $\sigma_1, \cdots \sigma_N$, are somewhat more complicated in form, and will be discussed in a later publication. The eigenvalues to which they correspond are fairly simple, however. The eigenvectors which are formed from the products of rth degree polynomials with $\mathbf{p}^{(0)}$ have eigenvalues

$$\nu = \nu_{m_1} + \nu_{m_2} + \cdots + \nu_{m_r}, \tag{113}$$

where the ν_{m_i} are given by (47), and the set of integers $m_1, \cdots m_r$ is selected from $0, 1 \cdots N-1$ with no repetitions. The number of such eigenvalues is given by the binomial coefficient $\binom{N}{r}$. The full set of 2^N eigenvalues is obtained by allowing r to range from 0 to N.

In particular, the largest eigenvalue is obtained for $r = N$ and is $\nu = N$. The eigenvector for this case is simply proportional to

$$p^{(N)}(\sigma_1, \cdots \sigma_N, t) = \prod_{j=1}^{N} \sigma_j e^{-N\alpha t}. \tag{114}$$

All of the foregoing discussion has been restricted to the case of nearest-neighbor coupling among spins in order to make contact with the familiar studies of the Ising model. The coupling may be extended to include the first n nearest neighbors by introducing the transition probability

$$w_j(\sigma_j) = \tfrac{1}{2}\alpha\left\{1 - \tfrac{1}{2}\sigma_j \sum_{l=1}^{n} \gamma_l(\sigma_{j-l} + \sigma_{j+l})\right\}, \tag{115}$$

where $\sum_l |\gamma_l| \le 1$. The methods of the preceding sections deal equally with the equations which follow from this more general type of coupling. The only significant change is that the quadratic equation, (55), for the short-range order is replaced by an equation of $2n$th degree which has n roots $\eta_1, \cdots \eta_n$ with absolute value less than unity. The equilibrium solution for the average spins, when the zeroth spin is fixed, is then an expression of the form

$$q_k = \sum_{j=1}^{n} c_j \eta_j^k, \tag{116}$$

where the coefficients c_j must be determined from the condition $q_0 = 1$ and the equations for $q_1, \cdots q_{n-1}$. These spin averages then determine the equilibrium spin correlations $r_{j,k}$ in precisely the way described earlier.

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APPENDIX

We have already noted that other forms of the transition probability than (9) are capable of bringing the stochastic model to the same equilibrium state as the Ising model. The condition that such a transition probability $w_j(\sigma_j)$ must satisfy is that the ratio $w_j(\sigma_j)/w_j(-\sigma_j)$ be equal to the equilibrium probability ratio (12). If we assume that $w_j(\sigma_j)$ depends symmetrically on the two neighboring spins σ_{j-1} and σ_{j+1} as well as on σ_j, then the condition just mentioned may be regarded as a functional equation for the transition probability. Its most general solution is given by the form

$$w_j(\sigma_j) = \tfrac{1}{2}\alpha\{1 + \delta\sigma_{j-1}\sigma_{j+1} - \tfrac{1}{2}\gamma(1+\delta)\sigma_j(\sigma_{j-1}+\sigma_{j+1})\}, \qquad (117)$$

in the absence of any magnetic field. In this form the parameter γ must still be identified with the constant (17), but the parameter δ has no analog in the discussions of the Ising model at equilibrium, and may evidently be chosen arbitrarily. It was assumed to vanish in our discussions of the time-dependent model since its presence materially complicates the equations for the spin expectation values.

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Correlations and Spontaneous Magnetization of the Two-Dimensional Ising Model*

ELLIOTT W. MONTROLL AND RENFREY B. POTTS†
International Business Machines Corporation, Thomas J. Watson Research Center, Yorktown Heights, New York
AND
JOHN C. WARD
Johns Hopkins University, Baltimore, Maryland
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In this paper we rederive, by simpler methods, the Onsager–Kaufman formulas for the correlations and the Onsager formula for the spontaneous magnetization of the rectangular two-dimensional Ising lattice. The Pfaffian approach is used to derive the correlations in terms of Pfaffians, and for the correlations in a row a single Toeplitz determinant is obtained which is proved equivalent to the Onsager–Kaufman result. The spontaneous magnetization is obtained as the limiting value of an infinite Toeplitz determinant and its evaluation is facilitated by use of the generalization of a result first published by Szego.

IN the days of Kepler and Galileo it was fashionable to announce a new scientific result through the circulation of a cryptogram which gave the author priority and his colleagues headaches. Onsager is one of the few moderns who operates in this tradition.

This paper concerns, among other things, the Onsager formula[1]

$$M = (1 - k^2)^{\frac{1}{8}}, \tag{0}$$

with

$$k = [\sinh (2J_1/kT) \sinh (2J_2/kT)]^{-1},$$

for the spontaneous magnetization of a two-dimensional Ising ferromagnet. This famous Onsager cryptogram required four years for its decipherment. It was first exposed to the public on 23 August 1948 on a blackboard at Cornell University on the occasion of a conference on phase transitions. Lazlo Tisza had just presented a paper on the General Theory of Phase Transitions. Gregory Wannier opened the discussion with a question concerning the compatability of the theory with some properties of the Ising model.[2] Onsager continued this discussion and then remarked that—incidentally the formula for the spontaneous magnetization of the two-dimensional model is just that given by (0). To tease a wider audience, the formula was again exhibited during the discussion which followed a paper by Rushbrooke at the first postwar IUPAP statistical mechanics meeting in Florence in 1948; it finally appeared in print as a discussion remark in reference (1). However, Onsager never published his derivation. The puzzle was finally solved by C. N. Yang[3] and its solution published in 1952.

Yang's analysis is very complicated. While many derivations of Onsager's thermodynamic formulas exist and are often presented in statistical mechanics courses, no new derivation of (0) appears in the literature nor is it considered to be appropriate as a classroom exercise.

In the main part of this paper we use the Pfaffian approach to derive the results of Kaufman and Onsager[4] and of Potts and Ward[5] on Ising spin correlations; we also show the equivalence of the apparently different formulas obtained in these two papers. This paper is essentially a continuation of the preceding one by P. Kasteleyn[6] on the Pfaffian approach to the dimer and Ising problems where it is shown that various combinatorial problems of the Kac and Ward[7] formulation of the Ising problem are avoided in the use of Pfaffians. The connection between the Ising problem and Pfaffians (and the "bathroom tile" lattice) was first noticed by Hurst and Green.[8,9] A rather detailed exposition of the Kasteleyn work is included in a survey of "Lattice

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* Part of this work was done while two of the authors (Elliott W. Montroll and John C. Ward) were visitors at the Brookhaven National Laboratories.

† On leave from the University of Adelaide, South Australia.

[1] L. Onsager, Nuovo Cimento, Suppl. 6, 261 (1949).

[2] Onsager's celebrated derivation of the partition function of the two-dimensional model is in Phys. Rev. 65, 117 (1944).

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[7] M. Kac and J. C. Ward, Phys. Rev. 88, 1332 (1952).

[8] C. A. Hurst and H. S. Green, J. Chem. Phys. 33, 1059 (1960).

[9] See also A. M. Dykhne and Yu B. Rumer, Soviet Phys—Usp. (English transl.) 75, 698 (1962).

Statistics" which has been prepared by one of the authors.[10]

We also present the details of a decipherment of the Onsager cryptogram (0) using a theorem on the evaluation of the determinant of a certain class of Toeplitz matrices. Evidentally, this is one of the methods used by Onsager himself. Mark Kac alerted the authors to a limit formula for the calculation of large Toeplitz determinants which happen to be of a type which appear naturally in the theory of spin correlations of a two-dimensional Ising lattice. This formula was first discussed by Szego.[11] Perusal of the Szego paper shows that the problem was proposed to Szego by the Yale mathematician S. Kakutani who apparently heard of it from Onsager. So, we wish to complete the circle from Onsager to Kakutani to Szego to Kac to us and now back to Onsager in this Onsager anniversary issue of the Journal of Mathematical Physics. Incidentally, Onsager promised the editor of this journal a manuscript on Toeplitz matrices for its inaugural issue. It has not yet arrived but we know it will be worth waiting for.

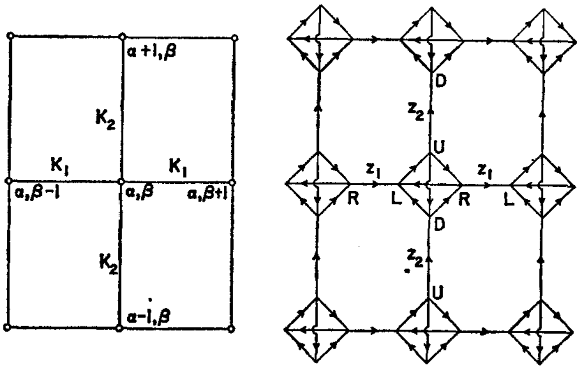
1. THE PARTITION FUNCTION

The partition function of a two-dimensional rectangular Ising lattice of N spins is given by[12]

$$Z = \sum_{\sigma=\pm 1} \prod_{\text{n.n.}} \exp\left(K_1\sigma_{\alpha,\beta}\sigma_{\alpha,\beta+1} + K_2\sigma_{\alpha,\beta}\sigma_{\alpha+1,\beta}\right), \quad (1)$$

where $\sigma_{\alpha,\beta} = \pm 1$ signifies the state of the spin at lattice site (α, β), $\pm kTK_1$ is the energy of interaction between horizontal pairs of neighboring spins, and $\pm kTK_2$ that between vertical pairs [see Fig. 1(a)]. The product is taken over all nearest-neighbor pairs and the summation over all N spins. If one defines

$$z_1 = \tanh K_1, \qquad z_2 = \tanh K_2, \quad (2)$$



(a) (b)

FIG. 1. The rectangular Ising lattice. (a) A typical site (α, β) and its neighbors; the spin at (α, β) interacts with the spins at the nearest neighbor sites $\alpha \pm 1, \beta$ and $\alpha, \beta \pm 1$. (b) By giving structure to the lattice sites, the "bathroom tile" lattice is obtained. The arrows give a possible set of directions which force a correct counting of polygons on the lattice.

then the partition function may be written

$$Z = (\cosh K_1 \cosh K_2)^N \sum \prod (1 + z_1\sigma_{\alpha,\beta}\sigma_{\alpha,\beta+1}) \times (1 + z_2\sigma_{\alpha,\beta}\sigma_{\alpha+1,\beta}). \quad (3)$$

As shown by Kasteleyn,[6] this partition function can be evaluated by constructing a Pfaffian $P(\mathbf{A})$ which counts dimer configurations on the "bathroom tile" lattice obtained from the rectangular lattice by giving structure to the corners as illustrated in Fig. 1(b). The value of the Pfaffian is calculated from the property that its square is the determinant of a skew-symmetric matrix $\mathbf{A}$ so that

$$Z^2 = (2 \cosh K_1 \cosh K_2)^{2N} |\mathbf{A}|. \quad (4)$$

The $4N \times 4N$ matrix $\mathbf{A}$ has the usual doubly cyclic structure reflecting the symmetry of the rectangular lattice and its nonvanishing elements are 4×4 matrices with the explicit values

$$\mathbf{A}(\alpha, \beta; \alpha, \beta) = \begin{array}{c|cccc} & \mathrm{R} & \mathrm{L} & \mathrm{U} & \mathrm{D} \\ \hline \mathrm{R} & 0 & 1 & -1 & -1 \\ \mathrm{L} & -1 & 0 & 1 & -1 \\ \mathrm{U} & 1 & -1 & 0 & 1 \\ \mathrm{D} & 1 & 1 & -1 & 0 \end{array}, \quad (5)$$

$$\mathbf{A}(\alpha, \beta; \alpha, \beta+1) = \begin{bmatrix} 0 & z_1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}, \quad (6)$$

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[10] E. W. Montroll, "Lattice Statistics," to appear as a chapter in a book entitled *Applied Combinatorial Mathematics*, edited by E. F. Beckenbach.

[11] G. Szego, "On Certain Hermitian forms associated with the Fourier series of a positive function," Communications du seminaire mathematique de l'université de Lund, tome supplementaire (1952) dedié a Marcel Riesz p. 228–238. See also V. Grenander and G. Szego, *Toeplitz Forms and their Applications* (University of California Press, Berkeley, California, 1958), as well as M. Kac, Duke Math. J. 21 (1954).

[12] In general, the notation of this paper will follow that of the review article by Newell and Montroll.[13] The variables K_1 and K_2 are chosen instead of K and K' to avoid an inconsistency in the use of this notation in the review article and in Kaufman's paper.[14] To compare our results with Kaufman and Onsager's[4] it is necessary to take $K_1 = H'$ and $K_2 = H$, and to compare with the results of Potts and Ward,[5] take $K_1 = H_2$ and $K_2 = H_1$.

[13] G. F. Newell and E. W. Montroll, Rev. Mod. Phys. **25**, 353 (1953).

[14] B. Kaufman, Phys. Rev. **76**, 1232 (1949).

$$\mathbf{A}(\alpha, \beta + 1; \alpha, \beta) = \begin{bmatrix} 0 & 0 & 0 & 0 \\ -z_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}, \quad (7)$$

$$\mathbf{A}(\alpha, \beta; \alpha + 1, \beta) = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & z_2 \\ 0 & 0 & 0 & 0 \end{bmatrix}, \quad (8)$$

$$\mathbf{A}(\alpha + 1, \beta; \alpha, \beta) = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & -z_2 & 0 \end{bmatrix}. \quad (9)$$

The arrow directions in Fig. 1(b), which are chosen to force a correct counting of the dimer configurations, enable one to write down these 4 × 4 matrices by inspection; it is only necessary to remember to use positive signs when a bond from a Right, Left, Up, or Down corner to another corner is in the direction of the arrowhead and negative signs otherwise. The value of $|\mathbf{A}|$ is easily determined from the determinant of

$$\begin{aligned} \mathbf{A}(\phi_1, \phi_2) = {} & \mathbf{A}(0, 0; 0, 0) \\ & + \mathbf{A}(0, 0; 1, 0)e^{i\phi_1} + \mathbf{A}(0, 0; -1, 0)e^{-i\phi_1} \\ & + \mathbf{A}(0, 0; 0, 1)e^{i\phi_2} + \mathbf{A}(0, 0; 0, -1)e^{-i\phi_2} \end{aligned}$$

$$= \begin{bmatrix} 0 & 1+z_1e^{i\phi_2} & -1 & -1 \\ -1-z_1e^{-i\phi_2} & 0 & 1 & -1 \\ 1 & -1 & 0 & 1+z_2e^{i\phi_1} \\ 1 & 1 & -1-z_2e^{-i\phi_1} & 0 \end{bmatrix}. \quad (10)$$

In fact, for large N,

$$\ln |\mathbf{A}| \sim \frac{N}{(2\pi)^2} \iint_{-\pi}^{\pi} \ln |\mathbf{A}(\phi_1, \phi_2)| \, d\phi_1 \, d\phi_2, \quad (11)$$

where

$$\begin{aligned} |\mathbf{A}(\phi_1, \phi_2)| = \Delta(\phi_1, \phi_2) = {} & (1 + z_1^2)(1 + z_2^2) \\ & - 2z_2(1 - z_1^2) \cos \phi_1 - 2z_1(1 - z_2^2) \cos \phi_2. \quad (12) \end{aligned}$$

In view of Eq. (2), these equations immediately lead to Onsager's celebrated formula[2]

$$\begin{aligned} N^{-1} \ln Z \sim \ln 2 + \frac{1}{(2\pi)^2} \iint_{-\pi}^{\pi} \ln (& \cosh 2K_1 \cosh 2K_2 \\ & - \sinh 2K_1 \cos \phi_2 \\ & - \sinh 2K_2 \cos \phi_1) \, d\phi_1 \, d\phi_2 \quad (13) \end{aligned}$$

for the partition function of the rectangular Ising lattice.

2. CORRELATION FUNCTIONS

The two spin correlation functions for a pair of spins located at sites (1, 1) and $(1 + l, 1 + m)$ is defined to be

$$\begin{aligned} \langle \sigma_{1,1}\sigma_{1+l,1+m} \rangle = {} & Z^{-1}(\cosh K_1 \cosh K_2)^N \\ & \times \sum_{\sigma=\pm 1} \sigma_{1,1}\sigma_{1+l,1+m} \\ & \times \prod_{\text{n.n.}} (1 + z_1\sigma_{\alpha,\beta}\sigma_{\alpha,\beta+1})(1 + z_2\sigma_{\alpha,\beta}\sigma_{\alpha+1,\beta}). \quad (14) \end{aligned}$$

Since boundary effects can be neglected for an infinite lattice, the correlations depend only on the relative separation of the spins and $\langle \sigma_{l',m'}\sigma_{l'+l,m'+m} \rangle = \langle \sigma_{1,1}\sigma_{1+l,1+m} \rangle$. The extra factor in (14) is advantageously written as

$$\begin{aligned} \sigma_{1,1}\sigma_{1+l,1+m} = {} & (\sigma_{1,1}\sigma_{1,2})(\sigma_{1,2}\sigma_{1,3}) \cdots (\sigma_{1,m}\sigma_{1,1+m}) \\ & \times (\sigma_{1,1+m}\sigma_{2,1+m})(\sigma_{2,1+m}\sigma_{3,1+m}) \cdots (\sigma_{l,1+m}\sigma_{1+l,1+m}) \\ = {} & \prod_{m'-1}^{m} (\sigma_{1,m'}\sigma_{1,1+m'}) \prod_{l'=1}^{l} (\sigma_{l',1+m}\sigma_{1+l',1+m}), \quad (15) \end{aligned}$$

a consequence of $\sigma^2 = 1$, which also implies identities[15] such as

$$\begin{aligned} & \sigma_{\alpha,\beta}\sigma_{\alpha,\beta+1}(1 + z_1\sigma_{\alpha,\beta}\sigma_{\alpha,\beta+1}) \\ & \qquad = z_1(1 + z_1^{-1}\sigma_{\alpha,\beta}\sigma_{\alpha,\beta+1}). \quad (16) \end{aligned}$$

Equation (14) can then be written

$$\begin{aligned} & Zz_1^{-m}z_2^{-l}\langle \sigma_{1,1}\sigma_{1+l,1+m} \rangle \\ & = (\cosh K_1 \cosh K_2)^N \sum_{\sigma=\pm 1} \prod_{m'=1}^{m} (1 + z_1^{-1}\sigma_{1,m'}\sigma_{1,1+m'}) \\ & \times \prod_{l'=1}^{l} (1 + z_2^{-1}\sigma_{l',1+m}\sigma_{1+l',1+m}) \\ & \times \prod_{\text{n.n.}}{}' (1 + z_1\sigma_{\alpha,\beta}\sigma_{\alpha,\beta+1})(1 + z_2\sigma_{\alpha,\beta}\sigma_{\alpha+1,\beta}), \quad (17) \end{aligned}$$

where $\prod'_{\text{n.n.}}$ is the product over all nearest-neighbor pairs not included in the first two products. The

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[15] The importance of these identities in the simplification of the Potts and Ward analysis of correlations has been observed independently by H. S. Green. While this paper was being prepared, we received a copy of a manuscript by H. S. Green and C. A. Hurst on the same subject. Although their treatment of correlation is similar to ours they have not taken advantage of the theorems on Toeplitz forms which are so helpful in spontaneous magnetization calculations. Their paper is to be published in a Max Born Festschrift issue of Z. Physik.

right-hand side of (17) is now precisely the expression (3) for the partition function Z, except that z_1 is replaced by z_1^{-1} for all factors corresponding to the horizontal pairs between (1, 1) and $(1, 1 + m)$ and z_2 by z_2^{-1} for vertical pairs between $(1, 1 + m)$ and $(1 + l, 1 + m)$. The correlations can therefore be evaluated by constructing a skew-symmetric matrix $\mathbf{A} + \boldsymbol{\delta}$ and using (4) to give

$$|\mathbf{A}|\, z_1^{-2m} z_2^{-2l} \langle \sigma_{1,1}\sigma_{1+l,1+m}\rangle^2 = |\mathbf{A} + \boldsymbol{\delta}|, \qquad (18)$$

or

$$\langle \sigma_{1,1}\sigma_{1+l,1+m}\rangle^2 = z_1^{2m} z_2^{2l}\, |\mathbf{I} + \mathbf{A}^{-1}\boldsymbol{\delta}|. \qquad (19)$$

All elements of the skew-symmetric matrix $\boldsymbol{\delta}$ are zero except those at which z_1 or z_2 are replaced by z_1^{-1} or z_2^{-1}, and there are in all $2l + 2m$ nonzero elements with values $\pm(z_1^{-1} - z_1)$ and $\pm(z_2^{-1} - z_2)$. Since most of the $4N \times 4N$ elements of $\boldsymbol{\delta}$ are zeros, (19) can be much simplified.

To illustrate this simplification, suppose that the only nonzero elements of $\boldsymbol{\delta}$ are δ_{12} and δ_{21}, so that (a_{jk}^{-1} representing an element of $\mathbf{A}^{-1}$)

$$\mathbf{I} + \mathbf{A}^{-1}\boldsymbol{\delta} = \mathbf{I} + \begin{bmatrix} a_{11}^{-1} & a_{12}^{-1} & a_{13}^{-1} & \cdot & \cdot \\ a_{21}^{-1} & a_{22}^{-1} & a_{23}^{-1} & \cdot & \cdot \\ a_{31}^{-1} & a_{32}^{-1} & a_{33}^{-1} & \cdot & \cdot \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}$$

$$\times \begin{bmatrix} 0 & \delta_{12} & 0 & \cdot & \cdot \\ \delta_{21} & 0 & 0 & \cdot & \cdot \\ 0 & 0 & 0 & \cdot & \cdot \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}$$

$$= \begin{bmatrix} 1 + a_{12}^{-1}\delta_{21} & a_{11}^{-1}\delta_{12} & 0 & \cdot & \cdot \\ a_{22}^{-1}\delta_{21} & 1 + a_{21}^{-1}\delta_{12} & 0 & \cdot & \cdot \\ a_{32}^{-1}\delta_{21} & a_{31}^{-1}\delta_{12} & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 \end{bmatrix}.$$

Then,

$$|\mathbf{I} + \mathbf{A}^{-1}\boldsymbol{\delta}| = \begin{vmatrix} 1 + a_{12}^{-1}\delta_{21} & a_{11}^{-1}\delta_{12} \\ a_{22}^{-1}\delta_{21} & 1 + a_{21}^{-1}\delta_{12} \end{vmatrix}$$

$$= \left| \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} a_{11}^{-1} & a_{12}^{-1} \\ a_{21}^{-1} & a_{22}^{-1} \end{bmatrix} \begin{bmatrix} 0 & \delta_{12} \\ \delta_{21} & 0 \end{bmatrix} \right|$$

$$= |\mathbf{I} + \mathbf{Q}\mathbf{y}|, \qquad (20)$$

where $\mathbf{y}$ is the submatrix of $\boldsymbol{\delta}$ obtained by taking only those rows and columns which contain nonzero elements and $\mathbf{Q}$ is the submatrix of $\mathbf{A}^{-1}$ obtained by taking these same rows and columns. It is important to note that on the left-hand side of (20), $\mathbf{I}$ refers to the unit matrix of order $4N$; while on the right-hand side it refers to the unit matrix of order 2. This should not cause confusion, of course, as $\mathbf{I}$ must be of the same order as the matrix to which it is added.

Returning to a consideration of Eq. (19), we can now replace it by

$$\langle \sigma_{1,1}\sigma_{1+l,1+m}\rangle^2 = z_1^{2m} z_2^{2l}\, |\mathbf{I} + \mathbf{Q}\mathbf{y}|, \qquad (21)$$

where $\mathbf{y}$ is the skew-symmetric matrix of order $2l + 2m$ which is the submatrix obtained from $\boldsymbol{\delta}$ by choosing only those rows and columns in which nonzero elements appear, and $\mathbf{Q}$ is the skew-symmetric matrix of order $2l + 2m$ which is the submatrix of $\mathbf{A}^{-1}$ formed with these same rows and columns.

If now we write

$$|\mathbf{I} + \mathbf{Q}\mathbf{y}| = |\mathbf{y}^{-1} + \mathbf{Q}|\, |\mathbf{y}| \qquad (22)$$

and observe that since $\mathbf{y}$ is skew symmetric, as is $\mathbf{y}^{-1}$ and hence $\mathbf{y}^{-1} + \mathbf{Q}$, we can write

$$|\mathbf{I} + \mathbf{Q}\mathbf{y}| = [P(\mathbf{y}^{-1} + \mathbf{Q})P(\mathbf{y})]^2, \qquad (23)$$

and hence

$$\langle \sigma_{1,1}\sigma_{1+l,1+m}\rangle = \pm z_1^m z_2^l P(\mathbf{y}^{-1} + \mathbf{Q})P(\mathbf{y}). \qquad (24)$$

The appropriate sign is chosen to make the correlation positive.

In general, of course, it is easiest to calculate the Pfaffians as the square roots of the determinants of the skew-symmetric matrices; but it will be seen that $P(\mathbf{y})$ is simple to determine as is $P(\mathbf{y}^{-1} + \mathbf{Q})$ when either l or m is zero. Before proceeding to an illustrative example we shall determine $\mathbf{A}^{-1}$ as required for the evaluation of $\mathbf{Q}$.

3. THE INVERSE MATRIX

Because of the simple structure of $\mathbf{A}$, its inverse can be easily obtained as

$$\mathbf{A}^{-1}(\alpha', \beta'; \alpha, \beta) = \frac{1}{(2\pi)^2}$$

$$\times \iint_{-\pi}^{\pi} e^{i[(\alpha'-\alpha)\phi_1 + (\beta'-\beta)\phi_2]} \mathbf{A}^{-1}(\phi_1, \phi_2)\, d\phi_1\, d\phi_2, \qquad (25)$$

where $\mathbf{A}^{-1}(\phi_1, \phi_2)$ is the inverse of the matrix $\mathbf{A}(\phi_1, \phi_2)$ given by

$$\mathbf{A}^{-1}(\phi_1,\phi_2)=\frac{1}{\Delta(\phi_1,\phi_2)}\begin{array}{c}\\ \mathrm{R}\\ \mathrm{L}\\ \mathrm{U}\\ \mathrm{D}\end{array}\!\!\begin{array}{cccc}\mathrm{R} & \mathrm{L} & \mathrm{U} & \mathrm{D}\\ \left[\begin{matrix}2iz_2\sin\phi_1 \\ -b^*-b+a^*b^*b \\ -2+a^*b \\ -2+a^*b^*\end{matrix}\right. & \begin{matrix}b+b^*-abb^* \\ -2iz_2\sin\phi_1 \\ 2-ab \\ -2+ab^*\end{matrix} & \begin{matrix}2-ab^* \\ -2+a^*b^* \\ -2iz_1\sin\phi_2 \\ -a^*-a+a^*ab^*\end{matrix} & \left.\begin{matrix}2-ab \\ 2-a^*b \\ a+a^*-aa^*b \\ 2iz_1\sin\phi_2\end{matrix}\right]\end{array}, \quad (26)$$

with

$$a=1+z_1e^{i\phi_2},\qquad b=1+z_2e^{i\phi_1},$$

$$b+b^*-abb^*=1-z_2^2-z_1e^{i\phi_2}(1+z_2^2+2z_2\cos\phi_1),$$

and

$$\Delta(\phi_1,\phi_2)=(1+z_1^2)(1+z_2^2) \qquad (27)$$
$$-2z_2(1-z_1^2)\cos\phi_1-2z_1(1-z_2^2)\cos\phi_2.$$

It will be seen that $\mathbf{A}^{-1}(\alpha',\beta';\alpha,\beta)$ is a function of the differences $\alpha-\alpha'$ and $\beta-\beta'$ and we shall find it convenient to introduce the abbreviated notation

$$\mathbf{A}^{-1}(\alpha',\beta';\alpha,\beta)_{\mathrm{RR}}=[\alpha-\alpha',\beta-\beta']_{\mathrm{RR}} \qquad (28)$$

and so on. Because $\Delta(\phi_1,\phi_2)$ is an even function of ϕ_1 and ϕ_2,

$$[0,\beta]_{\mathrm{RR}}=[0,\beta]_{\mathrm{LL}}=[\alpha,0]_{\mathrm{UU}}=[\alpha,0]_{\mathrm{DD}}=0. \quad (29)$$

To prove these relations we can show, for example, that

$$[0,\beta]_{\mathrm{RR}}=\frac{2iz_2}{(2\pi)^2}\int_{-\pi}^{\pi}d\phi_2\,e^{-i\beta\phi_2}\int_{-\pi}^{\pi}d\phi_1\,\frac{\sin\phi_1}{\Delta(\phi_1,\phi_2)}=0.$$

Also, since $b+b^*-abb^*=-(-b^*-b+a^*b^*b)^*$,

$$[0,\beta]_{\mathrm{RL}}=-[0,-\beta]_{\mathrm{LR}}$$

and similarly

$$[\alpha,0]_{\mathrm{UD}}=-[-\alpha,0]_{\mathrm{DU}}, \qquad (30)$$

and other such identities. The matrix elements can be expressed in terms of complete elliptic integrals by using the F functions discussed in Appendix A.

4. THE CORRELATION $\langle\sigma_{1,1}\sigma_{1,2}\rangle$

We are ready to begin calculation of the correlation functions and by way of illustration we shall carry through the computation of $\langle\sigma_{1,1}\sigma_{1,2}\rangle$ in detail. In this case one can write down the nonzero elements of $\boldsymbol{\delta}$ from inspection of Fig. 2 and the matrices (6) and (7):

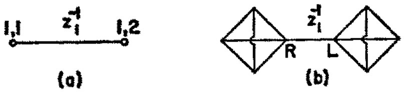

FIG. 2. The altered bond used in calculating $\langle\sigma_{1,1}\sigma_{1,2}\rangle$: (a) on the Ising lattice, and (b) on the "bathroom tile" lattice.

$$\text{RL element of }\boldsymbol{\delta}(1,1;1,2)=\ z_1^{-1}-z_1,$$
$$\text{LR element of }\boldsymbol{\delta}(1,2;1,1)=-(z_1^{-1}-z_1).$$

From $\boldsymbol{\delta}$ we now form the submatrix $\mathbf{y}$, using only the rows and columns of $\boldsymbol{\delta}$ which contain nonzero elements, obtaining the skew-symmetric matrix

$$\mathbf{y}=\begin{array}{c}\\ (1,1)\mathrm{R}\\ (1,2)\mathrm{L}\end{array}\!\!\begin{array}{cc}(1,1)\mathrm{R} & (1,2)\mathrm{L}\\ \left[\begin{matrix}0\\ -(z_1^{-1}-z_1)\end{matrix}\right. & \left.\begin{matrix}z_1^{-1}-z_1\\ 0\end{matrix}\right]\end{array}$$
$$=(z_1^{-1}-z_1)\begin{bmatrix}0 & 1\\ -1 & 0\end{bmatrix}. \qquad (31)$$

The 2×2 matrix $\mathbf{Q}$ obtained from $\mathbf{A}^{-1}$ by omitting all rows and columns except those labeled (1, 1)R and (1, 2)L is

$$\mathbf{Q}=\begin{bmatrix}[0,0]_{\mathrm{RR}} & [0,1]_{\mathrm{RL}}\\ [0,-1]_{\mathrm{LR}} & [0,0]_{\mathrm{LL}}\end{bmatrix}, \qquad (32)$$

which, by use of (29) and (30), reduces to the skew-symmetric form

$$\mathbf{Q}=\begin{bmatrix}0 & [0,1]_{\mathrm{RL}}\\ -[0,1]_{\mathrm{RL}} & 0\end{bmatrix}. \qquad (33)$$

To obtain the correlation

$$\langle\sigma_{1,1}\sigma_{1,2}\rangle=\pm z_1P(\mathbf{y}^{-1}+\mathbf{Q})P(\mathbf{y}) \qquad (34)$$

as given by (24), we require the Pfaffian of $\mathbf{y}$ and the Pfaffian of

$$\mathbf{y}^{-1}+\mathbf{Q}$$
$$=\begin{bmatrix}0 & -(z_1^{-1}-z_1)^{-1}+[0,1]_{\mathrm{RL}}\\ (z_1^{-1}-z_1)^{-1}-[0,1]_{\mathrm{RL}} & 0\end{bmatrix}. \qquad (35)$$

Since the Pfaffian[16] is the square root of the determinant of the associated antisymmetric matrix

$$P(\mathbf{y})=z_1^{-1}-z_1, \qquad (36)$$

and

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[16] There is more than one rule for evaluating Pfaffians. Perhaps the mathematical physicist should prefer that suggested by Thomson and Tait in their *Treatise on Natural Philosophy* (Cambridge University Press, Cambridge, England, (1879). In the 1962 Dover republication under the title *Principles of Mechanics and Dynamics*, the rule appears on p. 394 of Part I. See also E. Caianello, Nuovo Cimento, Suppl. 14, 177 (1959).

$$P(\mathbf{y}^{-1} + \mathbf{Q}) = -(z_1^{-1} - z_1)^{-1} + [0, 1]_{\mathrm{RL}}. \tag{37}$$

Substitution into (34) gives

$$\langle \sigma_{1,1}\sigma_{1,2}\rangle = \pm z_1(z_1^{-1} - z_1)\{-(z_1^{-1} - z_1)^{-1} + [0, 1]_{\mathrm{RL}}\}$$

$$= \pm\{z_1 - (1 - z_1^2)[0, 1]_{\mathrm{RL}}\}. \tag{38}$$

If now we introduce the double-integral expression for the inverse matrix element $[0, 1]_{\mathrm{RL}}$, this formula becomes

$$\begin{aligned}\langle \sigma_{1,1}\sigma_{1,2}\rangle &= \pm\frac{1}{(2\pi)^2}\iint_{-\pi}^{\pi} z_1 - (1 - z_1^2)\,\frac{e^{-i\phi_2}[1 - z_2^2 - z_1e^{i\phi_2}(1 + z_2^2 + 2z_2\cos\phi_1)]}{(1 + z_1^2)(1 + z_2^2) - 2z_2(1 - z_1^2)\cos\phi_1 - 2z_1(1 - z_2^2)\cos\phi_2}\,d\phi_1\,d\phi_2 \\ &= \pm\frac{1}{(2\pi)^2}\iint_{-\pi}^{\pi} \frac{2z_1(1 + z_2^2) - z_1^2(1 - z_2^2)e^{i\phi_2} - (1 - z_2^2)e^{-i\phi_2}}{(1 + z_1)^2(1 + z_2^2) - 2z_2(1 - z_1^2)\cos\phi_1 - 2z_1(1 - z_2^2)\cos\phi_2}\,d\phi_1\,d\phi_2, &&(39) \\ &= \frac{1}{2\pi}\int_{-\pi}^{\pi} e^{i\delta^*(\omega)}\,d\omega, &&(40)\end{aligned}$$

where $\delta^*(\omega)$ is the function introduced by Onsager.[2] It can be expressed in terms of z_1 and

$$z_2^* = (1 - z_2)/(1 + z_2) \tag{41}$$

as

$$e^{2i\delta^*} = \frac{(z_1z_2^*e^{i\omega} - 1)(z_1e^{i\omega} - z_2^*)}{(e^{i\omega} - z_1z_2^*)(z_2^*e^{i\omega} - z_1)}. \tag{42}$$

The positive sign is chosen in (40) since it is known that as $T \to 0$, $\delta^* \to 0$ and $\langle \sigma_{1,1}\sigma_{1,2}\rangle \to 1$.

The explicit evaluation of (39) can be carried out as shown in Appendix A, since in the notation used there,

$$\begin{aligned}\langle \sigma_{1,1}\sigma_{1,2}\rangle = {}& 2z_1(1 + z_2^2)F_{0,0} \\ & - z_1^2(1 - z_2^2)F_{0,1} - (1 - z_2^2)F_{0,-1}.\end{aligned} \tag{43}$$

For the special case when $z_1 = z_2$, the following results, in agreement with those of Kaufman and Onsager,[14] are obtained:

$$\begin{aligned}\langle \sigma_{1,1}\sigma_{1,2}\rangle &= (1 + k)^{\frac{1}{2}}\left\{\frac{1 - k}{\pi}K(k) + \tfrac{1}{2}\right\} \qquad \text{for } T < T_c \\ &= \left(\frac{1 + k}{k}\right)^{\frac{1}{2}}\left\{\frac{k - 1}{\pi}K(k) + \tfrac{1}{2}\right\}, \qquad \text{for } T > T_c,\end{aligned} \tag{44}$$

where

$$k = \begin{cases}1/\sinh^2(2K) & \text{if } T < T_c \\ \sinh^2(2K) & \text{if } T > T_c.\end{cases}$$

In these formulas, $K(k)$ is the elliptic integral of the first kind.

5. THE CORRELATION $\langle \sigma_{1,1}\sigma_{1,1+m}\rangle$

The above analysis can be easily generalized to obtain the correlation $\langle \sigma_{1,1}\sigma_{1,1+m}\rangle$ for any two spins in the same row. The nonzero elements of $\mathfrak{d}$ are obtained from an inspection of Fig. 3 and the matrices (6), (7):

$$\text{RL element of } \mathfrak{d}(1, m'; 1, 1 + m') = z_1^{-1} - z_1,$$

$$\text{LR element of } \mathfrak{d}(1, 1 + m'; 1, m') = -(z_1^{-1} - z_1),$$

$$m' = 1, 2, \cdots, m.$$

The $2m \times 2m$ skew-symmetric matrix $\mathbf{y}$ is therefore given by

$$\mathbf{y} = (z_1^{-1} - z_1)\cdot \begin{array}{cc|cccccccccc|} & & & & \mathrm{R} & & & & & \mathrm{L} & & \\ & & (1,1) & (1,2) & \cdot & \cdot & (1,m) & (1,2) & (1,3) & \cdot & \cdot & (1,1+m) \\ \hline \mathrm{R} & (1,1) & 0 & 0 & \cdot & \cdot & 0 & 1 & 0 & \cdot & \cdot & 0 \\ & (1,2) & 0 & 0 & \cdot & \cdot & 0 & 0 & 1 & \cdot & \cdot & 0 \\ & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ & (1,m) & 0 & 0 & \cdot & \cdot & 0 & 0 & 0 & \cdot & \cdot & 0 \\ \mathrm{L} & (1,2) & -1 & 0 & \cdot & \cdot & 0 & 0 & 0 & \cdot & \cdot & 0 \\ & (1,3) & 0 & -1 & \cdot & \cdot & 0 & 0 & 0 & \cdot & \cdot & 0 \\ & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ & (1,1+m) & 0 & 0 & \cdot & \cdot & -1 & 0 & 0 & \cdot & \cdot & 0 \\ \hline \end{array}, \tag{45}$$

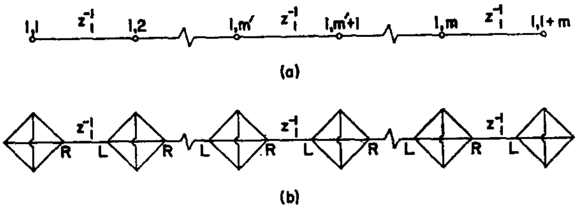

FIG. 3. The altered bonds used in calculating $\langle\sigma_{1,1}\sigma_{1,1+m}\rangle$: (a) on the Ising lattice; and (b) on the "bathroom tile" lattice.

or

$$\mathbf{y} = (z_1^{-1} - z_1)\begin{bmatrix} \mathbf{0} & \mathbf{I} \\ -\mathbf{I} & \mathbf{0} \end{bmatrix} \tag{46}$$

in obvious generalization of (31). The $2m \times 2m$ matrix $\mathbf{Q}$ obtained from $\mathbf{A}^{-1}$ by omitting all rows and columns except those in $\mathbf{y}$ is

$$\mathbf{Q} = \begin{bmatrix} \mathbf{0} & \mathbf{S} \\ -\mathbf{S} & \mathbf{0} \end{bmatrix}, \tag{47}$$

where S is the $m \times m$ matrix

$$\mathbf{S} = \begin{bmatrix} [0,1]_{\mathrm{RL}} & [0,2]_{\mathrm{RL}} & [0,3]_{\mathrm{RL}} & \cdot\ \cdot & [0,m]_{\mathrm{RL}} \\ [0,0]_{\mathrm{RL}} & [0,1]_{\mathrm{RL}} & [0,2]_{\mathrm{RL}} & \cdot\ \cdot & [0,m-1]_{\mathrm{RL}} \\ [0,-1]_{\mathrm{RL}} & [0,0]_{\mathrm{RL}} & [0,1]_{\mathrm{RL}} & \cdot\ \cdot & [0,m-2]_{\mathrm{RL}} \\ \vdots & \vdots & \vdots & \vdots\ \vdots & \vdots \\ [0,2-m]_{\mathrm{RL}} & [0,3-m]_{\mathrm{RL}} & [0,4-m]_{\mathrm{RL}} & \cdot\ \cdot & [0,1]_{\mathrm{RL}} \end{bmatrix}. \tag{48}$$

To obtain the correlation

$$\langle\sigma_{1,1}\sigma_{1,1+m}\rangle = \pm z_1^m P(\mathbf{y}^{-1} + \mathbf{Q})P(\mathbf{y}) \tag{49}$$

as given by (24), we require

$$P(\mathbf{y}) = (z_1^{-1} - z_1)^m, \tag{50}$$

and

$$P(\mathbf{y}^{-1} + \mathbf{Q}) = |-(z_1^{-1} - z_1)^{-1}\mathbf{I} + \mathbf{S}|. \tag{51}$$

In deriving (51), we have obtained from (46),

$$\mathbf{y}^{-1} = (z_1^{-1} - z_1)^{-1}\begin{bmatrix} \mathbf{0} & -\mathbf{I} \\ \mathbf{I} & \mathbf{0} \end{bmatrix}.$$

Substitution into (49) gives the result

$$\langle\sigma_{1,1}\sigma_{1,1+m}\rangle = \pm|z_1\mathbf{I} - (1 - z_1^2)\mathbf{S}|. \tag{52}$$

By defining

$$a_0 = z_1 - (1 - z_1^2)[0, 1]_{\mathrm{RL}}, \tag{53}$$

$$a_r = -(1 - z_1^2)[0, 1 + r]_{\mathrm{RL}}, \tag{54}$$

$$a_{-r} = -(1 - z_1^2)[0, 1 - r]_{\mathrm{RL}}$$

$$r = 1, 2, \cdots, m - 1, \tag{55}$$

the correlation can be written as the Toeplitz determinant

$$\langle\sigma_{1,1}\sigma_{1,1+m}\rangle = \begin{vmatrix} a_0 & a_1 & a_2 & \cdot\ \cdot\ \cdot & a_{m-1} \\ a_{-1} & a_0 & a_1 & \cdot\ \cdot\ \cdot & a_{m-2} \\ a_{-2} & a_{-1} & a_0 & \cdot\ \cdot\ \cdot & a_{m-3} \\ \vdots & & & & \vdots \\ a_{-m+1} & a_{-m+2} & a_{-m+3} & \cdot\ \cdot\ \cdot & a_0 \end{vmatrix}, \tag{56}$$

where the plus sign is chosen to render the correlation positive. The value of a_0 in terms of the function $\delta^*(\omega)$ has been found in (40) and, by an integration similar to that performed, there are obtained

$$a_r = \frac{1}{2\pi}\int_{-\pi}^{\pi} e^{-ir\omega}e^{i\delta^*(\omega)}\,d\omega, \tag{57}$$

so that the a_r are the coefficients in a series expansion of $e^{i\delta^*}$.

The form (56) for the correlation is the same as that obtained by Potts and Ward;[5] yet in the Kaufman-Onsager[4] result, two Toeplitz determinants appear. The identification of these two apparently different results is carried out in Appendix B.

6. THE CORRELATION $\langle\sigma_{1,1}\sigma_{2,2}\rangle$

Before calculating the general correlation function we shall sketch the derivation of the correlation $\langle\sigma_{1,1}\sigma_{2,2}\rangle$. Inspection of Fig. 4 assists one in writing down the nonzero elements of $\boldsymbol{\delta}$ as

RL element of $\boldsymbol{\delta}(1, 1; 1, 2) = z_1^{-1} - z_1$,
LR element of $\boldsymbol{\delta}(1, 2; 1, 1) = -(z_1^{-1} - z_1)$,
UD element of $\boldsymbol{\delta}(1, 2; 2, 2) = z_2^{-1} - z_2$,
DU element of $\boldsymbol{\delta}(2, 2; 1, 2) = -(z_2^{-1} - z_2)$.

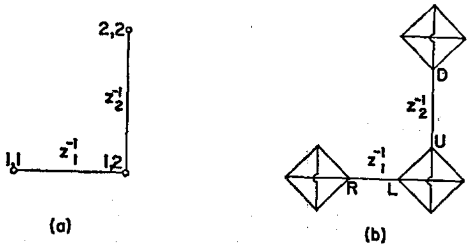

FIG. 4. The altered bonds used in calculating $\langle\sigma_{1,1}\sigma_{2,2}\rangle$: (a) on the Ising lattice, and (b) on the "bathroom tile" lattice.

The matrix $\mathbf{y}$ is, therefore,

$$\mathbf{y}=\begin{array}{c|cccc|} & (1,1)\mathrm{R} & (1,2)\mathrm{L} & (1,2)\mathrm{U} & (2,2)\mathrm{D} \\ (1,1)\mathrm{R} & 0 & z_1^{-1}-z_1 & 0 & 0 \\ (1,2)\mathrm{L} & -(z_1^{-1}-z_1) & 0 & 0 & 0 \\ (1,2)\mathrm{U} & 0 & 0 & 0 & z_2^{-1}-z_2 \\ (2,2)\mathrm{D} & 0 & 0 & -(z_2^{-1}-z_2) & 0 \end{array} \tag{58}$$

and

$$\mathbf{Q}=\begin{bmatrix} 0 & [0,1]_{\mathrm{RL}} & [0,1]_{\mathrm{RU}} & [1,1]_{\mathrm{RD}} \\ -[0,1]_{\mathrm{RL}} & 0 & [0,0]_{\mathrm{LU}} & [1,0]_{\mathrm{LD}} \\ -[0,1]_{\mathrm{RU}} & -[0,0]_{\mathrm{LU}} & 0 & [1,0]_{\mathrm{UD}} \\ -[1,1]_{\mathrm{RD}} & -[1,0]_{\mathrm{LD}} & -[1,0]_{\mathrm{UD}} & 0 \end{bmatrix}. \tag{59}$$

Since $P(\mathbf{y}) = (z_1^{-1} - z_1)(z_2^{-1} - z_2)$ (60)

and

$$\mathbf{y}^{-1}=\begin{bmatrix} 0 & -(z_1^{-1}-z_1)^{-1} & 0 & 0 \\ (z_1^{-1}-z_1)^{-1} & 0 & 0 & 0 \\ 0 & 0 & 0 & -(z_2^{-1}-z_2)^{-1} \\ 0 & 0 & (z_2^{-1}-z_2)^{-1} & 0 \end{bmatrix}, \tag{61}$$

substitution into (24) gives

$$\langle\sigma_{1,1}\sigma_{2,2}\rangle = (1-z_1^2)(1-z_2^2)\times\left|\begin{array}{ccc} -(z_1^{-1}-z_1)^{-1}+[0,1]_{\mathrm{RL}} & [0,1]_{\mathrm{RU}} & [1,1]_{\mathrm{RD}} \\ & [0,0]_{\mathrm{LU}} & [1,0]_{\mathrm{LD}} \\ & & -(z_2^{-1}-z_2)^{-1}+[1,0]_{\mathrm{UD}} \end{array}\right|, \tag{62}$$

the last factor on the right-hand side being the symbol for the Pfaffian $P(\mathbf{y}^{-1}+\mathbf{Q})$. We shall not evaluate this explicitly but proceed to the general correlation.

7. THE CORRELATION $\langle\sigma_{1,1}\sigma_{1+l,1+m}\rangle$

In the general case, the nonzero elements of $\boldsymbol{\delta}$ are:

RL element of $\boldsymbol{\delta}(1, m'; 1+m') = z_1^{-1} - z_1$,
LR element of $\boldsymbol{\delta}(1, 1+m'; 1, m) = -(z_1^{-1} - z_1)$,
UD element of $\boldsymbol{\delta}(l', 1+m; 1+l', 1+m) = z_2^{-1} - z_2$,
DU element of $\boldsymbol{\delta}(1+l', 1+m; l', 1+m) = -(z_2^{-1} - z_2)$,

where $m' = 1, 2, \cdots, m$ and $l' = 1, 2, \cdots, l$ [see Fig. 5].

The matrix $\mathbf{y}$ is obtained by choosing from $\boldsymbol{\delta}$ the $2l + 2m$ rows and columns ordered as

$$(1,1)\mathrm{R}, (1,2)\mathrm{R}, \cdots, (1,m)\mathrm{R},$$

then

$$(1,2)\mathrm{L}, (1,3)\mathrm{L}, \cdots, (1,1+m)\mathrm{L},$$

then

$$(1,1+m)\mathrm{U}, (2,1+m)\mathrm{U}, \cdots, (l,1+m)\mathrm{U},$$

and finally

$$(2,1+m)\mathrm{D}, (3,1+m)\mathrm{D}, \cdots, (1+l,1+m)\mathrm{D}.$$

In generalization of (58), (60), and (61),

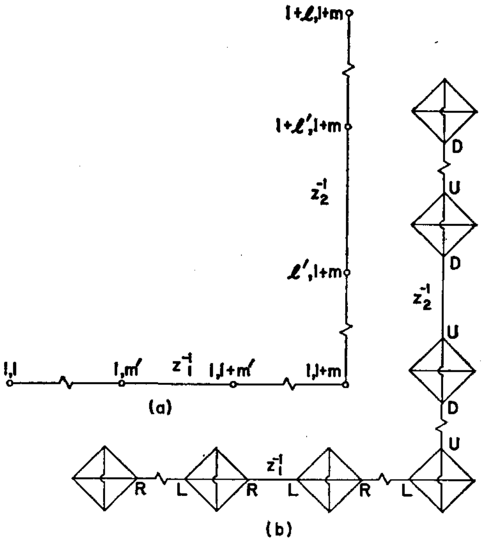

FIG. 5. The altered bonds used in calculationg $\langle\sigma_{1,1}\sigma_{1+l,1+m}\rangle$: (a) on the Ising lattice, and (b) the "bathroom tile" lattice.

$$\mathbf{y} = \begin{array}{c|cccc|} & \text{R} & \text{L} & \text{U} & \text{D} \\ \text{R} & 0 & (z_1^{-1} - z_1)\mathbf{I}_m & 0 & 0 \\ \text{L} & -(z_1^{-1} - z_1)\mathbf{I}_m & 0 & 0 & 0 \\ \text{U} & 0 & 0 & 0 & (z_2^{-1} - z_2)\mathbf{I}_l \\ \text{D} & 0 & 0 & -(z_2^{-1} - z_2)\mathbf{I}_l & 0 \end{array}, \tag{63}$$

$$P(\mathbf{y}) = (z_1^{-1} - z_1)^m (z_2^{-1} - z_2)^l, \tag{64}$$

and

$$\mathbf{y}^{-1} = \begin{bmatrix} 0 & -(z_1^{-1} - z_1)^{-1}\mathbf{I}_m & 0 & 0 \\ (z_1^{-1} - z_1)^{-1}\mathbf{I}_m & 0 & 0 & 0 \\ 0 & 0 & 0 & -(z_2^{-1} - z_2)^{-1}\mathbf{I}_l \\ 0 & 0 & (z_2^{-1} - z_2)^{-1}\mathbf{I}_l & 0 \end{bmatrix}. \tag{65}$$

The correlation is therefore given by

$$\langle \sigma_{1,1}\sigma_{1+l,1+m} \rangle = \pm(1 - z_1^2)^m (1 - z_2^2)^l P(\mathbf{y}^{-1} + \mathbf{Q}). \tag{66}$$

As the matrix Q is quite complicated in the general case, we shall not proceed further with this calculation except to make one remark. It is not necessary to go from 1, 1 to 1 + l, 1 + m along the horizontal line and then the vertical line; any other path connecting the two sites may be chosen. In certain cases other paths may give a simpler matrix $\mathbf{y}^{-1} + \mathbf{Q}$ whose Pfaffian has to be determined. For example, for calculating $\langle \sigma_{1,1}\sigma_{1+l,1+l} \rangle$ it is convenient to proceed from site (1, 1) to (1, 2) than to (2, 2), (2, 3), (3, 3) and so on in a staircase fashion.

8. SPONTANEOUS MAGNETIZATION

The spontaneous magnetization of the Ising model can be obtained from the formula

$$M^2 = \lim_{m \to \infty} \langle \sigma_{1,1}\sigma_{1,1+m} \rangle, \tag{67}$$

and the representation of the correlation function as the Toeplitz determinant given by (56). The method we use is that alluded to in the footnote in the Potts–Ward paper.[5] It is known from the theory of these determinants[11] that if $D_m(f)$ is the determinant of a Toeplitz matrix[17] whose elements are the coefficients in the Laurent expansion of a function $f(\omega)$ then

$$\lim_{m \to \infty} \frac{D_m(f)}{G(f)^{m+1}} = \exp\left(\sum_1^\infty n k_n k_{-n} \right), \tag{68}$$

where

$$G(f) = \exp \frac{1}{2\pi} \int_{-\pi}^{\pi} \ln f(\omega)\, d\omega, \tag{69}$$

and

$$\ln f(\omega) = \sum_{n=-\infty}^{\infty} k_n e^{in\omega}. \tag{70}$$

In the present problem, $f(\omega) = e^{i\delta^*}$ and hence

$$G(f) = \exp \frac{1}{2\pi} \int_{-\pi}^{\pi} i\delta^*\, d\omega = 1, \tag{71}$$

δ^* being an odd function of ω.

To determine k_n we require the Fourier expansion of

$$\ln f(\omega) = i\delta^*(\omega) = \frac{1}{2} \ln \frac{(z_1 z_2^* e^{i\omega} - 1)(z_1 e^{i\omega} - z_2^*)}{(e^{i\omega} - z_1 z_2^*)(z_2^* e^{i\omega} - z_1)}, \tag{72}$$

where we use the formula (42). Different expansions are required depending on whether the temperature is less than or greater than the critical temperature since

$$z_2^* < z_1 < 1 \quad \text{for} \quad T < T_c, \tag{73}$$

and

$$z_1 < z_2^* < 1 \quad \text{for} \quad T > T_c. \tag{74}$$

For temperatures below the critical temperature

$$\ln f(\omega) = \frac{1}{2} \ln \frac{(1 - z_1 z_2^* e^{i\omega})\left(1 - \dfrac{z_2^*}{z_1} e^{-i\omega}\right)}{(1 - z_1 z_2^* e^{-i\omega})\left(1 - \dfrac{z_2^*}{z_1} e^{i\omega}\right)}$$

$$= \frac{1}{2}\left[\ln(1 - z_1 z_2^* e^{i\omega}) + \ln\left(1 - \frac{z_2^*}{z_1} e^{-i\omega}\right) \right.$$

---

[17] Actually Eq. (68) has not appeared in the literature. The work of Szego[11] is restricted to the case of Hermitian Toeplitz forms so that the $k_n k_{-n}$ of (68) appears as $k_n k_n^*$ in his paper. However, the methods discussed in the Kac article can be applied immediately in the general case to derive (68).

$$- \ln(1 - z_1 z_2^* e^{-i\omega}) - \ln\left(1 - \frac{z_2^*}{z_1} e^{i\omega}\right)\Bigg]$$

$$= \frac{1}{2} \sum_{n=1}^{\infty} \frac{1}{n} [-(z_1 z_2^*)^n + (z_2^*/z_1)^n] e^{in\omega}$$

$$+ \frac{1}{n} [-(z_2^*/z_1)^n + (z_1 z_2^*)^n] e^{-in\omega}.$$

Hence

$$k_n = \frac{1}{2n} [(z_2^*/z_1)^n - (z_1 z_2^*)^n] = -k_{-n}, \qquad (75)$$

and

$$\sum_1^{\infty} n k_n k_{-n} = \frac{1}{4} \sum_1^{\infty} \frac{1}{n} [-(z_2^*/z_1)^{2n} + 2 z_2^{*2n} - (z_1 z_2^*)^{2n}]$$

$$= \frac{1}{4} \ln \frac{[1 - (z_2^*/z_1)^2][1 - (z_1 z_2^*)^2]}{[1 - z_2^{*2}]^2}$$

$$= \frac{1}{4} \ln \left[1 - \frac{(1 - z_1^2)^2 z_2^{*2}}{(1 - z_2^{*2})^2 z_1^2}\right].$$

Substitution into (68) gives

$$\lim_{m \to \infty} \frac{D_m(f)}{G(f)^{m+1}} = \lim_{m \to \infty} \langle \sigma_{1,1} \sigma_{1,1+m} \rangle$$

$$= \left[1 - \frac{(1 - z_1^2)^2 z_2^{*2}}{(1 - z_2^{*2})^2 z_1^2}\right]^{\frac{1}{4}}$$

$$= \left[1 - \frac{(1 - z_1^2)^2 (1 - z_2^2)^2}{16 z_1^2 z_2^2}\right]^{\frac{1}{4}}, \qquad (76)$$

and finally, for the spontaneous magnetization below the critical temperature,

$$M = \left[1 - \frac{(1 - z_1^2)^2 (1 - z_2^2)^2}{16 z_1^2 z_2^2}\right]^{\frac{1}{8}} \qquad (77)$$

$$= [1 - (\sinh 2K_1 \sinh 2K_2)^{-2}]^{\frac{1}{8}}, \quad T < T_c, \quad (78), (0)$$

the Onsager cryptogram (0). Our circle is now closed. However, for completeness we must show that $M = 0$ for $T > T_c$. Now $z_1 < z_2^* < 1$ and hence, from (72),

$$\ln f(\omega) = \frac{1}{2} \ln \frac{(1 - z_1 z_2^* e^{i\omega})[1 - (z_1/z_2^*) e^{i\omega}]}{e^{i2\omega}(1 - z_1 z_2^* e^{-i\omega})[1 - (z_1/z_2^*) e^{-i\omega}]}$$

$$= \frac{1}{2} \Bigg[\ln(1 - z_1 z_2^* e^{i\omega}) + \ln\left(1 - \frac{z_1}{z_2^*} e^{i\omega}\right)$$

$$- \ln(1 - z_1 z_2^* e^{-i\omega}) - \ln\left(1 - \frac{z_1}{z_2^*} e^{-i\omega}\right)\Bigg] - i\omega,$$

where the ω in the last term $-i\omega$ is the sawtooth function of period 2π. Then

$$\ln f(\omega) = \frac{1}{2} \sum_{n=1}^{\infty} \frac{1}{n} \left[-(z_1 z_2^*)^n - \left(\frac{z_1}{z_2^*}\right)^n + 2(-1)^n\right] e^{in\omega}$$

$$+ \frac{1}{n} \left[(z_1 z_2^*)^n + \left(\frac{z_1}{z_2^*}\right)^n - 2(-1)^n\right] e^{-in\omega},$$

since

$$-i\omega = \sum_1^{\infty} \frac{(-1)^n}{n} (e^{in\omega} - e^{in\omega}).$$

Hence

$$k_n = \frac{1}{2n} [-(z_1/z_2^*)^n - (z_1 z_2^*)^n + 2(-1)^n] = -k_{-n}, \quad (79)$$

and

$$\sum_1^{\infty} n k_n k_{-n} = \sum_1^{\infty} -\frac{1}{n} + \frac{(-1)^n}{n} \left[\left(\frac{z_1}{z_2^*}\right)^n + (z_1 z_2^*)^n\right]$$

$$- \frac{1}{4n} [(z_1/z_2^*)^n + (z_1 z_2^*)^n]^2$$

$$= -\infty,$$

as $\sum (1/n)$ is divergent. Hence

$$\lim_{m \to \infty} \langle \sigma_{1,1} \sigma_{1,1+m} \rangle = 0 \quad \text{for} \quad T > T_c, \qquad (80)$$

and

$$M = 0 \qquad T > T_c. \qquad (81)$$

ACKNOWLEDGMENT

The authors wish to thank Professor Mark Kac for several informative discussions concerning Toeplitz matrices and especially for bringing the work of Szego as well as his own to their attention.

APPENDIX A: SQUARE LATTICE GREEN'S FUNCTIONS

We derived formulas for correlation functions as Pfaffians and determinants whose elements were expressed in terms of the functions

$$F_{m_1,m_2} = \frac{1}{(2\pi)^2} \times \iint_{-\pi}^{\pi} \frac{\exp i(\phi_1 m_1 + \phi_2 m_2)\, d\phi_1\, d\phi_2}{a - \gamma_1 \cos\phi_1 - \gamma_2 \cos\phi_2}. \qquad (A1)$$

The parameters are

$$a = (1 + z_1^2)(1 + z_2^2) \quad \text{with} \quad z_j = \tanh K_j, \qquad (A2a)$$

$$\gamma_2 = 2z_1(1 - z_2^2) \quad \text{and} \quad \gamma_1 = 2z_2(1 - z_1^2). \qquad (A2b)$$

An alternative representation of these functions is

$$F_{m_1,m_2} = \int_0^{\infty} dx\, e^{-ax} \times \prod_{j=1}^{2} \left\{\frac{1}{2\pi} \int_{-\pi}^{\pi} \exp(i\phi_j m_j + \gamma_j \cos\phi_j)\, d\phi_j\right\}$$

$$= \int_0^{\infty} e^{-ax} I_{m_1}(x\gamma_1) I_{m_2}(x\gamma_2)\, dx, \qquad (A3)$$

$I_m(x\gamma)$ being the mth Bessel function of purely imaginary argument.

One special class of F's is those with $m_1 = m_2$. Then[18]

$$F_{mm} = \frac{1}{\pi(\gamma_1\gamma_2)^{\frac{1}{2}}}\, Q_{m-\frac{1}{2}}\left(\frac{a^2-\gamma_1^2-\gamma_2^2}{2\gamma_1\gamma_2}\right), \qquad \text{(A4)}$$

where $Q_n(x)$ is the nth Legendre function of the second kind. Now

$$Q_{-\frac{1}{2}}(\cosh\eta) = 2e^{-\eta/2}K(e^{-\eta}), \qquad \text{(A5)}$$

where $K(k)$ is the complete elliptic integral of the first kind. With the choice of parameters (A2) it is easily shown that

$$\frac{a^2-\gamma_1^2-\gamma_2^2}{2\gamma_1\gamma_2} = \frac{1}{2}\left\{\frac{(1-z_1^2)(1-z_2^2)}{4z_1z_2} + \frac{4z_1z_2}{(1-z_1^2)(1-z_2^2)}\right\}. \qquad \text{(A6)}$$

If we set this expression equal to $\cosh\eta$, then

$$e^{-\eta} = \begin{cases} (1-z_1^2)(1-z_2^2)/(4z_1z_2) & \text{if } (1-z_1^2)(1-z_2^2) < 4z_1z_2 \\ 4z_1z_2/(1-z_1^2)(1-z_2^2) & \text{if } (1-z_1^2)(1-z_2^2) > 4z_1z_2. \end{cases} \qquad \text{(A7)}$$

Since the phase transition occurs at the temperature T defined by

$$\sinh 2K_1 \sinh 2K_2 = 1, \qquad \text{(A8)}$$

and since $z_j = \tanh K_j$, (A7) is equivalent to

$$e^{-\eta} = \begin{cases} \sinh 2K_1 \sinh 2K_2 & \text{if } T > T_c \\ (\sinh 2K_1 \sinh 2K_2)^{-1} & \text{if } T < T_c. \end{cases} \qquad \text{(A9)}$$

We then find from (A4), (A5), and (A9)

$$F_{0,0} = \begin{cases} (2\pi \tanh K_1 \tanh K_2)^{-1}K([\sinh 2K_1 \sinh 2K_2]^{-1}) & \text{if } T < T_c \\ (2/\pi)\cosh^2 K_1 \cosh^2 K_2\, K(\sinh 2K_1 \sinh 2K_2) & \text{if } T > T_c. \end{cases} \qquad \text{(A10)}$$

Since the Legendre functions satisfy the recurrence formulas

$$(z^2-1)Q_n'(z) = nzQ_n(z) - n\,Q_{n-1}(z),$$

$Q_{-\frac{3}{2}}(z)$ can be obtained from $Q_{-\frac{1}{2}}(z)$ by setting $n = -\frac{1}{2}$. Then, if $z = \cosh\eta$,

$$\sinh^2\eta\,\frac{dQ_{-\frac{1}{2}}(\cosh\eta)}{d\cosh\eta} = -\tfrac{1}{2}\cosh\eta\, Q_{-\frac{1}{2}}(\cosh\eta) + \tfrac{1}{2}Q_{-\frac{3}{2}}(\cosh\eta), \qquad \text{(A11)}$$

where also

$$\sinh^2\eta\,\frac{dQ_{-\frac{1}{2}}(\cosh\eta)}{d\cosh\eta} = \sinh\eta\,\frac{dQ_{-\frac{1}{2}}(\cosh\eta)}{d\eta}. \qquad \text{(A12)}$$

Since

$$dK(k)/dk = E(k)/[k(1-k^2)] - K(k)/k,$$

where $E(k)$ is a complete elliptic integral of the second kind, we find from (A12),

$$\sinh^2\eta\,\frac{dQ_{-\frac{1}{2}}(\cosh\eta)}{d\cosh\eta} = (\sinh\eta)e^{-\eta/2}\{K(e^{-\eta}) - e^{\eta}E(e^{-\eta})\cosh\eta\},$$

so that (A11) implies

$$Q_{-\frac{3}{2}}(\cosh\eta) = 2e^{\eta/2}[K(e^{-\eta}) - E(e^{-\eta})] = Q_{\frac{1}{2}}(\cosh\eta). \qquad \text{(A13)}$$

The equality of $Q_{-\frac{3}{2}}$ and $Q_{\frac{1}{2}}$ follows from setting $n = -\frac{1}{2}$ in the recurrence formula

$$(2n+1)zQ_n(z) = (n+1)Q_{n+1}(z) + nQ_{n-1}(z). \qquad \text{(A14)}$$

Then returning to (A4) and noting from (A1) that

$$F_{m_1,m_2} = F_{-m_1,m_2} = F_{m_1,-m_2} = F_{-m_1,-m_2}, \qquad \text{(A15)}$$

we find

$$F_{1,1} = F_{1,-1} = F_{-1,1} = F_{-1,-1} = \frac{2e^{\eta/2}}{\pi(\gamma_1\gamma_2)^{\frac{1}{2}}}[K(e^{-\eta}) - E(e^{-\eta})]. \qquad \text{(A16)}$$

As in the case of $F_{0,0}$ two forms exist for $F_{1,1}$, one for $T > T_c$ and the other for $T < T_c$. These follow immediately from combining (A16) with (A9).

Now set $n = \frac{1}{2}$ in (A14). Then

$$Q_{\frac{3}{2}}(\cosh\eta) = \tfrac{2}{3}e^{\eta/2}(2e^{\eta} + e^{-\eta})K(e^{-\eta}) - \tfrac{8}{3}e^{\eta/2}E(e^{-\eta}), \qquad \text{(A17)}$$

so that

$$F_{22} = \frac{1}{\pi(\gamma_1\gamma_2)^{\frac{1}{2}}}\{\tfrac{2}{3}e^{\eta/2}(2e^{\eta} + e^{-\eta})K(e^{-\eta}) - \tfrac{8}{3}e^{\eta/2}E(e^{-\eta})\}. \qquad \text{(A18)}$$

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[18] A. Erdelyi, W. Magnus, F. Oberhettinger, and F. Tricomi, *Tables of Integral Transforms* (McGraw Hill Book Company, Inc., New York, 1954), Vol. 1, p. 183.

One can continue step by step to find each $F_{m,m}$, by repeated use of the recursion relation (A14).

Our Green's function (A1) also satisfies the difference equation

$$aF_{m_1,m_2} - \tfrac{1}{2}\gamma_1[F_{m_1+1,m_2} + F_{m_1-1,m_2}] - \tfrac{1}{2}\gamma_2[F_{m_1,m_2} + F_{m_1,m_2-1}] = \delta_{m_1,0}\delta_{m_2,0}. \tag{A19}$$

Physically these F's are connected to random-walk generating functions. Consider a walker who walks at random from lattice point to lattice point on a square lattice in such a manner that $p(l_1, l_2) = p(\mathbf{l})$ is the probability at any step he displaces himself by the vector (l_1, l_2) from his position before the step was taken. If his initial location is the origin and if $P_t(m_1, m_2) \equiv P_t(\mathbf{m})$ represents the probability of arrival at $\mathbf{m} = (m_1, m_2)$ after t steps, then the generating function for the walk is[10]

$$U(\mathbf{m}, z) = \sum_{t=0}^{\infty} z^t P_t(\mathbf{m}) = \frac{1}{(2\pi)^2} \times \iint_{-\pi}^{\pi} \frac{\exp - i(\phi_1 m_1 + \phi_2 m_2)\, d\phi_1\, d\phi_2}{1 - z\lambda(\phi_1, \phi_2)}, \tag{A20}$$

where

$$\lambda(\phi_1\phi_2) = \sum_{l} p(l_1 l_2) \exp i(\phi_1 l_1 + \phi_2 l_2). \tag{A21}$$

$U(\mathbf{m}, z)$ is related to (A1) in a walk in which at each opportunity for a step the walker moves only to a nearest-neighbor point or remains stationary until the next opportunity for a step arises. Suppose the probability of a step to the right, p_1, equals the probability of a step to the left and that the probability of a step upward, p_2, equals that of a step downward; and that p is the probability of remaining stationary. Then

$$2p_1 + 2p_2 + p = 1,$$

and

$$\lambda(\phi_1, \phi_2) = p + 2p_1 \cos\phi_1 + 2p_2 \cos\phi_2,$$

so that $U(-\mathbf{m}, z)$ is exactly F_{m_1,m_2} if one sets

$$a = 1 - zp,$$

$$\gamma_1 = 2zp_1 \quad \text{and} \quad \gamma_2 = 2zp_2.$$

We now obtain explicit expressions for a few more F's in the symmetrical case $\gamma_1 = \gamma_2 = \gamma$ by employing the difference equation (A19). In this case $F_{1,0} = F_{0,1} = F_{-1,0} = F_{0,-1}$. Hence,

$$aF_{0,0} - 2\gamma F_{1,0} = 1,$$

so that

$$F_{1,0} = (1/2\gamma)(aF_{0,0} - 1), \tag{A22}$$

$F_{0,0}$ being given by (A10). All other F's can be obtained as linear combinations of E and K by successive application of the difference equation (A19). For example,

$$aF_{1,1} - \gamma(F_{1,0} + F_{1,2}) = 0,$$

so that

$$F_{1,2} = (aF_{1,1} - \gamma F_{1,0})/\gamma = (aF_{1,1} - \tfrac{1}{2}aF_{0,0} + \tfrac{1}{2})/\gamma, \tag{A23}$$

where $F_{0,0}$ is given by (A4) and (A5) and $F_{1,1}$ by (A16).

To indicate how these formulas can be used for the calculation of correlation functions we find $\langle\sigma_{1,1}\sigma_{1,2}\rangle$ in a symmetric lattice with $K_1 = K_2 = K$. Then, from Eq. (43),

$$\langle\sigma_{1,1}\sigma_{1,2}\rangle = 2z(1 + z^2)F_{0,0} - (1 - z^2)(1 + z^2)F_{1,0}. \tag{A24}$$

But from (A22),

$$F_{1,0} = [4z(1 - z^2)]^{-1}[(1 + z^2)^2 F_{0,0} - 1].$$

Hence

$$\langle\sigma_{1,1}\sigma_{1,2}\rangle = \frac{(1 + z^2)}{4z} \times \{(z^2 + 2z - 1)(1 + 2z - z^2)F_{0,0} + 1\} = \frac{\cosh 2K}{2\sinh 2K}\left\{\frac{(\sinh^2 2K - 1)}{\cosh^4 K} F_{0,0} + 1\right\}. \tag{A25}$$

Substituting (A10) into (A25) we find

$$\langle\sigma_{1,1}\sigma_{1,2}\rangle = \begin{cases} (1 + k)^{\frac{1}{2}}\left\{\dfrac{(1 - k)}{\pi} K(k) + \tfrac{1}{2}\right\} \\ \quad \text{with } k = 1/\sinh^2 2K \quad \text{for } T < T_c \\ \left(\dfrac{1 + k}{k}\right)^{\frac{1}{2}}\left\{\dfrac{(k - 1)}{\pi} K(k) + \tfrac{1}{2}\right\} \\ \quad \text{with } k = \sinh^2 2K \quad \text{for } T > T_c, \end{cases}$$

a result first obtained by B. Kaufman and L. Onsager.

For completeness we make a few remarks concerning asymptotic formulas for F_{m_1,m_2}. Some of these have been discussed in reference 19. Others can be derived by methods discussed in connection with the three-dimensional Green's function of reference 20. When m_1 and m_2 are very large, the

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[19] E. W. Montroll, *Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability* (University of California Press, 1956), Vol. III, p. 209.

[20] A. A. Maradudin, E. W. Montroll, G. H. Weiss, R. Herman, and H. L. Milnes, Mem. Acad. Prog. de Belgique **XIV**, No. 1709 (1960).

integrand of (A1) oscillates very rapidly except in the neighborhood of $(\phi_1, \phi_2) = 0$. If, in the representation following (A2b), one expands $\cos\phi_1$ and $\cos\phi_2$ in a power series and only quadratic terms are retained, he obtains

$$F_{m_1,m_2} = \frac{1}{(2\pi)^2}\int_0^\infty dx\, e^{-x(a-\gamma_1-\gamma_2)}$$
$$\times \iint_{-\pi}^{\pi} \exp\{-\tfrac{1}{2}x(\gamma_1\phi_1^2 + \gamma_2\phi_2^2)$$
$$+ i(\phi_1 m_1 + \phi_2 m_2)\}\, d\phi_1\, d\phi_2.$$

The limits $(-\pi, \pi)$ can be extended to $(-\infty, \infty)$ since the ϕ integrand diminishes rapidly as one moves away from the origin. Hence

$$F_{m_1,m_2} \sim \frac{1}{2\pi(\gamma_1\gamma_2)^{\frac{1}{2}}}\int_0^\infty e^{-\frac{1}{2}R^2/x} e^{-x(a-\gamma_1-\gamma_2)}\, dx$$
$$= \frac{1}{\pi(\gamma_1\gamma_2)^{\frac{1}{2}}} K_0(R[2(a-\gamma_1-\gamma_2)]^{\frac{1}{2}}), \qquad \text{(A26)}$$

where

$$R^2 = (m_1^2/\gamma_1) + (m_2^2/\gamma_2),$$

and $K_0(z)$ is the modified Bessel function of the second kind of order zero. As $z \to \infty$,

$$K_0(z) \sim (\pi/2z)^{\frac{1}{2}} e^{-z}.$$

Corrections to (A26) can be obtained by following reference 20.

In the limit $a \to \gamma_1 + \gamma_2$, one combines (A4) with the asymptotic formula for the Legendre function (as $\epsilon \to 0$):

$$Q_{m-\frac{1}{2}}(1+\epsilon) \sim -\tfrac{1}{2}\log(\tfrac{1}{2}\epsilon) - \gamma - \psi(m+\tfrac{1}{2}) + \cdots,$$

where γ is Euler's gamma $= 0.57721$ and

$$\psi(x) = d\log\Gamma(x)/dx,$$

$\Gamma(x)$ being the well-known gamma function. One property of $\psi(x)$ is

$$\psi(n+x) - \psi(x) = \frac{1}{x} + \frac{1}{x+1} + \cdots + \frac{1}{x+n+1}.$$

If we let $a = \gamma_1 + \gamma_2 + \epsilon$ where ϵ is very small,

$$(a^2 - \gamma_1^2 - \gamma_2^2)/2\gamma_1\gamma_2 \sim 1 + \epsilon(\gamma_1+\gamma_2)/\gamma_1\gamma_2,$$

so that

$$F_{m,m} = \frac{1}{\pi(\gamma_1\gamma_2)^{\frac{1}{2}}}$$
$$\times\left\{-\frac{1}{2}\log\left[\frac{1}{2}\frac{\epsilon(\gamma_1+\gamma_2)}{\gamma_1\gamma_2}\right] - \gamma - \psi(m+\tfrac{1}{2}) \cdots\right\}$$

has a logarithmic divergence as $\epsilon \to 0$. Note that

$$F_{m,m} - F_{0,0}$$
$$= 2\left\{1 + \frac{1}{3} + \frac{1}{5} + \cdots + \frac{1}{2m-1}\right\}/\pi(\gamma_1\gamma_2)^{\frac{1}{2}},$$

while it is easy to show that for large m_1, m_2, m_3, and m_4, one has the limit result[19] as $\epsilon \to 0$:

$$F_{m_1,m_2} - F_{m_3,m_4} = \frac{1}{\pi(\gamma_1\gamma_2)^{\frac{1}{2}}}\log\left(\frac{\gamma_2 m_3^2 + \gamma_1 m_4^2}{\gamma_2 m_1^2 + \gamma_1 m_2^2}\right).$$

APPENDIX B. IDENTIFICATION OF TWO FORMULAS FOR ROW CORRELATIONS

There are two formulas for the correlations which are different in form but will be proved to be the same. The first is that obtained by Kaufman and Onsager,[4] in the form[21]

$$(-1)\,\langle\sigma_{1,1}\sigma_{1,1+m}\rangle$$
$$= c_2^{*2}\begin{vmatrix} b_{-1} & b_{-2} & b_{-3} & \cdots & b_{-m} \\ b_0 & b_{-1} & b_{-2} & \cdots & b_{1-m} \\ b_1 & b_0 & b_{-1} & \cdots & b_{2-m} \\ \vdots & \vdots & \vdots & & \vdots \\ b_{m-2} & b_{m-3} & b_{m-4} & \cdots & b_{-1} \end{vmatrix}$$
$$- s_2^{*2}\begin{vmatrix} b_1 & b_2 & b_3 & \cdots & b_m \\ b_0 & b_1 & b_2 & \cdots & b_{m-1} \\ b_{-1} & b_0 & b_1 & \cdots & b_{m-2} \\ \vdots & \vdots & \vdots & & \vdots \\ b_{2-m} & b_{3-m} & b_{4-m} & \cdots & b_{-1} \end{vmatrix}, \qquad \text{(B1)}$$

where

$$c_2^* = \cosh K_2^*,\quad s_2^* = \sinh K_2^*,\quad \tanh K_2 = e^{-2K_2^*}, \qquad \text{(B2)}$$

$$b_r = \frac{1}{\pi}\int_0^\pi \cos[\delta'(\omega) - r\omega]\, d\omega, \qquad \text{(B3)}$$

$$\sin\delta'(\omega)\sinh 2K_2^* = \sin\delta^*(\omega)\sinh 2K_1, \qquad \text{(B4)}$$

$$\cos\delta'(\omega) = \sin\delta^*(\omega)\sin\omega\cosh 2K_2^*$$
$$- \cos\delta^*(\omega)\cos\omega. \qquad \text{(B5)}$$

The second formula is that obtained by Potts and Ward[5] and given by (56) and (57) above:

$$\langle\sigma_{1,1}\sigma_{1+m}\rangle = \begin{vmatrix} a_0 & a_1 & a_2 & \cdots & a_{m-1} \\ a_{-1} & a_0 & a_1 & \cdots & a_{m-2} \\ a_{-2} & a_{-1} & a_0 & \cdots & a_{m-3} \\ \vdots & \vdots & \vdots & & \vdots \\ a_{1-m} & a_{2-m} & a_{3-m} & \cdots & a_0 \end{vmatrix}, \qquad \text{(B6)}$$

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[21] Equation (43) of their paper contains a misprinted sign. To change from their notation to ours note that $\sum_r = b_{-r}$; $H = K_2$, $H' = K_1$.

with

$$a_r = \frac{1}{2\pi}\int_{-\pi}^{\pi} e^{-ir\omega}e^{i\delta^*(\omega)}\,d\omega$$

or

$$a_r = \frac{1}{\pi}\int_0^{\pi} \cos\left[\delta^*(\omega) - r\omega\right]d\omega. \qquad \text{(B7)}$$

It seems surprising that formula (B1), containing two determinants, should give the same result as the simpler formula (B6), a single determinant. We show this to be true by establishing the following matrix identity:

$$\begin{bmatrix} 1 & 0 & \cdot & \cdot & \cdot & 0 & 0 \\ 0 & & & & & & 0 \\ \cdot & & & & & & \cdot \\ \cdot & & & s_1\mathbf{I}_m - c_1\mathbf{R}_m & & & \cdot \\ 0 & & & & & & 0 \\ 0 & 0 & \cdot & \cdot & \cdot & 0 & 1 \end{bmatrix}$$

$$\times \begin{bmatrix} 1 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & & & & & \\ \cdot & & & & & \\ \cdot & & c_2^*\mathbf{I}_{m+1} + s_2^*\mathbf{R}_{m+1} & & & \\ \cdot & & & & & \\ 0 & & & & & \end{bmatrix} \begin{bmatrix} 0 & c_2^* & 0 & \cdot & \cdot & s_2^* \\ s_2^* & & & & & \\ 0 & & & & & \\ \cdot & & & \mathbf{B}_{m+1} & & \\ \cdot & & & & & \\ -c_2^* & & & & & \end{bmatrix}$$

$$\times \begin{bmatrix} 1 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & & & & & \\ \cdot & & & & & \\ \cdot & & -s_2^*\mathbf{I}_{m+1} + c_2^*\mathbf{R}_{m+1} & & & \\ \cdot & & & & & \\ 0 & & & & & \end{bmatrix} \begin{bmatrix} 1 & 0 & \cdot & \cdot & \cdot & 0 & 0 \\ 0 & & & & & & 0 \\ \cdot & & & & & & \cdot \\ \cdot & & & c_1\mathbf{I}_m + s_1\mathbf{R}_m & & & \cdot \\ 0 & & & & & & 0 \\ 0 & 0 & \cdot & \cdot & \cdot & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} 0 & \cdot & \cdot & \cdot & 0 & 1 \\ \cdot & & & & & ? \\ \cdot & & \mathbf{A}_m & & & ? \\ \cdot & & & & & ? \\ 0 & & & & & ? \\ -1 & ? & ? & ? & ? & ? \end{bmatrix}, \qquad \text{(B8)}$$

or briefly

$$\mathbf{P}_1\mathbf{P}_2\mathbf{P}_3\mathbf{P}_4\mathbf{P}_5 = \mathbf{P}_6, \qquad \text{(B9)}$$

with the following notation:

$$s_1 = \sinh K_1, \qquad c_1 = \cosh K_1, \qquad \text{(B10)}$$

$$? = \text{elements which are irrelevant}, \qquad \text{(B11)}$$

$$\mathbf{I}_m = \text{unit matrix of order } m, \qquad \text{(B12)}$$

$$\mathbf{R}_m = m \times m \text{ matrix} \begin{bmatrix} & & & 1 \\ & 0 & 1 & \\ & & \cdot & \\ & \cdot & & \\ & 1 & 0 & \\ 1 & & & \end{bmatrix}, \qquad \text{(B13)}$$

and $\mathbf{A}_{m+1}$ and $\mathbf{B}_{m+1}$ are the Toeplitz matrices

$$\mathbf{A}_{m+1} = \begin{bmatrix} a_0 & a_1 & \cdot & \cdot & a_m \\ a_{-1} & a_0 & \cdot & \cdot & a_{m-1} \\ \vdots & & & & \\ a_{-m} & a_{1-m} & \cdot & \cdot & a_0 \end{bmatrix},$$

$$\mathbf{B}_{m+1} = \begin{bmatrix} b_0 & b_1 & \cdot & \cdot & b_m \\ b_{-1} & b_0 & \cdot & \cdot & b_{m-1} \\ \vdots & & & & \\ b_{-m} & b_{1-m} & \cdot & \cdot & b_0 \end{bmatrix}. \qquad \text{(B14)}$$

To establish the identity we use the relations

$$s_2^*c_2^*(b_{-r} - b_r) = s_1c_1(a_{-r} - a_r), \qquad \text{(B15)}$$

$$c_2^{*2}b_r - s_2^{*2}b_{-r} = s_1^2a_{r-1} - c_1^2a_{1-r}, \qquad \text{(B16)}$$

which follow from identities between δ' and δ^*. These relations imply therefore that

$$s_2^*c_2^*(\mathbf{B}'_{m+1} - \mathbf{B}_{m+1}) = s_1c_1(\mathbf{A}'_{m+1} - \mathbf{A}_{m+1}) \qquad \text{(B17)}$$

$$(c_2^{*2}\mathbf{B}_{m+1} - s_2^{*2}\mathbf{B}_{m+1})\mathbf{R}_{m+1}$$

$$= \begin{bmatrix} & & & ? \\ & (s_1^2\mathbf{A}_m - c_1^2\mathbf{A}_m')\mathbf{R}_m & & ? \\ & & & ? \\ ? & ? & ? & ? \end{bmatrix}, \qquad \text{(B18)}$$

where the prime denotes matrix transposition. Then

$$\mathbf{P}_2\mathbf{P}_3\mathbf{P}_4 = \begin{bmatrix} 0 & \cdot & \cdot & 0 & 1 \\ \vdots & & \mathbf{X} & & \\ 0 & & & & \\ -1 & & & & \end{bmatrix}, \qquad \text{(B19)}$$

where

$$\mathbf{X} = (c_2^*\mathbf{I}_{m+1} + s_2^*\mathbf{R}_{m+1})\mathbf{B}_{m+1}(-s_2^*\mathbf{I}_{m+1} + c_2^*\mathbf{R}_{m+1})$$

$$= s_2^*c_2^*(\mathbf{B}'_{m+1} - \mathbf{B}_m) + (c_2^{*2}\mathbf{B}_{m+1} - s_2^{*2}\mathbf{B}_{m+1})\mathbf{R}_{m+1}$$

$$= \begin{bmatrix} & & & ? \\ & \mathbf{Y} & & ? \\ & & & ? \\ ? & ? & ? & ? \end{bmatrix},$$

and where

$$\mathbf{Y} = s_1c_1(\mathbf{A}_m' - \mathbf{A}_m) + s_1^2\mathbf{A}_m - c_1^2\mathbf{A}_m')\mathbf{R}_m. \qquad \text{(B20)}$$

In deriving this result, (B17) and (B18) have been used, as well as

$$\mathbf{RM} = \mathbf{M'R}, \qquad \text{(B21)}$$

for any matrix **M**. The matrix identity is finally proved from

$$(s_1\mathbf{I}_m - c_1\mathbf{R}_m)\mathbf{Y}(c_1\mathbf{I}_m + s_1\mathbf{R}_m)$$

$$= (s_1\mathbf{I}_m - c_1\mathbf{R}_m)(-s_1\mathbf{A}_m - c_1\mathbf{A}_m'\mathbf{R}_m)$$

$$= \mathbf{A}_m.$$

We can now take determinants of the identity (B8), (B9), giving

$$|\mathbf{P}_1\mathbf{P}_2\mathbf{P}_3\mathbf{P}_4\mathbf{P}_5| = |\mathbf{P}_6|,$$

or

$$|\mathbf{P}_1\mathbf{P}_5|\;|\mathbf{P}_2\mathbf{P}_4|\;|\mathbf{P}_3| = |\mathbf{P}_6|,$$

so that

$$\begin{vmatrix} 1 & 0 & \cdot & \cdot & 0 \\ 0 & & & & \\ \cdot & & -\mathbf{R}_m & & \\ \cdot & & & & \\ 0 & & & & \end{vmatrix} \; \left|\mathbf{R}_{m+1}\right| \; |\mathbf{P}_3| = |\mathbf{P}_6|,$$

or simply

$$|\mathbf{P}_3| = |\mathbf{P}_6|.$$

But

$$|\mathbf{P}_3| = (-1)^m c_2^{*2} \begin{vmatrix} b_{-1} & b_{-2} & \cdot & \cdot & b_{-m} \\ b_0 & b_{-1} & \cdot & \cdot & b_{1-m} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ b_{m-2} & b_{m-1} & \cdot & \cdot & b_{-1} \end{vmatrix} + (-1)^{m+1} s_2^{*2} \begin{vmatrix} b_1 & b_2 & \cdot & \cdot & b_m \\ b_0 & b_1 & \cdot & \cdot & b_{m-1} \\ \cdot & & & & \\ b_{2-m} & b_{1-m} & \cdot & \cdot & b_1 \end{vmatrix}, \qquad \text{(B22)}$$

which is the Kaufman–Onsager formula (B1) for $\langle\sigma_{1,1}\sigma_{1,1+m}\rangle$, and

$$|\mathbf{P}_6| = |\mathbf{A}_m| = \begin{vmatrix} a_0 & a_1 & \cdot & \cdot & a_{m-1} \\ a_{-1} & a_0 & \cdot & \cdot & a_{m-2} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ a_{1-m} & a_{2-m} & \cdot & \cdot & a_0 \end{vmatrix},$$

which is the Potts–Ward formula. And hence the two formulas are the same.