

Distribution Functions and Quantum Statistics

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A formulation of quantum statistical mechanics is given, in terms of distribution functions. It is shown that all quantities of interest are obtained directly from nonlocal distribution functions

$$\gamma^{(1)}(x_1', x_1, \beta), \quad \gamma^{(2)}(x_1', x_2', x_1 x_2, \beta), \dots$$

In a uniform system the Fourier transform of $\gamma^{(1)}(x_1', x_1, \beta)$ is the distribution of particles in k space, $n(k, \beta)$. Various schemes for calculating these distribution functions directly are discussed. An approximate integral equation for $n(k, \beta)$ is found, which can be solved by a converging iteration process. Some remarks are included on the application of the virial theorem.

1. INTRODUCTION

THERE has been a great deal of attention recently to the problem of applying modern perturbation and field-theoretic techniques to quantum statistical mechanics. In this general area perhaps one should especially mention Montroll and Ward,¹ Martin and Schwinger,² Yang, and Lee,³ and Matsubara, Bloch, and deDominicis *et al.*⁴ The following investigation has points of contact mainly with the first two, but proceeds in a somewhat different direction.

Most previous work in this general area has been directed toward systematic calculations of the grand partition function (g.p.f.). Once the g.p.f. is known, all thermodynamic quantities (internal energy, pressure, density, susceptibility, magnetization, etc.) are found very easily. The g.p.f. treatment is thus rather satisfying, but it is not the only possible one. For example, the same thermodynamic quantities may be found directly from a certain function: $\gamma^{(2)}(x_1' x_2'; x_1 x_2; \beta)$ by integration. This is not so straightforward as differentiation, but there are two compensating advantages: First, the diagonal element of the $\gamma^{(2)}$ function has a direct physical meaning, being the distribution of pairs of particles; moreover, if we integrate over the coordinates of one particle (say x_2), removing the prime, we obtain a function whose diagonal element is proportional to the density of particles, and whose Fourier transform is the distribution of particles in momentum space, $n(k, \beta)$. All of these are directly, or almost directly, measurable by experiment. To obtain the same information starting from the g.p.f. is a problem as difficult as calculating, for example, the energy.

The second advantage is in a sense fortuitous. It turns out that in the process of looking for differential

equations which determine the distribution functions it is very natural to introduce an effective potential operator K which is essentially the reaction matrix of many-body perturbation theory. Since the equations derived in the present treatment are not exact the advantage here is merely that we can assume the K matrix is known once-for-all and proceed from there. The actual calculation of K for a given interaction is a separate problem.

In an exact treatment,⁵⁻⁷ which we hope to give later, the use of the K matrix is useful also inasmuch as it makes it possible to carry over certain results of a general nature to statistical mechanics. In particular one might mention the famous "linked cluster expansion."

2. THE DENSITY MATRIX

The density matrix Γ may be defined as the solution of the Bloch equation

$$-(\partial/\partial\beta)\Gamma_{\mu\nu} = \mathcal{H}\Gamma_{\mu\nu}. \quad (2.1)$$

For a Hamiltonian which is independent of temperature, one has the formal solution

$$\Gamma_{\mu\nu} = \Phi_\mu \exp(-\beta\mathcal{H})\Phi_\nu, \quad \lim_{\beta \rightarrow 0} \Gamma_{\mu\nu} = \delta_{\mu\nu} \quad (2.2)$$

where the Schrödinger equation $\mathcal{H}\Phi_\nu = E_\nu\Phi_\nu$ determines the eigenvalues and eigenfunctions. The partition function Z for a canonical ensemble is defined by

$$Z = \sum_\nu \exp(-\beta E_\nu) = \text{Tr}\{\exp(-\beta\mathcal{H})\}, \quad (2.3)$$

where the sum is over all states in a complete set corresponding to the given β . The average of any quantum

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¹ E. Montroll and J. Ward, *Phys. Fluids* **1**, 55 (1958).

² P. C. Martin and J. Schwinger, *Phys. Rev.* **115**, 1342 (1959).

³ C. N. Yang and T. D. Lee, *Phys. Rev.* **113**, 1165 (1959); **116**, 25 (1959).

⁴ T. Matsubara, *Progr. Theoret. Phys. (Kyoto)* **14**, 351 (1955); C. Bloch, *Nuclear Phys.* **7**, 451 (1958); C. Bloch and C. de Dominicis, *Nuclear Phys.* **7**, 459 (1958); **10**, 181 (1958); **10**, 509 (1958); also A. Glassgold, W. Heckrotte, and K. Watson, *Phys. Rev.* **115**, 1374 (1959).

⁵ A complete bibliography can be found in "The Many-Body Problem," course given in the Summer School of Theoretical Physics, Grenoble, 1958 (unpublished); also, K. A. Brueckner, C. A. Levinson, and H. Mahmoud, *Phys. Rev.* **95**, 217 (1954); K. A. Brueckner, *Phys. Rev.* **96**, 508 (1954); **97**, 1353 (1955); K. A. Brueckner and C. A. Levinson, *Phys. Rev.* **97**, 1344 (1955); K. M. Watson, *Phys. Rev.* **103**, 172 (1956); W. Riesenfeld and K. M. Watson, *Phys. Rev.* **104**, 492 (1956).

⁶ K. A. Brueckner and M. Gell-Mann, *Phys. Rev.* **106**, 364 (1957).

⁷ L. Van Hove, *Physica* **21**, 901 (1955); **22**, 343 (1956); L. Van Hove and N. M. Hugenholtz, *Physica* **24**, 363 (1958); J. Goldstone, *Proc. Roy. Soc. (London)* **A239**, 627 (1957).

mechanical operator over the canonical ensemble is given by

$$\bar{O}_{(\text{ensemble})} = \text{Tr}\{O \exp(-\beta \mathcal{H})\} / \text{Tr}\{\exp(-\beta \mathcal{H})\}. \quad (2.4)$$

It is actually more convenient to work in the grand canonical ensemble. The grand partition function is given by

$$Z^G = \sum_N z^N Z_N = \text{Tr}\{\exp(-\beta \mathcal{H}_N + \beta \mu N)\}. \quad (2.5)$$

where μ is the chemical potential and $z = \exp(\beta \mu)$ is the fugacity of the system. The average over the grand canonical ensemble is, of course,

$$\bar{O}_{(\text{grand ensemble})} = \text{Tr}\{O \exp(-\beta \mathcal{H} + \beta \mu N)\} / \text{Tr}\{\exp(-\beta \mathcal{H} + \beta \mu N)\}. \quad (2.6)$$

Before discussing distribution functions in the grand ensemble, we consider the situation when the number of particles N is fixed. A configuration representation is

$$\Gamma^{(N)}(\mathbf{x}^{N'}, \mathbf{x}^N) = \Sigma_{\nu} \Phi_{\nu}^*(\mathbf{x}^{N'}) \exp(-\beta \mathcal{H}) \Phi_{\nu}(\mathbf{x}^N) = \Gamma^{(N)}(N' | N), \quad (2.7)$$

where $\mathbf{x}^N = \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N$ is a $3N$ -dimensional vector (including spin coordinates, if any) and $\Phi(\mathbf{x}^N)$ is the correct many-body Schrödinger wave function. Now define a set of generalized distribution functions (these are the same as Löwdin's⁸ reduced density matrices, except for the factor $n!/Z_N$):

$$\begin{aligned} \gamma^{(1)}(1' | 1) &= \frac{N}{Z_N} \int \dots \int \Gamma^{(N)}(1', N-1' | 1, N-1) d\{N-1\}, \\ \gamma^{(2)}(1'2' | 12) &= \frac{N(N-1)}{Z_N} \times \\ &\int \dots \int \Gamma^{(N)}(1', 2', N-2 | 1, 2, N-2) d\{N-2\}, \\ &\dots, \\ \gamma^{(N)}(N' | N) &= \frac{N!}{Z_N} \Gamma^{(N)}(N' | N), \end{aligned} \quad (2.8)$$

using an obvious notation. The primes are removed from the particle coordinates being integrated and, of course, every integration includes the appropriate sum over spin coordinates. The quantities on the left are nonlocal distribution functions for 1-particle, 2-particles, 3-particles, etc. It is clear from the definitions that the m th and $(m+1)$ st matrices are related as follows:

$$\begin{aligned} \gamma^{(m)}(1', 2', \dots, m' | 1, 2, \dots, m) &= \frac{1}{N-m} \int \gamma^{(m+1)} \\ &\times (1', 2', \dots, m', m+1 | 1, 2, \dots, m, m+1) d^3 x_{m+1}, \end{aligned} \quad (2.9)$$

⁸ P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).

where the coordinates of the $(m+1)$ st particle are integrated out.

Note that removing the primes from all primed variables and integrating over configuration space is equivalent to taking the trace, so that:

$$\begin{aligned} 1 &= \frac{1}{N} \int \gamma^{(1)}(1' | 1) d^3 x_1 \\ &= \frac{1}{N(N-1)} \int \int \gamma^{(2)}(1'2' | 12) d^3 x_1 d^3 x_2 \\ &= \dots = \frac{1}{N!} \int \dots \int \gamma^{(N)}(N' | N) d\{N\}. \end{aligned} \quad (2.10)$$

The diagonal element $\gamma^{(1)}(1 | 1)$ depends on the coordinate of only one particle. It is clear that this can be interpreted in terms of the density, i.e.,

$$\gamma(1 | 1) = \rho(r_1), \quad (2.11)$$

where $\rho(r_1)$ is the density of particles as a function of position. If the N particles are evenly distributed in a volume Ω , then, of course, $\rho(r) = \rho_0 = N/\Omega$. In statistical mechanics problems this is generally the case. One alternative is where the particles actually form a collective boundstate (at zero pressure),⁹ e.g., an atomic nucleus. A third distinct possibility (also corresponding to zero pressure) is that the particles form a lattice structure like a crystalline solid, in which case the density is periodic. Most physical problems, therefore, fall quite neatly into three classes: (1) uniform gases or liquids and (2) finite systems at zero pressure, and (3) crystalline solids. In case (1) the diagonal elements of $\gamma^{(2)}$, $\gamma^{(3)}$, \dots depend only on the *relative* positions of the particles, not on their location with respect to a fixed coordinate system. This is a consequence of the invariance of the Hamiltonian under translations. Thus,

$$\begin{aligned} \gamma^{(1)}(1 | 1) &= \rho_0, \\ \gamma^{(2)}(12 | 12) &= \rho_0^2 \rho_2(r_{12}), \\ \gamma^{(3)}(123 | 123) &= \rho_0^3 \rho_3(r_{12}, r_{23}, r_{31}). \end{aligned} \quad (2.12)$$

A modified kind of invariance occurs if the ensemble is considered to be subject to a periodic external potential. This approximates the actual situation of electrons in a metal, for example. This is neither case (1) nor case (3), exactly, because we are dealing with a two-component system where the electrons are in the liquid or gas phase, and the ions are in the crystalline phase.

⁹ It has been pointed out to the author by J. Lebowitz that there are probably no real systems which have *exactly* zero pressure. Even a tightly bound system has a finite probability of dissociation, and consequently if it is enclosed in a finite volume there will be a finite "vapor pressure." In the case of nuclei this correction is extremely small, being essentially proportional to the ratio of the thermal energy kT to the binding energy. There will also be a negligible correction arising from the kinetic energy of motion of the nucleus *as a whole* inside the confining volume Ω .

Any operator O can be divided into 1-body, 2-body, 3-body operators, e.g.,

$$O = O^{(0)} + \sum_i O_i^{(1)} + \sum_{i < j} O_{ij}^{(2)} + \sum_{i < j < k} O_{ijk}^{(3)} + \dots, \quad (2.13)$$

and one has quite generally, for the expectation value of O ,

$$\begin{aligned} \langle O \rangle &= O^{(0)} + \int O_1^{(1)} \gamma^{(1)}(1' | 1) d^3 x_1 \\ &+ \frac{1}{2!} \int \int O_{12}^{(2)} \gamma^{(2)}(1' 2' | 12) d^3 x_1 d^3 x_2 \\ &+ \frac{1}{3!} \int \int \int O_{123}^{(3)} \gamma^{(3)}(1' 2' 3' | 123) d^3 x_1 d^3 x_2 d^3 x_3. \end{aligned} \quad (2.14)$$

In practically all problems of physical interest one may ignore terms other than those indicated; moreover all the known three-body forces are apparently rather small compared to two-body interactions. If the operator depends on spin or isospin it can be expressed in terms of appropriate exchange operators operating on the exact wave function. For a system of Fermi particles the total wave function is, of course, antisymmetric and it is easy to see that in this case *all* the reduced density matrices have the property of vanishing when two or more coordinates (including spin and isospin) are set equal. However, details of this nature are more properly discussed in relation to specific problems.

What is more important is the following observation: if all terms beyond the m -body term are negligible, then the physical properties of the system are determined once for all if we know $\gamma^{(m)}$. Naturally, we are mainly concerned where $O = \mathcal{H}$, the Hamiltonian operator, and where $m=2$, meaning that 3-body and higher-order many-body forces are unimportant. The quantum mechanical virial theorem throws an interesting sidelight on the above remarks. In general the theorem states that

$$\langle T \rangle = \langle \Xi \rangle, \quad (2.15)$$

where Ξ is the virial operator, defined

$$\begin{aligned} \Xi &= \frac{1}{2} \sum_i \{ \mathbf{r}_i \cdot \text{grad}_i [\sum_{i < j} V_{ij} + \sum_{i < j < k} V_{ijk} + \dots] \} \\ &+ (\text{V.E.F.}), \end{aligned} \quad (2.16)$$

where (V.E.F.) = virial of external forces. The term in square brackets represents all the interparticle interactions,¹⁰ including both central and noncentral

¹⁰ The argument as given here holds for local potentials. Since the most general kind of interaction is nonlocal (e.g., velocity dependent), the usual form of the quantum mechanical virial theorem must be modified. For a nonlocal interaction of the form $\int V(N', N) \Phi(N') d\{N'\}$ the virial takes the form

$$\begin{aligned} \Xi &= \frac{1}{2} \sum_i \left\{ \mathbf{r}_i \cdot \text{grad}_i \int V(N', N) \Phi(N') d\{N'\} \right. \\ &\quad \left. - \int V(N', N) \mathbf{r}_i' \cdot \text{grad}_i \Phi(N') d\{N'\} \right\} + \text{V.E.F.}, \end{aligned}$$

forces and any combination of exchange operators. The differentiation refers only to the spatial variables leaving the spin and isospin operators (if any) unchanged. The spatial dependence of V_{ij} , V_{ijk} , ..., etc. must be upon relative coordinates only, whence the expression above can be simplified as follows:

$$\begin{aligned} \Xi &= \frac{1}{2} \left[\sum_{i < j} \mathbf{r}_{ij} \frac{\partial}{\partial \mathbf{r}_{ij}} V_{ij} + \sum_{i < j < k} \left(\mathbf{r}_{ij} \frac{\partial}{\partial \mathbf{r}_{ij}} + \mathbf{r}_{ik} \frac{\partial}{\partial \mathbf{r}_{ik}} \right. \right. \\ &\quad \left. \left. + \mathbf{r}_{jk} \frac{\partial}{\partial \mathbf{r}_{jk}} \right) V_{ijk} + \dots \right] + \text{V.E.F.}, \end{aligned} \quad (2.17)$$

whence

$$\begin{aligned} \langle T \rangle &= \langle \Xi \rangle = \frac{1}{4} \int \int \left[\mathbf{r}_{12} \frac{\partial}{\partial \mathbf{r}_{12}} V_{12} \right] \gamma^{(2)}(12 | 12) d^3 x_1 d^3 x_2 \\ &+ \frac{1}{12} \int \int \int \left[\left(\mathbf{r}_{12} \frac{\partial}{\partial \mathbf{r}_{12}} + \mathbf{r}_{13} \frac{\partial}{\partial \mathbf{r}_{13}} + \mathbf{r}_{23} \frac{\partial}{\partial \mathbf{r}_{23}} \right) V_{123} \right] \\ &\quad \times \gamma^{(3)}(1' 2' 3' | 123) d^3 x_1 d^3 x_2 d^3 x_3 + (\text{V.E.F.}), \end{aligned} \quad (2.18)$$

where by definition $\langle \text{V.E.F.} \rangle = \frac{3}{2} p \Omega$.^{10a} It is understood, in interpreting the above integrals, that spin and isospin operators act only on unprimed variables, before the primes are removed.

It is clear from the foregoing that as long as the spatial interaction potential is local and provided there are no external forces ($p\Omega=0$), both the kinetic energy and the potential energy are determined by the diagonal elements of $\gamma^{(2)}$, $\gamma^{(3)}$, Assuming only 2-body forces, the diagonal element of $\gamma^{(2)}$ above is sufficient to determine the energy. This is a fact of considerable practical importance since the above criteria are satisfied to a good approximation by several physical systems, including nuclei. The only qualification one need make is that the nuclear potential V_{ij} may have some non-locality (velocity dependence) of a rather short-range character. But the nucleon scattering data may be

and, breaking the interaction into 2-body, 3-body, components as before, we obtain

$$\begin{aligned} \Xi &= \frac{1}{4} \int \int \left(\mathbf{r}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + \mathbf{r}_2 \cdot \frac{\partial}{\partial \mathbf{r}_2} \right) \left\{ \int \int V_{12}(r_{12}, r_{12}'') \right. \\ &\quad \times \gamma^{(2)}(1' 2' | 1'' 2'') d^3 r_1'' d^3 r_2'' \} d^3 r_1 d^3 r_2 \\ &\quad - \frac{1}{4} \int \int \int \int V_{12}(r_{12}, r_{12}'') \left(\mathbf{r}_1'' \cdot \frac{\partial}{\partial \mathbf{r}_1''} + \mathbf{r}_2'' \cdot \frac{\partial}{\partial \mathbf{r}_2''} \right) \\ &\quad \times \gamma^{(2)}(1' 2' | 1'' 2'') d^3 r_1'' d^3 r_2'' d^3 r_1 d^3 r_2 + \text{V.E.F.} + 3\text{-body terms.} \end{aligned}$$

In the first term the requisite spin and isospin terms operate on $\gamma^{(2)}$ *first*; then the single primes are changed to double primes, and all integrations are performed. In the second term the differentiation is carried out on the doubly primed variables first, followed by the operations indicated by V_{12} (these two steps can be taken in either order as long as V_{12} only involves operations on spinors). Finally, the single primes are changed to double primes as formerly, and all integrations carried out. The differentiation on the density matrix directly is an explicit sign of the velocity dependence of the nonlocal interaction.

^{10a} Note added in proof. Here we have assumed (a) no exchange forces and (b) isotropy. In general the pressure is a tensor quantity.

satisfied up to quite high energies by local potentials with a hard core, so that the assumption of local forces is probably quite reasonable.

A further remark may be appropriate with regard to the convergence of perturbation methods. Perturbation techniques are predicated, generally speaking, on the assumption that the potential energy (from the perturbing part of the Hamiltonian) is much smaller than the kinetic energy contribution (due to the unperturbed Hamiltonian). The great advantage of the Brueckner theory⁵ is that it maximizes the contribution of the unperturbed Hamiltonian by finding the best possible "effective" single-particle potential. This is discussed briefly in the next section. However, sooner or later, all perturbative techniques become impossibly complicated when more and more many-particle collisions take place, unless, as in the electron-gas problem, one can sum whole classes of terms at a stroke.⁶ The virial theorem may give one an estimate of the contribution of the potential energy as compared with the kinetic energy in the liquid fraction of a condensing state, which may be of use in estimating the convergence of perturbation theory.

3. ON THE SUFFICIENCY OF THE γ MATRICES

A number of questions arise in connection with this topic, and we shall touch on only a few of them, and only briefly. To begin with, it is obvious that if all the energy eigenvalues are known, then at a given reciprocal temperature β all the thermodynamic properties of the system are completely determined, via the partition function Z_N . We have already remarked that for a system with only 2-body forces the matrix $\gamma^{(2)}$ is sufficient to determine the average energy E . Moreover, if the particles only interact through *local* potentials (not velocity dependent), and systems in equilibrium with external forces, the diagonal element of $\gamma^{(2)}$ alone is sufficient.

Löwdin⁸ has discussed the application of the density matrix formulation to the Hartree-Fock problem, following earlier treatments by Fock¹¹ and Dirac.¹² These authors showed that for the ground state $\beta \rightarrow \infty$ in the "independent particle model," where the many-body wave function is constructed entirely from single-particle wave functions (e.g., as a Slater determinant) all the density matrices can be constructed explicitly from the single-particle function $\gamma_{\beta \rightarrow \infty}^{(1)}(1'|1)$. Of course, the independent-particle model fails to take into account pair correlations or higher-order effects. However, by a simple extension of some arguments due to Brueckner and others it can be shown that a knowledge of $\gamma_{\beta \rightarrow \infty}^{(1)}(1'|1)$ is in principle sufficient to determine the energy, including all two-particle correlations. This is a stronger result than Löwdin's. We shall sketch the proof briefly, for the most general nonlocal spin-

dependent two-body interaction. Ignoring three-body collisions, the energy of such a system is given by

$$E = \sum_i \epsilon_i = \sum_i \int \varphi_i^*(x_1) T_i \varphi_i(x_1) d^3 \\ + \sum_{i < j} \sum_l^{occ} c_l \int \int \int \int \varphi_i^*(x_1) \varphi_i(x_1') \\ \times (r_{12} | K_l | r_{12}') \varphi_j^*(x_2) \varphi_j(x_2') \\ \times d^3 x_1 d^3 x_1' d^3 x_2 d^3 x_2', \quad (3.1)$$

where φ_i are a set of single-particle functions and the C_l are statistical factors associated with summing over spins (if any). The sums are over occupied states. The Hartree-Fock equation determining the single-particle functions φ_i are obtained in the usual way by varying the above expression with respect to φ_i^* , subject to the normalization condition

$$\sum_i \int \varphi_i^*(x) \varphi_i(x) d^3 x = N. \quad (3.2)$$

The K matrix is determined by solving the following integral equation in which the single-particle energies occur:

$$K_{ij,kl} = v_{ij,kl} + \sum_{m,n}^{occ} \frac{v_{ij,mn} K_{mn,kl}}{\epsilon_k + \epsilon_l + \epsilon_m - \epsilon_n}, \quad (3.3)$$

and of course the matrix element involves the single-particle functions in question. The procedure of Brueckner and collaborators is to look for a solution by a self-consistent procedure, starting at any point, and iterating until convergence is obtained. It should be noted that the Hartree-Fock equations are nonlinear integro-differential equations, and because of the non-linearity one expects more than one possible solution. Indeed on physical grounds one would expect quite different solutions, depending on the initial conditions. It is easy to show that plane waves satisfy the H-F equations, leading to one form of the K matrix which has actually been computed numerically by Brueckner and Gammel¹³; namely, the case corresponding to infinite nuclear matter. Solutions corresponding to finite nuclei are now being sought.

For present purposes the significant point is the fact that in the ground state

$$\sum_i^{occ} \psi_i^*(x_1') \psi_i(x_1) = \gamma_{\beta \rightarrow \infty}^{(1)}(1'|1). \quad (3.4)$$

Any choice of $\gamma^{(1)}(1'|1)$ which is inserted in the H-F equations serves to linearize the equation and make it possible to "solve" by routine methods, but this solution would not, in general, satisfy the self-consistency con-

¹¹ V. Fock, Z. Physik **61**, 126 (1930).

¹² P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930); **27**, 240 (1931).

¹³ K. A. Brueckner and J. Gammel, Phys. Rev. **109**, 1023 (1958); K. A. Brueckner, J. Gammel, and H. Weitzner, Phys. Rev. **110**, 431 (1958).

dition between the output and the input. The correct choice, of course, determines the energy eigenvalues and eigenfunctions for a given form of the K matrix. It only remains to determine $K_{ij,kl}$ itself by solving the integral equation, recomputing the eigenvalues, and so on until the process converges.

4. BLOCH-TYPE EQUATION FOR THE γ MATRICES

The fundamental equation is the Bloch equation

$$-(\partial/\partial\beta)\Gamma = \mathcal{H}\Gamma, \quad (4.1)$$

with the boundary condition

$$\lim_{\beta \rightarrow 0} \Gamma(\mathbf{x}'^N, \mathbf{x}^N, \beta) = \delta(\mathbf{x}'^N - \mathbf{x}^N).$$

Here we assume only 2-body forces, e.g.,

$$\mathcal{H} = \sum_{i=1}^N T_i + \sum_{i < j=1}^N V_{ij}. \quad (4.2)$$

$$-\frac{1}{Z_N} \frac{\partial}{\partial\beta} Z_N \gamma^{(2)}(1'2'|12) = \left(E - \frac{\partial}{\partial\beta}\right) \gamma^{(2)}(1'2'|12)$$

$$= (T_1 + T_2 + V_{12}) \gamma^{(2)}(1'2'|12) + \int (T_3 + V_{13} + V_{23}) \gamma^{(3)}(1'2'3|123) d^3x_3$$

$$+ \frac{1}{2} \int \int V_{34} \gamma^{(4)}(1'2'34|1234) d^3x_3 d^3x_4. \quad (4.4)$$

The general case is obtained in a similar way, e.g.,

$$\left(E - \frac{\partial}{\partial\beta}\right) \gamma^{(m)}(1'2' \dots m'|12 \dots m)$$

$$= \left(\sum_{i=1}^m T_i + \sum_{i < j=1}^m V_{ij}\right) \gamma^{(m)}(1'2' \dots m'|12 \dots m) + \int (T_p + \sum_{i=1}^m V_{ip}) \gamma^{(m+1)}(1'2' \dots m', p|12 \dots m p) d^3x_p$$

$$+ \frac{1}{2} \int \int V_{pq} \gamma^{(m+2)}(1'2' \dots m', pq|12 \dots m p q) d^3x_p d^3x_q. \quad (4.5)$$

These equations can be easily checked by integrating the remaining coordinates making use of the conditions 2.10, 2.14.

A boundary condition is supplied by the symmetry requirements on the matrices. On exchanging unprimed variables we have

$$\gamma^{(2)}(1'2'|12) = \pm \gamma^{(2)}(1'2'|21), \quad (4.6)$$

$$\gamma^{(3)}(1'2'3'|123) = \pm \gamma^{(3)}(1'2'3'|132) = \dots, \quad (4.7)$$

and similarly for the primed variables. The extension to higher-order matrices is immediate. A further requirement is that the matrices be symmetric across the diagonal (Hermiticity), i.e., for $\gamma^{(2)}$,

$$\gamma^{(2)}(1'2'|12) = \gamma^{(2)*}(12|1'2'). \quad (4.8)$$

Now integrate both sides over all particle coordinates but one, and multiply through by N/Z_N to obtain the single-particle equation. It is also convenient to eliminate Z_N , using $E = -(\partial/\partial\beta) \ln Z_N$:

$$-\frac{1}{Z_N} \frac{\partial}{\partial\beta} Z_N \gamma^{(1)}(1'|1) = \left(E - \frac{\partial}{\partial\beta}\right) \gamma^{(1)}(1'|1)$$

$$= T_1 \gamma^{(1)}(1'|1) + \int (T_2 + V_{12}) \gamma^{(2)}(1'2'|12) d^3x_2$$

$$+ \frac{1}{2} \int \int V_{23} \gamma^{(3)}(1'23|123) d^2x_2 d^3x_3. \quad (4.3)$$

The two-particle equation is found by integrating over all but two particle coordinates and multiplying by $N(N-1)/Z_N$. As before,

$$-\frac{1}{Z_N} \frac{\partial}{\partial\beta} Z_N \gamma^{(2)}(1'2'|12) = \left(E - \frac{\partial}{\partial\beta}\right) \gamma^{(2)}(1'2'|12)$$

$$= (T_1 + T_2 + V_{12}) \gamma^{(2)}(1'2'|12) + \int (T_3 + V_{13} + V_{23}) \gamma^{(3)}(1'2'3|123) d^3x_3$$

$$+ \frac{1}{2} \int \int V_{34} \gamma^{(4)}(1'2'34|1234) d^3x_3 d^3x_4. \quad (4.4)$$

The general case is obtained in a similar way, e.g.,

$$\left(E - \frac{\partial}{\partial\beta}\right) \gamma^{(m)}(1'2' \dots m'|12 \dots m)$$

$$= \left(\sum_{i=1}^m T_i + \sum_{i < j=1}^m V_{ij}\right) \gamma^{(m)}(1'2' \dots m'|12 \dots m) + \int (T_p + \sum_{i=1}^m V_{ip}) \gamma^{(m+1)}(1'2' \dots m', p|12 \dots m p) d^3x_p$$

$$+ \frac{1}{2} \int \int V_{pq} \gamma^{(m+2)}(1'2' \dots m', pq|12 \dots m p q) d^3x_p d^3x_q. \quad (4.5)$$

This fixes the dependence of the primed variables in terms of the unprimed variables.

It is interesting to derive the equations in the grand canonical ensemble. The appropriate distribution functions are defined by

$$\gamma_G^{(m)} = \frac{1}{Z_G} \sum_{N=m}^{\infty} z^N Z_N \gamma_N^{(m)}. \quad (4.9)$$

The equations determining the grand canonical distribution functions are easily found by multiplying the above equations through by $(Z_N/Z_G) z^N$ and summing over N . The result turns out to give exactly the same equations as before, with Z_N replaced by Z_G and $\gamma_N^{(m)}$ by $\gamma_G^{(m)}$. It is useful as before to eliminate Z_G from

the equations, using the relation $E = -(\partial/\partial\beta) \ln Z_G$. The result is, for $m < N$

$$\begin{aligned} \left(E - \frac{\partial}{\partial\beta}\right) \gamma_G^{(1)}(1'|1) \\ = T_1 \gamma_G^{(1)}(1'|1) + \int (T_2 + V_{12}) \gamma_G^{(2)}(1'2|12) d^3x_2 \\ + \frac{1}{2} \int \int V_{23} \gamma_G^{(3)}(1'23|123) d^3x_2 d^3x_3, \quad (4.10) \end{aligned}$$

$$\begin{aligned} \left(E - \frac{\partial}{\partial\beta}\right) \gamma_G^{(2)}(1'2'|12) \\ = (T_1 + T_2 + V_{12}) \gamma_G^{(2)}(1'2'|12) \\ + \int (T_3 + V_{13} + V_{23}) \gamma_G^{(3)}(1'2'3|123) d^3x_3 \\ + \frac{1}{2} \int \int V_{34} \gamma_G^{(4)}(1'2'34|1234) d^3x_3 d^3x_4, \quad (4.11) \end{aligned}$$

and similarly for the general case. We have made use of the fact that $\gamma_N^{(m)}$ is identically zero by definition for $N < m$, which expresses the fact that there can be no probability of finding m particles in any configuration if the total number of particles N is smaller than m . Since the equations for $\gamma_N^{(m)}$ and $\gamma_G^{(m)}$ are the same, for $m < N$, we conclude that $\gamma_N^{(m)} \cong \gamma_G^{(m)}$, for $m \ll N$. Hence we drop all subscripts hereafter.

A more suggestive way of writing the equations is to break things down in terms of the energy per particle E/N using the identity

$$E\gamma^m = m \frac{E}{N} \gamma^m + \int \frac{E}{N} \gamma^{(m+1)} d^3x_{m+1},$$

and defining the Hamiltonian for m particles,

$$\mathcal{H}^{(m)} = \sum_{i=1}^m T_i + \sum_{i < j=1}^m V_{ij}; \quad (3.12)$$

we obtain

$$\begin{aligned} \left[m \frac{E}{N} - \frac{\partial}{\partial\beta} - \mathcal{H}^{(m)} \right] \gamma^{(m)} \\ = \int \left(T_p + \sum_{i=1}^m V_{ip} - \frac{E}{N} \right) \gamma^{(m+1)} d^3x_p \\ + \frac{1}{2} \int \int V_{pq} \gamma^{(m+2)} d^3x_p d^3x_q. \quad (3.14) \end{aligned}$$

The integro-differential equations above do not define $\gamma^{(1)}$, $\gamma^{(2)}$ uniquely except in terms of higher-order matrices, $\gamma^{(3)}$, $\gamma^{(4)}$. These in turn are determined by a hierarchy of further equations which are derived in the same way.

The various terms in the two equations can be identified as follows:

(a) The term involving $\gamma^{(1)}$ would be present if the single particle were isolated.

(b) Terms involving $\gamma^{(2)}$ would appear if there were only two particles in the system. They represent the effects of the interaction of the first particle with any second particle or the mutual interaction of a pair in the absence of any other particles.

(c) Terms involving $\gamma^{(3)}$ would appear if there were only three particles in the system. They take into account the effect on the first particle of interactions between any other pair, or interactions of one of the original pair with any third particle. All such interactions are equivalent.

(d) Terms involving $\gamma^{(4)}$ appear if there are four or more particles in the system and represent the indirect effect, on the original pair, of interactions between other pairs of particles. All such interactions are again equivalent. Of course, higher-order matrices appear in the equations determining $\gamma^{(3)}$, $\gamma^{(4)}$.

The systematics of the hierarchy are obvious. The first equation is related to the Hartree-Fock equation (at finite temperature) where the first particle moves in an effective potential due to all the others. The third term is essentially the "single-particle potential," while the second and fourth terms give, in effect, a momentum dependence. The second equation treats two particles explicitly, and, of course, the m th equation treats m particles explicitly. All the equations of the hierarchy are equivalent in that the solution of any one must give the energy and thermodynamic quantities correctly.

5. APPROXIMATION METHODS—SUPERPOSITION PRINCIPLE

It is worth re-emphasizing that the hierarchy of integro-differential equations described in the last section constitute a complete formulation of the many-body problem in quantum statistics, although an unwieldy one. To make further progress it will evidently be necessary to cut off the sequence at some point by approximating one of the higher-order matrices in terms of a lower-order one. One is led naturally to consider something like the well-known "superposition approximation" of Kirkwood¹⁴ which has been used in classical statistical mechanics. As an example consider the two-particle equation derived in the last section:

¹⁴ J. Kirkwood, J. Chem. Phys. 3, 300 (1935).

$$\left[\frac{E}{N} - \frac{\partial}{\partial \beta} - 3\mathcal{C}^{(2)} \right] \gamma^{(2)}(1'2'|12) \\ = \int \left(T_3 + V_{13} + V_{23} - \frac{E}{N} \right) \gamma^{(3)}(1'2'3|123) d^3x_3 \\ + \frac{1}{2} \int \int V_{34} \gamma^{(4)}(1'2'34|1234) d^3x_3 d^3x_4. \quad (5.1)$$

If $\gamma^{(3)}$ and $\gamma^{(4)}$ are approximated in terms of $\gamma^{(2)}$, the resulting (approximate) solution is found by an iterative process in which we use $\gamma_{(0)}^{(2)}$ to construct the higher-order matrices and solve the inhomogeneous but linear integral equation which results. [Actually there may be little justification for going beyond the first iteration, even in principle, since there is no real guarantee that a better approximation for $\gamma^{(3)}$ is obtained by superposing the $(n+1)$ st iterate $\gamma_{(n+1)}^{(2)}$ than was obtained by the n th iterate $\gamma_{(n)}^{(2)}$ for arbitrarily large n . It is clear, therefore, that though the iteration process for $\gamma^{(2)}$ may converge, it will *not* converge to the correct solution of the actual problem unless the superposition principal also happens to be correct, which is generally not the case.]

Classically, the superposition approximation was used by Kirkwood to express $\gamma^{(3)}$ in terms of $\gamma^{(2)}$, e.g.,

$$\rho_0^3 \gamma^{(3)}(1'2'3'|123) \cong \gamma^{(2)}(1'2'|12) \\ \times \gamma^{(2)}(2'3'|23) \gamma^{(2)}(3'1'|31). \quad (5.2)$$

Evidently the above can easily be generalized to the quantum-mechanical problem, since the three-particle matrix is automatically symmetric or antisymmetric, on exchanging two particle coordinates (either primed or unprimed variables), according to the symmetry properties of the two-particle matrices. This can be verified by inspection.

We must generalize the idea, however, to apply to matrices of any order. Define the superposition approximation as follows: Any product or sum of products of m -particle matrices which contains the coordinates of $m+n$ particles and obeys the correct symmetry and Hermiticity requirements for the $(m+n)$ -particle matrix will be known as a superposition approximation of the $(m+n)$ -particle matrix.

The treatment of the equation of $\gamma^{(1)}$ requires a superposition approximation involving only $\gamma^{(1)}$. Clearly a suitable choice for $\gamma^{(2)}$ is

$$\gamma_{\text{super}}^{(2)}(1'2'|12) = \gamma^{(1)}(1'|1) \gamma^{(1)}(2'|2) \\ \pm \gamma^{(1)}(1'|2) \gamma^{(1)}(2'|1).$$

A convenient notation for generalizing to higher orders is to use determinants or permanents, which we denote by means of subscripts \pm , e.g.,

$$\gamma_{\text{super}}^{(2)}(1'2'|12) = \begin{vmatrix} \gamma^{(1)}(1'|1) & \gamma^{(1)}(1'|2) \\ \gamma^{(1)}(2'|1) & \gamma^{(1)}(2'|2) \end{vmatrix}_{\pm}, \quad (5.3)$$

and

$$\gamma_{\text{super}}^{(3)}(1'2'3'|123) \\ \pm \begin{vmatrix} \gamma^{(1)}(1'|1) & \gamma^{(1)}(1'|2) & \gamma^{(1)}(1'|3) \\ \gamma^{(1)}(2'|1) & \gamma^{(1)}(2'|2) & \gamma^{(1)}(2'|3) \\ \gamma^{(1)}(3'|1) & \gamma^{(1)}(3'|2) & \gamma^{(1)}(3'|3) \end{vmatrix}_{\pm}, \quad (5.4)$$

where the (+) sign signifies a permanent and the (−) sign a determinant. Evidently the first case corresponds to Bose-Einstein statistics and the second case to Fermi-Dirac statistics.

As long as the many-particle wave function can be constructed from a properly symmetrized product of single-particle functions, the superposition principle is exact. This holds for free particles or for particles moving in a single-particle potential (for example the nuclear shell model). We shall come back to this point later on.

When a two-body interaction is introduced, however, the superposition is no longer exact, and there is a definite inconsistency between successive γ matrices, viz.,

$$\frac{1}{N-1} \int \gamma_{\text{super}}^{(2)}(1'2'|12) d^3x_2 \neq \gamma^{(1)}(1'|1), \quad (5.5)$$

$$\frac{1}{N-2} \int \gamma_{\text{super}}^{(3)}(1'2'3'|123) d^3x_3 \neq \gamma^{(2)}(1'2'|12). \quad (5.6)$$

This inconsistency is characteristic of the approximation. Since the equations must hold true (with the equality) when $\gamma_{\text{super}}^{(3)}$ and $\gamma_{\text{super}}^{(2)}$ are replaced by the exact $\gamma^{(3)}$ and $\gamma^{(2)}$, we have a useful criterion for estimating the validity of the superposition approximation for a given problem, in terms of the magnitude of the discrepancy between the right-hand and left-hand sides of (5.5) and (5.6).

Returning now to the equation of $\gamma^{(2)}$ we need an appropriate superposition approximation for $\gamma^{(3)}$ and $\gamma^{(4)}$ in which two-particle correlations are included. One method which suggests itself is to start with a first approximation $\gamma_{(0)}^{(2)}$ and first integrate over the \mathbf{x}_2 coordinates to obtain the corresponding matrix $\gamma_{(0)}^{(1)}$, then use the determinant (permanent) constructions illustrated above to obtain $\gamma_{(0),\text{super}}^{(3)} \gamma_{(0),\text{super}}^{(4)}$. It is clear that there is again an inconsistency if we integrate over \mathbf{x}_3 in $\gamma_{(1),\text{super}}^{(3)}$. In fact we will obtain a new matrix $\gamma_{(1),\text{super}}^{(2)}$ which is different from the original $\gamma_{(0)}^{(2)}$. That this is not a convergent process should be clear. One could indeed obtain an infinite sequence of $\gamma^{(2)}$ matrices by repeatedly integrating and using the superposition approximation, and the error will merely increase each time.¹⁵

¹⁵ Further insight into the situation may be gained by the following consideration: suppose we make the plausible requirement that $\gamma^{(3)}$ be determined by the superposition principle *and* that it be consistent with $\gamma^{(2)}$ in the sense of (5.6). This means

In practice therefore it would seem advisable not to use the determinant method already outlined. Instead one might use the simple product already illustrated in (5.2) for $\gamma^{(3)}$ extending it for $\gamma^{(4)}$ as well:

$$\rho_0^3 \gamma_{\text{super}}^{(3)}(1'2'3'|123) = \gamma^{(2)}(1'2'|12) \gamma^{(2)}(2'3'|23) \gamma^{(2)}(3'1'|31), \quad (5.2)$$

$$\begin{aligned} \rho_0^8 \gamma_{\text{super}}^{(4)}(1'2'3'4'|1234) \\ = \gamma^{(2)}(1'2'|12) \gamma^{(2)}(2'3'|23) \gamma^{(2)}(3'4'|34) \\ \times \gamma^{(2)}(4'1'|41) \gamma^{(2)}(1'3'|13) \gamma^{(2)}(2'4'|24). \end{aligned} \quad (5.7)$$

Another type of superposition approximation has been introduced by Schwinger and Martin² in their work, involving products of matrices of different order. They approximate the three-particle Green's functions by a sum of products of two-particle Green's functions and one-particle Green's functions. The choice of one version or the other is largely a question of mathematical expediency.

6. SOLUTION OF EQUATION FOR $\gamma^{(1)}$ BY SUPERPOSITION METHOD: IDEAL GAS

The simplest application of the formalism is to calculate the single-particle distribution function for the ideal Bose and Fermi gas. The equation for $\gamma_{\text{ideal}}^{(1)}$ [using (5.3), which is exact in this case] is

$$\begin{aligned} \left(E - \frac{\partial}{\partial \beta}\right) \gamma_{\text{ideal}}^{(1)}(1'|1) \\ = T_1 \gamma_{\text{ideal}}^{(1)}(1'|1) + \int T_2 [\gamma_{\text{ideal}}^{(1)}(1'|1) \gamma_{\text{ideal}}^{(1)}(2'|2) \\ \pm \gamma_{\text{ideal}}^{(1)}(1'|2) \gamma_{\text{ideal}}^{(1)}(2'|1)] d^3 x_2. \end{aligned} \quad (6.1)$$

We drop the clumsy subscript for convenience in the following. Since the gas is presumed to be uniform, $\gamma^{(1)}$ depends only on the relative coordinate $|r_i' - r_j|$. Define the Fourier transform

we look at the set of functions $\tilde{\gamma}^{(2)}$ which satisfy the integral equation

$$\frac{1}{N-2} \int \tilde{\gamma}^{(2)}(2'3'|23) \gamma^{(2)}(3'1'|31) d^3 x_3 = \rho_0^3.$$

We know, of course, that $\tilde{\gamma}^{(2)}$ cannot be a solution of the Bloch equation. However, it might seem not unreasonable to use the functions $\tilde{\gamma}^{(2)}$ as approximate choices for a variational calculation of the energy, by minimizing the energy (a functional of $\tilde{\gamma}^{(2)}$) subject to the requirement above. However, nothing useful can come from such a program because, at closer analysis it is seen that there are no nontrivial solutions of the integral equation. Consider the case of a system sufficiently large so that boundary effects may be ignored. Then $\tilde{\gamma}_{\text{diag.}}^{(2)}$ will depend only on the relative coordinates. By introducing the Fourier transform of $\tilde{\gamma}_{\text{diag.}}^{(2)}$, it is easily seen that the left-hand side is a function of $|\mathbf{r}_1 - \mathbf{r}_2|$ whereas the right-hand side is a constant. (More generally the l.h.s. will be a function of $\mathbf{r}_1, \mathbf{r}_1', \mathbf{r}_2, \mathbf{r}_2'$.) Consequently the integral equation cannot be satisfied by any reasonable function $\tilde{\gamma}^{(2)}$, and the superposition approximation cannot be used in conjunction with a variational approach.

$$\begin{aligned} \sum_{\text{spin}} \gamma^{(1)}(i'|j) &= \gamma^{(1)}(|r_i' - r_j|) \\ &= \int n(k, \beta) e^{ik \cdot (r_i' - r_j)} d^3 k. \end{aligned} \quad (6.2)$$

Evidently $n(k, \beta)$ represents the number of particles possessing momentum $\mathbf{p} = \hbar \mathbf{k}$. Using the definition of the kinetic energy operator,

$$T_i = -(\hbar^2/2m) \nabla_i^2, \quad (6.3)$$

we obtain the equation for $n(k, \beta)$:

$$\begin{aligned} \left(E - \frac{\partial}{\partial \beta}\right) n(k, \beta) \\ = \frac{\hbar^2}{2m} \left\{ k^2 n(k, \beta) + n(k, \beta) \int k'^2 n(k', \beta) d^3 k' \right. \\ \left. + \lambda k^2 n^2(k, \beta) \right\}, \end{aligned} \quad (6.4)$$

where λ is a statistical factor depending on spin and symmetry, which we shall define later. But the energy $E(\beta)$ is easily shown to be

$$E(\beta) = \frac{\hbar^2}{2m} \Omega \int k'^2 n(k', \beta) d^3 k', \quad (6.5)$$

so there is a cancellation and the equation reduces to

$$-\frac{\partial}{\partial \beta} n(k, \beta) + \frac{\hbar^2 k^2}{2m} n(k, \beta) [1 + \lambda n(k, \beta)]. \quad (6.6)$$

The equation is nonlinear but it can be integrated partially with respect to β in straightforward fashion introducing one constant of integration. The result is, as expected,

$$\begin{aligned} n_{\text{ideal}}(k, \beta) &= \left[C \exp\left(\frac{\hbar^2 k^2 \beta}{2m}\right) - \lambda \right]^{-1} \\ &= (\lambda)^{-1} \left[z^{-1} \exp\left(\frac{\hbar^2 k^2 \beta}{2m}\right) - \text{sgn} \lambda \right]^{-1}, \end{aligned} \quad (6.7)$$

where we let $C = z^{-1} |\lambda|$. Note that $|\lambda|^{-1}$ may be interpreted as the number of particles which may occupy a given k state for Fermi statistics, while z may be interpreted as the fugacity; z is eliminated in the conventional way by making use of the condition that the number of particles in the system is fixed to be N .^{15a} It may be worth pointing out here that the procedure we

^{15a} Note added in proof. In the case of a degenerate Bose gas z becomes unity, and a δ function term appears in $n(k, \beta)$ corresponding to 'condensed' particles having zero momentum and energy. The coefficient of the δ function gives the number of particles in the condensed state, and is determined by the normalization condition.

have followed is only unambiguous if we stick to the grand canonical ensemble, where the fugacity z is treated as an independent variable. Thus we have put no actual restriction on the implicit temperature dependence of our constant of integration. The pair-distribution function is the diagonal element of $\gamma^{(2)}$, namely

$$\begin{aligned}\gamma_{\text{ideal}}^{(2)}(12|12) &= \gamma^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|) \\ &= \rho_0^2 + \lambda [\gamma^{(1)}(|\mathbf{r}_1 - \mathbf{r}_2|)]^2 \\ &= \rho_0^2 + \text{sgn} \lambda |\lambda|^{-1} \left[\int \left[z^{-1} \exp \frac{\hbar^2 k^2 \beta}{2m} \right. \right. \\ &\quad \left. \left. - \text{sgn} \lambda \right] e^{i\mathbf{k} \cdot \mathbf{r}_i - i\mathbf{k} \cdot \mathbf{r}_j} d^3 k \right]^2. \quad (6.8)\end{aligned}$$

It is seen that when $\lambda = +1$ the above formula is precisely the pair-distribution function for an ideal Bose gas first given by London and Placzek.¹⁶ It is evidently a simple matter to give the corresponding formulae for $\gamma_{\text{ideal}}^{(3)}$, $\gamma_{\text{ideal}}^{(4)}$, etc. It remains to define the factor λ . Since spatially symmetric wave functions clearly correspond to $\lambda = +1$ and spatially antisymmetric wave functions to $\lambda = -1$, it is evident that λ must be the fraction of pairs in space-symmetric states

minus the fraction in space-antisymmetric states. Since the wave function must include the internal coordinates of the system, if any, these also contribute to the symmetry so that some of the pairs will be in symmetric and others in antisymmetric space states. The physically important cases are as follows:

Bosons, such as He^4 , have spin zero; thus all pairs are in space-symmetric states, whence $\lambda = 1$.

Among the fermions, electrons (positive and negative), and He^3 have spin $\pm \frac{1}{2}$; thus $\frac{1}{4}$ of all pairs are in space-symmetric states and $\frac{3}{4}$ in space-antisymmetric states, whence $\lambda = \frac{1}{4} - \frac{3}{4} = -\frac{1}{2}$. Nucleons have spin $\pm \frac{1}{2}$ and isospin $\pm \frac{1}{2}$; thus (assuming equal numbers of neutrons and protons) $\frac{3}{8}$ of all pairs are in space-symmetric states and $\frac{5}{8}$ in space-antisymmetric states, whence $\lambda = \frac{3}{8} - \frac{5}{8} = -\frac{1}{4}$.

It is barely conceivable that non-relativistic statistical mechanics might be applied to certain other cases, such as π -meson clouds. However at the moment such applications seem rather far-fetched, so for present purposes they can be ignored.

7. SOLUTION OF EQUATION FOR $\gamma^{(1)}$ BY SUPERPOSITION METHOD: EFFECTIVE INTERACTION

Assume spinless particles interacting through a 2-body potential $V(r_{ij})$. The complete single-particle equation in the superposition approximation is evidently

$$\begin{aligned}\left(E - \frac{\partial}{\partial \beta} - T_1\right) \gamma^{(1)}(1'|1) &= \int (T_2 + V_{12}) \begin{vmatrix} \gamma^{(1)}(1'|1) & \gamma^{(1)}(1'|2) \\ \gamma^{(1)}(2'|1) & \gamma^{(1)}(2'|2) \end{vmatrix}_{\pm} d^3 x_2 \\ &+ \frac{1}{2} \int \int V_{23} \begin{vmatrix} \gamma^{(1)}(1'|1) & \gamma^{(1)}(1'|2) & \gamma^{(1)}(1'|3) \\ \gamma^{(1)}(2'|1) & \gamma^{(1)}(2'|2) & \gamma^{(1)}(2'|3) \\ \gamma^{(1)}(3'|1) & \gamma^{(1)}(3'|2) & \gamma^{(1)}(3'|3) \end{vmatrix}_{\pm} d^3 x_2 d^3 x_3. \quad (7.1)\end{aligned}$$

We have no means of solving a nonlinear integro-differential equation such as the above, so an iterative scheme is appropriate. Suppose in the nonlinear terms on the right we replace $\gamma^{(1)}$ by the solution for the ideal

gas (previous section) $\gamma_{\text{ideal}}^{(1)} = \gamma_0^{(1)}$. The equation is now a linear but inhomogeneous ordinary differential equation. For the m th iterate,

$$\begin{aligned}\left(E - \frac{\partial}{\partial \beta} - T_1\right) \gamma_{(m)}^{(1)}(1'|1) &= \int (T_2 + V_{12}) \begin{vmatrix} \gamma_{(m-1)}^{(1)}(1'|1) & \gamma_{(m-1)}^{(1)}(1'|2) \\ \dots & \dots \end{vmatrix} d^3 x_2 \\ &+ \frac{1}{2} \int \int V_{23} \begin{vmatrix} \gamma_{(m-1)}^{(1)}(1'|1) & \gamma_{(m-1)}^{(1)}(1'|2) & \gamma_{(m-1)}^{(1)}(1'|3) \\ \dots & \dots & \dots \end{vmatrix}_{\pm} d^3 x_2 d^3 x_3. \quad (7.2)\end{aligned}$$

The analogy with the usual Hartree-Fock method is now clear, for the two terms on the right-hand side involving the interaction are integrated to an *effective* 1-particle potential.

The idea of an "effective" 2-particle interaction can therefore be introduced at this point. Suppose an

effective potential $K(r_{ij})$ is defined conceptually as that operator which, operating on properly symmetrized plane-waves, is equivalent to $V(r_{ij})$ operating on the correct wave function.¹⁷ If V_{12} is replaced by such an operator the superposition approximation is again

¹⁶ F. London, J. Chem. Phys. **11**, 203 (1943); G. Placzek, Proceedings Berkeley Symposium on Mathematical Statistics and Probability, 1950 (unpublished), p. 281.

¹⁷ This is oversimplified, since it becomes the question of whether such an operator exists in the form specified. The omission will be rectified.

plausible, and we obtain the modified Hartree-Fock equation

$$\left(E - \frac{\partial}{\partial \beta} - T_1\right) \gamma^{(1)}(1'|1) = \int (T_2) \begin{vmatrix} \gamma^{(1)}(1'|1) & \gamma^{(1)}(1'|2) \\ \gamma^{(1)}(2'|1) & \gamma^{(1)}(2'|2) \end{vmatrix}_{\pm} d^3x_2 \\ + \int K_{12} \begin{vmatrix} \gamma_0^{(1)}(1'|1) & \gamma_0^{(1)}(1'|2) \\ \gamma_0^{(1)}(2'|1) & \gamma_0^{(1)}(2'|2) \end{vmatrix} d^3x_2 + \frac{1}{2} \int \int K_{23} \begin{vmatrix} \gamma_0^{(1)}(1'|1) & \gamma_0^{(1)}(1'|2) & \gamma_0^{(1)}(1'|3) \\ \gamma_0^{(1)}(2'|1) & \gamma_0^{(1)}(2'|2) & \gamma_0^{(1)}(2'|3) \\ \gamma_0^{(1)}(3'|1) & \gamma_0^{(1)}(3'|2) & \gamma_0^{(1)}(3'|3) \end{vmatrix}_{\pm} d^3x_2 d^3x_3, \quad (7.3)$$

where $\gamma_0^{(1)}(i'|j)$ is the solution of (6.1). If the system is very large and has a uniform density $\rho_0 = N/V = \gamma_{(0)}^{(1)}$, then $\gamma^{(1)}$ depends only on $|\mathbf{x}_1' - \mathbf{x}_1|$. Define the Fourier transforms

$$\sum_{\text{spins}} \gamma^{(1)}(i'|j) = \gamma^{(1)}(|\mathbf{r}_i' - \mathbf{r}_j|) \\ = \int n(k, \beta) e^{i\mathbf{k} \cdot (\mathbf{r}_i' - \mathbf{r}_j)} d^3k, \quad (7.4)$$

$$K(k) = \sum_{\text{spins}} \int K(\mathbf{r}_{ij}) e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} d^3r_{ij}, \quad (7.5)$$

and of course let $T_i = -(\hbar^2/2m)\nabla_i^2$. The energy is easily seen to be from (2.8) and (2.14)

$$E = \frac{\hbar^2 \Omega}{2m} \int n(k) k^2 d^3k \\ + \Lambda(\beta) \int \int K_{12}(x_1 x_2) \gamma_0^{(2)}(x_1 x_2, \beta) d^3x_1 d^3x_2, \quad (7.6)$$

where $\Lambda(\beta) = Z_0^{(N)}(\beta)/Z^{(N)}(\beta)$. The quantity $\Lambda(\beta)$ is determined by the differential equation

$$\frac{\partial}{\partial \beta} \ln \Lambda(\beta) = -\frac{\hbar^2}{2m} \Omega \int k^2 (n_0(k, \beta) - n(k, \beta)) d^3k \\ + \Lambda(\beta) \int \int K_{12}(x_1 x_2) \gamma_0^{(2)}(x_1 x_2, \beta) d^3x_1 d^3x_2. \quad (7.7)$$

In first approximation the first term on the right vanishes and the solution of (7.7) is

$$\Lambda(\beta) = -1 / \int \int K_{12}(x_1 x_2) \gamma_0^{(2)}(x_1 x_2, \beta) d^3x_1 d^3x_2. \quad (7.8)$$

On expanding the determinants and using the above definitions one easily obtains the following integro-differential equation for $n(k, \beta)$:

$$-\frac{\partial}{\partial \beta} n(k, \beta) = \frac{\hbar^2 k^2}{2m} [n(k, \beta) + \lambda n^2(k, \beta)] + \Lambda(\beta) \left[-n(k, \beta) \int \int K(x_1 x_2) \gamma_0^{(2)}(x_1 x_2, \beta) d^3x_1 d^3x_2 \right. \\ \left. + \int \int K(x_1 x_2) \gamma_0^{(2)}(x_1' x_1 x_2, \beta) e^{i\mathbf{k} \cdot (\mathbf{x}_1' - \mathbf{x}_1)} d^3x_2 d^3x_1' d^3x_1 \right. \\ \left. + \frac{1}{2} \int \int \int K(x_2 x_3) \gamma_0^{(3)}(x_1' x_1 x_2 x_3, \beta) e^{i\mathbf{k} \cdot (\mathbf{x}_1' - \mathbf{x}_1)} d^3x_3 d^3x_2 d^3x_1' d^3x_1 \right]. \quad (7.9)$$

This equation is rather difficult to solve. A simpler approximation in the same spirit is obtained by replacing $\gamma_0^{(2)}$, $\gamma_0^{(3)}$ in (7.3) by superpositions of the $\gamma^{(1)}$'s (instead of $\gamma_0^{(1)}$'s as above). The resulting equation is

$$-\frac{\partial}{\partial \beta} n(k, \beta) = (n(k, \beta) + \lambda n^2(k, \beta)) \left\{ \frac{\hbar^2 k^2}{2m} + \Lambda(\beta) \rho_0 K(0) + \Lambda(\beta) \lambda \int K(k' - k) n(k', \beta) d^3k' \right\}. \quad (7.10)$$

Now it is perfectly consistent with the approximations made so far to replace $n(k', \beta)$ on the right-hand side by $n_0(k', \beta)$. The integration with respect to β can then be carried out leading to the algebraic equation

$$n(k, \beta) = |\lambda|^{-1} \left\{ z^{-1} \exp \left[\frac{\hbar^2 k^2 \beta}{2m} + \lambda \int_0^\beta \Lambda(\beta') d\beta' \int d^3k' K(k' - k) n_0(k_2', \beta') \right] - \text{sgn} \lambda \right\}^{-1}, \quad (7.11)$$

where z is the fugacity. Our object has been to take into account the correlations due to two-body interactions,

while retaining the superposition principle. A more strictly justifiable use of the K operator would lead to

the following equations instead of (7.3):

$$\begin{aligned} & \left(E - \frac{\partial}{\partial \beta} - T_1\right) \gamma^{(1)}(1'|1) \\ &= \int T_2 \gamma^{(2)}(1'2'|12) d^3 x_2 \\ &+ \Lambda(\beta) \int K_{12}(12) \gamma_0^{(2)}(1'2,12) d^3 x_2 \\ &+ \Lambda(\beta) \frac{1}{2} \int \int K_{23}(2,3) \gamma_0^{(3)}(1'23|123) d^3 x_2 d^3 x_3 \end{aligned}$$

but the above cannot be solved easily in this form because of the presence of $\gamma^{(2)}$. Evidently (7.3) is obtained from the above by using the superposition approximation for $\gamma^{(2)}$.

For the sake of simplicity it has been tacitly assumed throughout the foregoing derivation that the operator K_{12} depends on space variables $\mathbf{x}_1, \mathbf{x}_2$ in the same way as V_{12} . Actually, this is not strictly true, e.g., K_{12} cannot be expressed in purely "local" form. This is because the effect of the medium (the other $N-1$ particles) is momentum dependent. The correct procedure is to let K be a nonlocal operator, depending on both the primed and unprimed variables:

$$K = K(x_1' x_2'; x_1 x_2).$$

The whole derivation can be carried through in this more general case, leading to a parallel but more complicated equation. The justification for not doing so is simply that in practice the nonlocality has a rather short range, which means that $K(x_1' x_2'; x_1 x_2)$ is zero everywhere except when it is nearly diagonal, e.g., when $|\mathbf{x}_0' - \mathbf{x}_1|$ and $|\mathbf{x}_2' - \mathbf{x}_2|$ are very small. Therefore it is usual to expand the nonlocal density function $\gamma^{(1)}$ in a Taylor series,

$$\begin{aligned} \gamma^{(1)}(i'|j) &\equiv \gamma^{(1)}(x_i', x_j) \\ &= \gamma^{(1)}(0) + (\mathbf{x}_i' - \mathbf{x}_j) \cdot \nabla_j \gamma^{(1)}(i'|j)|_{i'=j} \\ &+ \frac{1}{2} (\mathbf{x}_i' - \mathbf{x}_j)^2 \nabla_j^2 \gamma^{(1)}(i'|j)|_{i'=j} + \dots; \quad (7.12) \end{aligned}$$

when this has been done the subsequent integration over the primed variables can be carried out explicitly on the K matrix, yielding the local form

$$K(r_{12}) = \int K(x_1' x_2; x_1 x_2) d^3 x_1' d^3 x_2'. \quad (7.13)$$

The corrections display an explicit momentum dependence, since

$$\mathbf{p}_i = i\hbar \nabla_i.$$

8. EFFECTIVE INTERACTION: REACTION MATRIX

The effective interaction K has been defined as the operator which, operating on properly symmetrized

plane waves, is equivalent to $V(12)$ operating on the correct wave function. Although a similar idea is rather well known in ordinary many-body theory, it is perhaps not immediately obvious that the same approach is applicable here. The connection becomes clearer if we introduce a set of functions $G^{(m)}(x^{m'}, x^m, s)$ defined by the Laplace transform:

$$G^{(m)}(x^{m'}, x^m, s) = \int_0^\infty e^{-\beta s} \gamma^{(m)}(x^{m'}, x^m, \beta) d\beta. \quad (8.1)$$

In particular it is easy to see that, when $m=N$,

$$\begin{aligned} (s - \mathcal{H}^{(N)}) G^{(N)}(x^{N'}, x^N, s) \\ = \frac{1}{2} [\delta(x^{N'} - x^N) \pm \delta(x^N - x^{N'})], \quad (8.2) \end{aligned}$$

where $H^{(N)}$ is the N -particle Hamiltonian and s is the total energy. Evidently $G^{(N)}$ is a Green's function for the entire system at the energy s .

The wave function satisfies the equation

$$(s - \mathcal{H}^{(N)}) \Psi^{(N)}(x^{N'}, x^N, s) = 0. \quad (8.3)$$

Writing $\mathcal{H}^{(N)} = T^{(N)} + V^{(N)}$, we have

$$(s - T^{(N)}) \Phi_0^{(N)}(x^{N'}, x^N, s), \quad (8.3a)$$

$$(s - T^{(N)}) G_0^{(N)}(x^{N'}, x^N, s). \quad (8.2a)$$

The K operator for the many-body wave function is introduced through the equations

$$\begin{aligned} \Psi^{(N)} &= \Phi_0^{(N)} + G^{(N)} V^{(N)} \Phi_0^{(N)} \\ &= \Phi_0^{(N)} + G_0^{(N)} V^{(N)} \Psi^{(N)} \\ &= \Phi_0^{(N)} + G_0^{(N)} \tilde{K}^{(N)} \Phi_0^{(N)}. \end{aligned} \quad (8.4)$$

By a straightforward algebraic manipulation we obtain the general relations

$$G^{(N)} = G_0^{(N)} + G_0^{(N)} \tilde{K}^{(N)} G_0^{(N)}, \quad (8.5)$$

$$\tilde{K}^{(N)} = V^{(N)} + V^{(N)} G_0^{(N)} \tilde{K}^{(N)}. \quad (8.6)$$

An exact treatment of the problem must start from this point. We shall return to this later on. Our use of the K matrix in Sec. 7 is not exact as was already pointed out. However, both the foregoing treatment and any exact treatment depend upon the assumption that the K matrix is independent of temperature (independent of β). It is sufficient to show that \tilde{K} as defined by (8.4) is independent of the true energy eigenvalue s . Once this is established the argument proceeds as follows: inserting (8.5) in (8.2) we take the inverse Laplace transform. Since \tilde{K} is independent of s by hypothesis, the inverse Laplace transformation acts only upon $G_0^{(N)}(s)$. The result is in exact Bloch equation involving only $\Gamma_0^{(N)}$ and $\tilde{K}^{(N)}$. Since $\tilde{K}^{(N)}$ is defined by (8.4), where β does not occur, we can set $\tilde{K}^{(N)} = K^{(N)}$, and note that it is also independent of β .

The approximation in Sec. 7 also assumes that the many-body operator $K^{(N)}$ can be decomposed into a

sum of two-body operators,

$$K^{(N)} = \sum_{i < j} K_{ij}.$$

This means that all three-body and higher terms in the general expansion of $K^{(N)}$ are dropped. Either of the operator equations (8.5), (8.6), which determine both $G^{(N)}$ and $K^{(N)}$ in terms of $G_0^{(N)}$ and $V^{(N)}$, can be replaced by the operator relation $K^{(N)}G_0^{(N)} = V^{(N)}G^{(N)}$. Once having established that $K^{(N)}$ is independent of s we can inverse Laplace transform both sides, obtaining $K^{(N)}\Gamma_0^{(N)} = V^{(N)}\Gamma^{(N)}$. Since both $K^{(N)}$ and $V^{(N)}$ are decomposed into two-body operators, the thermal averaging process gives

$$\begin{aligned} & \int \int K_{12} \Gamma_0^{(2)}(1, 2, \beta) d^3 x_1 d^3 x_2 \\ &= \int \int V_{12} \Gamma^{(2)}(1, 2, \beta) d^3 x_1 d^3 x_2, \\ \text{or} \\ & \Lambda(\beta) \int \int K_{12} \gamma_0^{(2)}(1, 2, \beta) d^3 x_1 d^3 x_2 \\ &= \int \int V_{12} \gamma^{(2)}(1, 2, \beta) d^3 x_1 d^3 x_2, \quad (8.7) \end{aligned}$$

which leads to (7.6).

The next step is to establish that a two-body K matrix exists and K_{12} is independent of S .

The actual proof turns out to be equivalent to the proof that unlinked clusters in Schrödinger many-body perturbation theory cancel to all orders. This proof was given by Goldstone⁷ and will not be repeated. A brief outline of the derivation of the two-body K matrix follows Rodberg's¹⁸ paper.

For the many-body problem, assuming two-body forces, the Schrödinger equation can be written

$$s\Psi = [\sum_i (T_i + U_i) - \sum_{i < j} V_{ij}'] \Psi,$$

where U_i is an arbitrary single-particle potential and V_{ij}' is the "residual" two-body interaction, to be discussed later. Expand Ψ in a complete set of eigenfunctions,

$$\begin{aligned} \Psi &= \sum_{\eta} a_{\eta} \Phi_{\eta}, \\ [s - \sum_i (T_i + U_i)] \Psi &= \sum_{i < j} V_{ij}' \Psi, \\ \sum_{\eta} a_{\eta} [s - E_{\eta}] \Phi_{\eta} &= \sum_{i < j} V_{ij}' \Psi, \end{aligned}$$

whence

$$\Psi = \sum_{\eta} \frac{\Phi_{\eta} \langle \Phi_{\eta} | \sum_{i < j} V_{ij}' | \Psi \rangle}{s - E_{\eta}}. \quad (8.8)$$

It is convenient to normalize $\langle \Phi_0 | \Psi \rangle = 1$ (so $\langle \Psi | \Psi \rangle > 1$), and obtain

$$\Psi = \Phi_0 + \sum_{\eta \neq 0} \frac{\Phi_{\eta} \langle \Phi_{\eta} | \sum_{i < j} V_{ij}' | \Psi \rangle}{s - E_{\eta}}, \quad (8.9)$$

$$s = E_0 + \langle \Phi_0 | \sum_{i < j} V_{ij}' | \Psi \rangle. \quad (8.10)$$

We now wish to pick out the pair 12 and an operator \tilde{K}_{12} such that

$$\langle \Phi_{\mu} | \tilde{K}_{12} | \Psi_{12} \rangle = \langle \Phi_{\mu} | V_{12}' | \Psi \rangle, \quad (8.11)$$

where Ψ_{12}' is the wave function *not* containing correlations of the pair 12 but containing all others:

$$\Psi_{12}' = \Psi - \sum_{\eta \neq 0} \frac{\Phi_{\eta} \langle \Phi_{\eta} | V_{12}' | \Psi \rangle}{s - E_{\eta}}, \quad (8.12)$$

$$V_{12}' \Psi = V_{12}' \left[\Psi_{12}' + \sum_{\eta \neq 0} \frac{\Phi_{\eta} \langle \Phi_{\eta} | V_{12}' | \Psi \rangle}{s - E_{\eta}} \right]. \quad (8.13)$$

Taking the matrix element with Φ_i , we obtain

$$\begin{aligned} \langle \Phi_i | V_{12}' | \Psi \rangle &= \langle \Phi_i | V_{12}' | \Psi_{12}' \rangle \\ &+ \sum_{\eta \neq 0} \frac{\langle \Phi_i | V_{12}' | \Phi_{\eta} \rangle \langle \Phi_{\eta} | V_{12}' | \Psi \rangle}{s - E_{\eta}}, \quad (8.14) \end{aligned}$$

or

$$\begin{aligned} \langle \Phi_i | \tilde{K}_{12} | \Psi_{12}' \rangle &= \langle \Phi_i | V_{12}' | \Psi_{12}' \rangle \\ &+ \sum_{\eta \neq 0} \frac{\langle \Phi_i | V_{12}' | \Phi_{\eta} \rangle \langle \Phi_{\eta} | \tilde{K}_{12} | \Psi_{12}' \rangle}{s - E_{\eta}}. \quad (8.15) \end{aligned}$$

Expanding Ψ_{12}' in the orthonormal set, $\Psi_{12} = \sum_j a_j \Phi_j$, one finds that (8.15) is implied by

$$\tilde{K}_{ij} = V_{ij}' + \sum_{\eta \neq 0} \frac{V_{i\eta}' \tilde{K}_{\eta j}}{s - E_{\eta}}. \quad (8.16)$$

To complete the formulation, we note that

$$s = E_0 + \langle \Phi_0 | \sum_{i < j} \tilde{K}_{ij} | \Psi_{ij}' \rangle, \quad (8.17)$$

$$\Psi_{ij}' = \Phi_0 + \sum_{\eta \neq 0} \frac{\langle \Phi_{\eta} | \Phi_{\eta} | \sum_{k < l}^{(i,j)} \tilde{K}_{kl} | \Psi_{kl}' \rangle}{(s - E_{\eta})}. \quad (8.18)$$

The last equation can be iterated, and then combined with the expression for the energy, to give a rapidly convergent (in general) perturbation expression which is exact if carried out to all orders. The so-called Brueckner approximation¹⁹ is to take just the leading

¹⁸ L. Rodberg, Ann. Phys. 2, 199 (1957).

¹⁹ This is not the only approximation possible, nor is it necessarily a good one. For example, if V_{12} is the Coulomb potential, the terms left out of the Brueckner approximation are extremely important. A quite different type of approximation is needed in this instance, in which contributions from all orders of perturbation theory are included in each term. The simplest version of this is known as the "ring-integral" approximation.

term:

$$s = E_0 + \langle \Phi_0 | \sum_{i < j} \tilde{K}_{ij} | \Phi_0 \rangle + \dots \quad (8.19)$$

More detailed consideration of these equations leads to three important remarks, justification for which is found in the literature:

(1) The energy denominators as shown are in an inconvenient form for calculation (the Wigner form), which must be replaced by the more practical Schrödinger form by iteration and expansion. This introduces terms which apparently have the wrong N dependence. However, Goldstone showed that these terms (unlinked clusters) cancel exactly in all orders of perturbation theory. As a result one can redefine \tilde{K}_{ij} using E_0 instead of s in the denominators:

$$\tilde{K}_{ij} = V_{ij}' + \sum_{\eta \neq 0} \frac{V_{i\eta}' \tilde{K}_{\eta j}}{E_0 - E_\eta} \quad (8.20)$$

This shows that \tilde{K} depends on the energy spectrum, but *not* on the total energy. Thus the s dependence is eliminated and $\tilde{K} = K$ as stated.

(2) The formulation is independent of the choice of U_i , which is arbitrary. It is possible to choose U_i to minimize corrections to the "Brueckner approximation," or in essence to maximize E_0 with respect to

$$\langle \Phi_0 | \sum_{i < j} K_{ij} | \Phi_0 \rangle.$$

The residual two-body interaction V_{ij}' is defined so that

$$\sum_{i < j} V_{ij}' = \sum_{i < j} V_{ij} - \sum_j U_i. \quad (8.21)$$

A choice of U_i which makes the second-order energy vanish is the following:

$$U_i = \sum_j^{occ} \langle \varphi_j | K_{ij} | \varphi_j \rangle, \quad (8.22)$$

where φ_i are single-particle wave functions, and the sum is over the states which are occupied in the "chosen configuration" Φ_0 . The choice is arbitrary however, and one could choose $U_i = 0$ in which case E_0 is just the kinetic energy. This may simplify the energy denominators, but leads to slower convergence of the perturbation series.

(3) When the potential V_{ij} is singular the equations must be recast to avoid divergences. One way of doing this is to introduce a nonsingular "pseudopotential" \tilde{V}_{ij} which is equivalent to V_{ij} when it operates on the correct wave function Ψ . The ideal was first suggested by Fermi²⁰ for the scattering of hard spheres, and extended by Huang, Yang, and Lee²¹ to the many-body problem of a hard-sphere gas. A more general discussion of pseudopotentials has been given by Abe.²² A different

approach is due to Bethe and Goldstone²³ who rewrite the Brueckner equations in differential form, where the spurious divergence disappears. The reader is referred to the above authors for details.

In regard to the energy denominators, perhaps it would be worth while to proceed a little further in order to see how (3.3) is obtained. We have the sum:

$$\sum_{\eta \neq 0} V_{i\eta}' K_{\eta j} / E_0 - E_\eta,$$

where E_0 is the N -particle ground state and E_η is one of the excited N -particle states. Such excitations occur when two or more particles are removed from the ground-state configuration described by ϕ_0 . The most important contributions occur when only two particles are excited, as seen from the supposed convergence of (8.19). Therefore in terms of "single-particle levels" we have

$$E_0 - E_\eta = \epsilon_k + \epsilon_l - \epsilon_m - \epsilon_n,$$

where k, l represent "particles" outside the chosen configuration and m, n represent "holes" left by the excitation. The sum over η represents the sum over all such excitations, plus three-particle and more complicated excitations, but since three-particle correlations have been left out, it is consistent to include only the two-particle terms. This means summing over all k, l, m, n , subject to the requirement that momentum be conserved, which puts one restriction on the sum. If the particles obey Fermi statistics the Pauli principle puts a second restriction on the sum, viz., the k, l sum over states in ϕ_0 and m, n over states *not* in ϕ_0 .

It was stated earlier that an exact theory must begin from the pair of equations (8.5) and (8.6). Thus,

$$\Gamma^{(N)}(\dots\beta) = \int_{c-i\infty}^{c+i\infty} G^{(N)}(\dots s) e^{i\beta s} ds. \quad (8.23)$$

Since $\tilde{K}^{(N)} = K^{(N)}$ is independent of s , (8.5) is equivalent to

$$\Gamma^{(N)}(\dots\beta) = \Gamma_0^{(N)}(\dots\beta) + \int_0^\infty \Gamma_0^{(N)}(\dots\beta') K^{(N)} \Gamma_0^{(N)}(\dots\beta' - \beta) d\beta', \quad (8.24)$$

making use of the Laplace-transform representation of the δ -function. We now integrate over all variables except m (where $m = 1, 2, \dots$) to obtain an exact hierarchy of equations involving only $\Gamma_0^{(1)}$ or $\gamma_0^{(1)}$, since $\Gamma_0^{(N)}$ is simply a superposition. These equations will be investigated in detail elsewhere.

9. ELIMINATION OF FUGACITY

It is necessary to go one step beyond the expression (7.10) to be in a position to utilize this approximation in any practical problem. The final step is to eliminate the fugacity z . In the following we assume that the

²⁰ E. Fermi, *Ricerca sci.* **7**, 13 (1936).

²¹ K. Huang and C. N. Yang, *Phys. Rev.* **105**, 767 (1957); T. D. Lee, K. Huang, and C. N. Yang, *Phys. Rev.* **106**, 1135 (1957).

²² R. Abe, *Progr. Theoret. Phys. (Kyoto)* **19**, 1, 699 (1958).

²³ H. Bethe and J. Goldstone, *Proc. Roy. Soc. (London)* **A238**, 55 (1956).

potential energy is small compared to the kinetic energy and introduce an expansion parameter ζ which will later be set equal to unity.

Assume first a spinless Fermi gas, with $\lambda = -1$. Introducing the above mentioned expansion parameter ζ , (7.10) becomes

$$n(k, \beta) = \frac{1}{z^{-1} \exp \left[\frac{\hbar^2 k^2}{2m} \beta - \zeta \int^{\beta'} \Lambda(\beta') d\beta' \int d^3 k' K(k' - k) n_0(k', \beta') \right] + 1}. \quad (9.1)$$

Now expand z^{-1} around its value for an ideal gas z_0^{-1}

$$z^{-1} = z_0^{-1} + \left. \frac{\partial z^{-1}}{\partial \zeta} \right|_{\zeta=0} + \frac{1}{2} \zeta^2 \left. \frac{\partial^2 z^{-1}}{\partial \zeta^2} \right|_{\zeta=0} + \dots \quad (9.2)$$

$$= z_0^{-1} + \zeta z_1^{-1} + \frac{1}{2} \zeta^2 z_2^{-1} + \dots$$

Similarly, expand $n(k, \beta)$ in a Taylor series around $\zeta = 0$:

$$n(k, \beta) = n_0(k, \beta) + \zeta \left. \frac{\partial n(k, \beta, \zeta)}{\partial \zeta} \right|_{\zeta=0} + \frac{1}{2} \zeta^2 \left. \frac{\partial^2 n(k, \beta, \zeta)}{\partial \zeta^2} \right|_{\zeta=0} + \dots, \quad (9.3)$$

where

$$\frac{\partial n(k, \beta, \zeta)}{\partial \zeta} = -n^2(k, \beta, \zeta) \left\{ \frac{\partial z^{-1}}{\partial \zeta} - z^{-1} \int^{\beta} \Lambda(\beta') d\beta' \right. \\ \left. \times \int d^3 k' K(k' - k) n_0(k', \beta') \right\} \exp[\dots].$$

We would not be justified by our earlier approximations in going beyond first order, so

$$\left. \frac{\partial n}{\partial \zeta} \right|_{\zeta=0} = -[n_0(k, \beta) - n_0^2(k, \beta)] \\ \times \left\{ z_1^{-1} - z_0^{-1} \int^{\beta} \Lambda(\beta') d\beta' \right. \\ \left. \times \int d^3 k' K(k' - k) n_0(k', \beta') \right\}. \quad (9.4)$$

Now the normalization condition is fulfilled for $n_0(k, \beta)$:

$$\int n(k, \beta) d^3 k \equiv \int n_0(k, \beta) d^3 k;$$

whence

$$0 = \int \left. \frac{\partial n(k, \beta, \zeta)}{\partial \zeta} \right|_{\zeta=0} d^3 k \\ \equiv \int \left. \frac{\partial^2 n(k, \beta, \zeta)}{\partial \zeta^2} \right|_{\zeta=0} d^3 k \equiv \dots \quad (9.5)$$

By inserting (9.4) in (9.5) we immediately deter-

mine z_1^{-1} :

$$z_1^{-1} = z_0^{-1} \int d^3 k (n_0(k, \beta) - n_0^2(k, \beta)) \\ \times \int^{\beta} d\beta' \Lambda(\beta') \int d^3 k' K(k' - k) n_0(k', \beta') \\ \times 1 / \int (n_0(k, \beta) - n_0^2(k, \beta)) d^3 k. \quad (9.6)$$

The process can be repeated indefinitely, if desired, to determine z_2^{-1} , z_3^{-1} , \dots . Combining (9.6) with (9.4) we obtain the first correction to $n(k, \beta)$. Some idea of the effect of the approximations introduced in Sec. 7 may be had by noticing that at absolute zero ($\beta \rightarrow \infty$) all the corrections to $n_0(k, \beta)$ vanish identically because of the presence of a factor $(n_0 - n_0^2)$ in front of each one. Thus the extreme low temperature limit is not accurately treated here, and the exact theory is needed.

In the case of Bose systems the same difficulty at very low temperatures is likely to occur, and we therefore shall not waste any effort discussing the case of a strongly degenerate Bose gas, which is characterized by $z = 1$ and in which a finite fraction of particles occupies the state of zero momentum ($k = 0$). On the other hand above the critical temperature the elimination of the fugacity in the case of a Bose gas proceeds exactly as above. We merely alter the signs in a few places. Thus the factors

$$n_0(k, \beta) - n_0^2(k, \beta)$$

are replaced by

$$n_0(k, \beta) + n_0^2(k, \beta),$$

and one replaces $\Lambda(\beta')$ by $-\Lambda(\beta')$ in (9.6) and (9.4).

10. CONCLUSION

We have defined in Sec. 2 a set of distribution functions $\gamma^{(m)}(1'2' \dots m' | 12 \dots m; \beta)$ related to the density matrix, and showed how the average value of any operator in either the canonical or grand canonical ensemble is obtained. A hierarchy of equations determining the $\gamma^{(m)}$ matrices has been displayed in Sec. 4 and an approximate technique for solving the equations (the "superposition approximation") has been discussed in some detail in Sec. 5. The equations for the ideal gas are treated in Sec. 6. A technique for recasting the

equations so that the superposition principle is more useful is then proposed in Sec. 7, in analogy with the many-body perturbation theory developed by Brueckner and others. The equation for the single-particle matrix $\gamma^{(1)}$ is put into an interesting form (7.11), making use of the familiar Brueckner K matrix.^{5,13,18} Section 8 is devoted to a derivation of the K matrix and proof that it is independent temperature. In the process another set of functions $G^{(m)}(1'2'\dots m'|12\dots m; s)$ are defined which are seen on inspection to be the m -body Green's functions of the many-body Schrödinger equation. These are similar to the functions investigated exhaustively by Martin and Schwinger.² The result is proved that the statistical distribution functions are obtained from the Green's functions by an inverse Laplace transformation. In Sec. 9 we give a brief discussion of difficulties in the low-temperature limit and show how the fugacity is eliminated from the distribution functions.

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APPENDIX A: CALCULATION OF $\gamma^{(2)}(x_1'x_2'; x_1x_2; \beta)$ FOR AN ISOLATED PAIR OF PARTICLES

The simplest way of computing $\gamma^{(2)}(1'2'|12)$ for an isolated pair is to make use of (2.8); e.g., when there are only two particles in the system,

$$\gamma^{(2)}(1'2'|12) = (2!/Z_{(2)})\Gamma^{(2)}(1'2'|12), \quad (\text{A.1})$$

where $Z_{(2)}$ is the partition function for just two particles,

$$Z_{(2)} = \int \int \Gamma^{(2)}(12|12) d^3x_1 d^3x_2. \quad (\text{A.2})$$

The density matrix $\Gamma^{(2)}(1'2'|12)$ satisfies the Bloch equation

$$-(\partial/\partial\beta)\Gamma^{(2)}(1'2'|12) = (T_1 + T_2 + V_{12})\Gamma^{(2)}(1'2'|12), \quad (\text{A.3})$$

subject to the boundary condition at infinite temperature ($\beta=0$)

$$\lim_{\beta \rightarrow 0} \Gamma^{(2)}(1'2'|12) = \frac{1}{2} [\delta(x_1' - x_1) \delta(x_2' - x_2) \pm \delta(x_1 - x_1') \delta(x_2 - x_2')], \quad (\text{A.4})$$

depending on the statistics. Summing over internal coordinates, we get

$$\lim_{\beta \rightarrow 0} \sum_{\text{spin}} \Gamma^{(2)}(1'2'|12) = \frac{1}{2} [\delta(x_1' - x_1) \delta(x_2' - x_2) + \lambda \delta(x_1 - x_1') \delta(x_2 - x_2')], \quad (\text{A.5})$$

λ having been defined at the end of Sec. 6. A fairly complete derivation of $\Gamma^{(2)}$ can be found in an article

by Blatt,²⁴ so only the results will be quoted here. The two-particle Hamiltonian splits into two contributions, one from center-of-mass motion and one from relative motion:

$$\mathcal{H}^{(2)} = T_1 + T_2 + V_{12} = -\frac{\hbar^2}{4m} \nabla_{x_{12}}^2 - \frac{\hbar^2}{m} \nabla_{r_{12}}^2 + V(r_{12}), \quad (\text{A.6})$$

where

$$\mathbf{X}_{12} = \mathbf{x}_1 + \mathbf{x}_2, \quad \mathbf{r}_{12} = \mathbf{x}_1 - \mathbf{x}_2.$$

The two parts of the Hamiltonian commute, so $\Gamma^{(2)}$ may be factored as follows:

$$\sum_{\text{spin}} \Gamma^{(2)}(x_1'x_2'; x_1x_2; \beta) = U(x_{12}', x_{12}, \beta) W(r_{12}', r_{12}, \beta), \quad (\text{A.7})$$

where

$$U(x_{12}', x_{12}, \beta) = \left(\frac{m}{\pi \hbar^2 \beta} \right)^{\frac{3}{2}} \exp \left[-\frac{m}{\hbar^2 \beta} (x_{12}' - x_{12})^2 \right], \quad (\text{A.8})$$

and

$$\begin{aligned} W(r_{12}', r_{12}, \beta) &= \frac{1}{4} \left[(1+\lambda) \sum_{l \text{ even}} + (1-\lambda) \sum_{l \text{ odd}} \right] (2l+1) \\ &\times \left\{ \sum_i \bar{R}_{li}(r_{12}') \bar{R}_{li}(r_{12}) \exp(-\beta \epsilon_{li}^{(-)}) \right. \\ &\quad \left. + \frac{2}{\pi} \int_0^\infty \exp \left(-\frac{\hbar^2 k^2 \beta}{m} \right) R_l(r_{12}', k) R_l(r_{12}, k) \right. \\ &\quad \left. \times P_l(\mathbf{r}_{12}' \cdot \mathbf{r}_{12}) k^2 dk \right\}. \quad (\text{A.9}) \end{aligned}$$

The sum over l is over relative angular momentum states, the sum over i is over all discrete bound states of the two-body potential (if any), and the integral is over all continuum (scattering) states. The radial scattering wave functions satisfy

$$\frac{d^2}{dr^2} [r R_l(r, k)] + \left(k^2 - \frac{l(l+1)}{r^2} + \frac{m}{\hbar^2} V(r) \right) r R_l(r, k) = 0, \quad (\text{A.10})$$

and the (normalized) bound-state radial wave functions satisfy

$$\frac{d^2}{dr^2} [r \bar{R}_{li}(r)] + \left(-\epsilon_{li}^{(-)} - \frac{l(l+1)}{r^2} + \frac{m}{\hbar^2} V(r) \right) r \bar{R}_{li}(r) = 0, \quad (\text{A.11})$$

where

$$\int_0^\infty \bar{R}_{li}^2(r) dr = 1. \quad (\text{A.12})$$

Substituting into (A.2) and (A.1), one obtains $\gamma^{(2)}$ as promised.

²⁴ J. Blatt, Nuovo cimento 4, 430 (1956).