Irreversible Processes in Isolated Systems

EDWARD N. ADAMS
International Business Machine Research Center, Yorktown Heights, Hew York
(Received May 10, 1960)

The point of view is taken that the irreversibility paradox of Loschmitt and Zermelo arises because there are two valid transport equations, one causal, the other anticausal, each consistent with the fundamental equations of mechanics. From this point of view the problem of irreversibility is to characterize a given nonequilibrium distribution as to which transport equation it will obey. Using the transport theories of Kohn and Luttinger and of Van Hove, we obtain a statistical criterion capable of so characterizing distribution functions of both stationary and time varying types. We discuss the question of how experimental procedures consistently bring about a situation to which the causal transport equation applies; we answer the question for a very simple kind of experimental situation.

I. INTRODUCTION

RECENTLY a number of authors[1–8] have studied means of deriving rigorously from the equations of mechanics the basic macroscopic equations governing one or another simple irreversible process. In these theories the emphasis has been on obtaining the macroscopic kinetic equations governing the irreversible process from a sound theoretical treatment, free of arbitrary and unsatisfactory features present in older theories. The authors have had various particular objectives: they have wished to understand, e.g., how to avoid the intuitive use of distribution functions, how to go beyond the lowest order Born approximation in treating collision terms in the transport equation, how to view the conservation of energy condition in scattering, why the old condition of disappearance of phase coherence between collisions gives too restrictive conditions for validity of the transport equation, etc.

It is a feature of several of these theories that the transport situation is discussed by means of an idealized system which is thermally isolated and which obeys Hamiltonian equations of motion. Our work to be reported here arose from a consideration of the manner in which these theories deal with the irreversibility problem,[9] which arises when an irreversible process is described in terms of the fundamental laws of mechanics. We have arrived at some simple ideas of general significance which are latent in some of these papers,[2–4] but which we think have not been adequately discussed there. We will explain these ideas by means of simple specific examples, and in the main refer to existing theory for their mathematical substantiation. What we are principally concerned to understand is the relation of the theory of the very artificial and oversimplified transport situation which can be treated by Hamiltonian mechanics to the more complex situation which might exist under experimental circumstances.

In the following paragraphs we will establish that, from a certain point of view, the problem of irreversibility arises from the existence of not one but two transport equations, each valid under its own conditions. From existing theory we will arrive at a statistical characterization of a nonequilibrium distribution adequate to determine which of the two transport equations will govern its time variation. We will then discuss the relation of the two transport equations to the results of experiments. We will finally discuss the formulation of mathematical initial conditions to describe experimental situations in transport.

II. REVERSIBILITY-IRREVERSIBILITY PROBLEM

In elementary discussions of kinetic theory Boltzmann's equation for the distribution function in the six-dimensional coordinate-velocity space is commonly deduced from the fundamental equations of mechanics by means of heuristic arguments involving merely the conservation of particles and certain assumptions concerning the statistical properties of the scattering interaction (Stosszahlansatz). Such familiar treatments make it appear that Boltzmann's equation is an approximation to the Liouville equation, valid provided only that there is no particular average correlation between the position and the velocity of an electron. On such a basis Boltzmann's equation should be valid at almost every moment in a typical system. Against this view there is the objection raised by Loschmitt[9] that because the Boltzmann equation predicts irreversible effects it cannot be an approximation to the reversible equations of mechanics: For every motion of a system which has an associated distribution function satisfying Boltzmann's equation, there is another possible motion, obtained from the first by reversing all velocities, in which the system point in multidimensional coordinate space

[1] V. R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).
[2] W. Kohn and J. M. Luttinger (KLI), Phys. Rev. **108**, 590 (1957); (KLII) **109**, 1892 (1958).
[3] L. Van Hove, Physica **21**, 517 (1955).
[4] R. Brout and I. Prigogine, Physica **22**, 621 (1956). See also contribution to *Symposium on Transport Processes in Statistical Mechanics* (Interscience Publishers, Inc., New York, 1958).
[5] M. Lax, Phys. Rev. **109**, 1921 (1958).
[6] D. A. Greenwood, Proc. Phys. Soc. (London) **71**, 585 (1958).
[7] S. F. Edwards, Phil. Mag. **3**, 1020 (1958).
[8] H. L. Lewis, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7.
[9] M. Kac, *Lectures in Applied Mathematics* (Interscience Publishers, Inc., London, 1959), Vol. 1, Chap. 3, gives a discussion of the reversibility paradox with some historical references. See also Appendix I, by G. E. Uhlenbeck, especially pp. 185, 186, and 198.

moves along the same trajectory as for the first motion but in the opposite sense; the second motion has an associated distribution function which satisfies an "anti-Boltzmann equation" in which the irreversible terms, the scattering terms, have the "wrong" sign. The one-to-one correspondence between these two possible motions of the system shows that there are as many distribution functions associated to possible motions of a system that fail to satisfy Boltzmann's equation as there are distribution functions that satisfy it. The existence of these other motions is sometimes referred to as the "paradox" of the Boltzmann equation or the "reversibility-irreversibility problem." For brevity we will speak of these velocity-reversed motions as "duals" of the original motion.

As an example we apply the Loschmitt argument to the decay of electric current in a closed loop of wire in which there is no emf. On simple assumptions about the collision terms the Boltzmann equation will have the form

$$\partial f/\partial t = (f_0 - f)/\tau, \qquad (2.1)$$

in which τ is the time of momentum relaxation: Equation (2.1) predicts that the current will decay like $e^{-t/\tau}$. If we assume that the forces exerted by the scatterers are purely electric, hence are even functions of the time, then the equations of motion of the electrons in the wire are invariant under the transformation $t \rightarrow -t$ and the same equations of motion apply if the trajectories of the electrons are all reversed. For this dual motion with the trajectories reversed the distribution function satisfies

$$\partial f/\partial t = -(f_0 - f)/\tau, \qquad (2.2)$$

and the current builds up like $e^{t/\tau}$. We have called Eq. (2.2) the "anti-Boltzmann" equation because of the change in sign of the scattering term; it describes what we will call "anticausal" behavior. Loschmitt's argument shows that macroscopic motions which satisfy Eq. (2.2) are in some sense as common as those which satisfy (2.1).

The existence of the dual motions implies that Boltzmann's equation does not follow from the equations of motion alone: Boltzmann's equation is not an approximation to the equations of motion. The most that could be true—and it is true—is that many distributions exist which change with time according to Boltzmann's equation. In principle, then, to ensure that a nonequilibrium distribution obeys Boltzmann's equation, one must specify some property of the distribution, e.g., some initial condition. (In a particular experimental problem this might be inferred from the initial configuration of the apparatus.)

The existence of the Loschmitt dual motions does not depend, in an essential way, on the equations of motion having time-reversal symmetry: "Irreversible" motions of the anticausal type exist in systems having no particular time symmetry. We will show this by considering an example from the theory of electrical conduction. We consider a thought experiment in which electrical conduction is studied by means of observations made on the current in a closed loop of wire in which there is no emf. The current will be zero or very small most of the time, and only at exceedingly great intervals will the current become macroscopically large. However, when a very large fluctuation does come along, its decay is governed by the Boltzmann equation. We want to discuss the manner of growth of such a large fluctuation. We assert that the growth, like the decay, is governed by a macroscopic transport equation. This equation is, in general, what we will call the anti-Boltzmann equation to emphasize its anticausal nature. In simple cases, for which the equations of motion are reversible in time, the anti-Boltzmann equation may be obtained from the Boltzmann equation by reversing the signs of the scattering terms as we obtained Eq. (2.2) from Eq. (2.1). If the equations of motion do not have time reversal symmetry, there is, in general, no simple relation between the forms of the two transport equations. However, *there will in any case be an anti-Boltzmann transport equation which describes the most probable course of departure of a nonequilibrium distribution function from equilibrium just as the Boltzmann equation describes the most probable course of approach of a nonequilibrium distribution function to equilibrium.* Thus, (generalized) Loschmitt dual motions exist, even when the equations of motion do not have time symmetry.

The above considerations indicate that fundamentally the problem of irreversibility does not involve time symmetry as such. Instead it involves the existence of two possible valid macroscopic transport equations: The problem is to know of a given, mathematically specified, nonequilibrium distribution function which of the two transport equations would describe its time behavior. From another point of view, the irreversibility problem is to understand why only one of the two transport equations is of use in predicting future behavior of experimental systems.

III. RATE EQUATIONS FOR ELECTRICAL CONDUCTION

In respect to the deduction of rate equations governing observable irreversible processes, there are two questions which should be answered:

1. What feature of a nonequilibrium distribution function determines which of the two transport equation it will obey?
2. Why is it that only the Boltzmann equation is useful in predicting the future of an experimental irreversible process?

We will discuss the first question in this section and return to the second in a later section. In trying to characterize a distribution function that obeys, e.g., the Boltzmann equation, we might specify either some characteristics of its history or some characteristics of it at a given time. In either case there is the technical

difficulty that the systems of interest are so very complicated that even knowing exact initial conditions and equations of motion one cannot practicably carry through straightforwardly the calculations required to ascertain even the qualitative behavior that the initial conditions imply. Thus, the only practical possibility for characterizing a distribution function as to which transport equation it satisfies, would be to find some statistical property of the distribution function of the system which would serve to characterize it satisfactorily.

We will obtain the required characterization of the distribution function first for a steady state problem studied by Kohn and Luttinger[2] (KLI) in their theory of the dc electrical conduction of an isolated electron gas. In the following paragraphs we will deduce the desired characteristic directly from the equations of Kohn and Luttinger. In the interest of brevity we will not rederive these equations here, but will merely recapitulate the ones we require, since the interested reader can find a full discussion of detailed questions arising in the derivation in the paper of reference. We will, however, discuss in detail how the equations of that theory should be solved since the method of KLI must be refined so that we can obtain both transport equations of interest to us.

In the problem of Kohn and Luttinger the electrons are scattered by an interaction λV which results from the action of identical, randomly situated scatterers of uniform mean density. The total Hamiltonian H_T of the system is the sum of three parts, H_0 the part describing the motion of the system in the absence of scattering, λV described above, and H_F which describes the action of the electric field $E(t)$. The electric field $E(t)$ is of the form $E_0 e^{st}$ in which s is the rate of switching on of the electric field. The state of the system is described by a total density matrix ρ_T which is written as the sum of an initial density matrix ρ and a density matrix ρ_F which is linear in the field. ρ is assumed to be a function of $H_0+\lambda V$, the initial Hamiltonian. ρ_F is assumed to be of the form fe^{st} so that it will describe a situation for which the induced current is at all times exactly proportional to the applied field. The diagonal elements of f are denoted f_k, the off-diagonal elements $f_{kk'}$. The equations are formulated in the representation for which velocity is diagonal, so the current will depend only on the f_k. The equations of motion of f_k and $f_{kk'}$ tre, in adequate approximation for our purposes [see (KLI) Eqs. (25) combined with (33), Eq. (26) with $C_{kk'}=0$]

$$-isf_k=ieE_\alpha\partial\rho/\partial k_\alpha +\lambda \textstyle\sum_{k'}{}' [f_{kk'}V_{k'k}-V_{kk}f_{k'k}], \quad (3.1)$$

$$(\omega_{kk'}-is)f_{kk'}=\lambda V_{kk'}(f_k-f_{k'}) +\lambda \textstyle\sum_{k''}{}'(f_{kk''}V_{k''k'}-V_{kk''}f_{k''k'}), \quad (3.2)$$

in which ρ_k means $\rho(E_k)$, α is, e.g., a cartesian index for the vector E_α, the notation superscript prime on the summation means that no two subscripts appearing on any two-subscript symbol can be the same, $\omega_{kk'}$ denotes $(E_k-E_{k'})/\hbar$, and λ is a dimensionless parameter used to define the various orders of perturbation theory. In the approximation (3.2) the equilibrium density matrix ρ has been treated as though it were diagonal in the momentum representation. This approximation, which affects only higher corrections to the transport equation, is only made for the sake of brevity; our procedure is equally valid if we keep the terms $C_{kk'}$ which we have dropped.

As formulated, these equations are intended to describe the situation in an ensemble of isolated electron gases, each originally in an energy eigenstate with the electrons moving about randomly, when an electric field is slowly turned on; Eqs. (3.1) and (3.2) apply only if the current is exactly proportional to the field. We have remarked in the last section that there are two macroscopic transport equations which govern the time behavior of fluctuations: We will now demonstrate that either of these two transport equations could apply to a situation as described above, and will also show in what way the corresponding distributions differ. We will make use of Kohn and Luttinger's perturbation analysis in which the interaction parameter λ is taken as small and the density matrix f determined by a series of successive approximations. (However, our method of solution of the equations differs from theirs in an important way.) As shown in KLI, the function $f_k\sim O(\lambda^{-2})$, the function $f_{kk'}\sim O(\lambda^{-1})$ for vanishing λ, so we can get a given approximation to $f_{kk'}$ in (3.2) by using the next lowest approximation to $f_{k''}$, $f_{k''k'}$ where they appear in the summation on the right-hand side, which is one order higher in λ. When an approximate solution for $f_{kk'}$ is substituted into Eq. (3.1), a corresponding approximation to the transport equation is obtained.

The approximate solution of (3.2) in powers of the interaction parameters is not entirely straightforward. We desire for our case to discuss steady state transport, so we want a solution of the equations that doesn't depend on s. This we can get if s is small compared to all of the natural frequencies of the problem, including the scattering rate (slow turn-on limit), for then we may let s approach zero without changing the current. From elementary considerations we know that for sufficiently small λ the scattering time τ is of order λ^{-2}. But the slow-turn-on conditions above would require that $sf_{kk'}$, which is apparently of order λ^{-1} be always smaller than $f_{kk'}/\tau$ which is of the order λ^{+1}. Thus, for fixed value of s the limit $\lambda\rightarrow 0$ cannot be taken without giving up the condition of slow-turn-on. Since the validity of the perturbation treatment depends on passing to the limit $\lambda\rightarrow 0$, we will modify the above equations so that that limit can be taken. The simplest formal procedure is to write s as $\bar{s}\lambda^2$ with the consequence that the limits $\bar{s}\rightarrow 0$, $\lambda\rightarrow 0$ can be taken in either order. We now find as the lowest order (in λ) approximation to $f_{kk'}$

$$f_{kk'}\approx\lambda V_{kk'}(f_k-f_{k'})/\omega_{kk'}. \quad (3.3)$$

Inserting (3.3) in (3.1) we find that the terms involving $V_{kk'}$ cancel one another and that the solution of (3.1) does not correspond to a transport process of the usual sort at all, since it does not depend on the scattering and it has no limit as the rate of turning on the field is made indefinitely small.

In order to get the transport solution of Eq. (3.1) we must retain terms in Eq. (3.2) that are of order $\lambda^2 f_{kk'}$, since these terms are essential to describe the $f_{kk'}$ for which the energy difference $\omega_{kk'}$ is approximately zero. In order to display all terms of order λ^{+1} we need to substitute in the summation expressions for $f_{kk''}$, $f_{k''k'}$ that are correct to order λ^0. We cannot get the required expressions by direct iteration of Eq. (3.2), so we resort to an indirect method which has much in common with simple minded renormalization procedures in field theory. We rewrite Eq. (3.2) as

$$\begin{aligned}(\omega_{kk'}-i\bar{s}\lambda^2-i\Gamma_{kk'}\lambda^2)f_{kk'} &= \lambda V_{kk'}(f_k-f_{k'})-i\lambda^2\Gamma_{kk'}f_{kk'}\\ &+\lambda \sum\nolimits_{k''}{}'(f_{kk''}V_{k''k'}-V_{kk''}f_{k''k'}). \end{aligned}\tag{3.4}$$

We wish to choose $\Gamma_{kk'}$ so as to cancel out the terms proportional to $f_{kk'}$ arising when series developments for $f_{kk''}$, $f_{k''k'}$ are put into the summation on the right-hand side of (3.4). That choice of $\Gamma_{kk'}$ will result in a cancellation of the second term on the right-hand side of Eq. (3.4) with certain terms in the summation there; these cancellations have the sole consequence that when the series is inserted for $f_{kk''}$, $f_{k''k'}$ further restrictions must be imposed on the range of the summation indices in addition to those implied by the prime on the summation in (3.4), so that no two indices in the summand can be the same. We will indicate that these additional restrictions are to be observed by the symbol $''$ on the summation. Incorporating these simplifications into Eq. (3.4) and defining

$$d_{kk'}=\omega_{kk'}-i\lambda^2\bar{s}-i\lambda^2\Gamma_{kk'}, \tag{3.5}$$

we obtain for $f_{kk'}$ the simpler form

$$f_{kk'}=\frac{\lambda V_{kk'}(f_k-f_{k'})}{d_{kk'}}+\lambda \sum\nolimits_{k''}{}'' \frac{(f_{kk''}V_{k''k'}-V_{kk''}f_{k''k'})}{d_{kk'}}. \tag{3.6}$$

Equation (3.6) may now be readily solved by iterative substitution into itself.

Explicit expressions for $\Gamma_{kk'}$ may be obtained by iterating (3.6) and collecting the terms which are omitted in virtue of the second prime on the summation in (3.6). For the exposition of the irreversibility problem it is entirely sufficient to take the first nonvanishing approximation to $\Gamma_{kk'}$, which comes from the first substitution of the summation into itself. The first approximation to $\Gamma_{kk'}$ is found to satisfy

$$\lambda^2\Gamma_{kk'}=-i\lambda^2 \sum\nolimits_{k''}\left[\frac{|V_{k'k''}|^2}{d_{kk''}}+\frac{|V_{kk''}|^2}{d_{k''k'}}\right]. \tag{3.7}$$

Since the $\Gamma_{kk'}$ occur in the denominators on the right-hand side of Eq. (3.7), Eq. (3.7 actually gives a set of simultaneous equations to be solved for the $\Gamma_{kk'}$. We can easily find good solutions of these equations for the case that λ is very small, because the values of the integrals on the right-hand side of (3.7), are almost independent of the magnitude of the small imaginary quantities in the denominator. The real part of $\lambda^2\Gamma_{kk'}$ is something like the mean scattering rate in the states k,k' os $\lambda^2\Gamma_{kk'}$ is, by the hypothesis of slow turn on, large compared to $\lambda^2\bar{s}$. It follows that the solutions of (3.7) are independent of $\bar{s}$ for small $\bar{s}$.

What is essential for our purpose is that the self-consistent solutions of (3.7) may have either a positive or a negative real part. The corresponding two solutions for $\Gamma_{kk'}$ lead respectively to the causal and anticausal transport equations inferred in the previous section. The two equations may be found directly by substituting

$$f_{kk'}\doteq\lambda V_{kk'}(f_k-f_{k'})/d_{kk'}, \tag{3.8}$$

into Eq. (3.1). $f_{kk'}$ with the positive value of $\Gamma_{kk'}$ leads to the usual steady-state Boltzmann equation, $f_{kk'}$ with the negative value of $\Gamma_{kk'}$ to the steady-state anti-Boltzmann equation, each with the scattering terms given in lowest order Born approximation.

We have given the above discussion in detail for several reasons. For one reason, we have found that the intuitive arguments of the previous section do not immediately convince some reasonable people of the existence of the anticausal type transport equation for systems lacking time symmetry. For another, our treatment shows the extreme sensitivity of the results of the theory to the treatment of the initial condition as implied in the various limiting processes. Finally, the mathematical form of the above discussion enables us (by extension) to characterize mathematically for a more general system the motions of the system that satisfy the Boltzmann equation. We conclude that in general it is the sign of $\Gamma_{kk'}$ appearing in its density matrix elements that characterizes the transport equation the distribution will obey: Positive and negative signs of $\Gamma_{kk'}$ in the expression (3.5) correspond, respectively, to causal and anticausal behavior. The sign of $\Gamma_{kk'}$ is of importance only for pairs of states of about the same energy; for these pairs of states it determines the phase of the off-diagonal density matrix elements. With respect to the classical six-space distribution function, these matrix elements have the significance of position-velocity correlations. Thus we conclude that the existence of systematic nonzero long-wavelength position-velocity correlations is necessary for the validity of a transport equation, and the phase of these correlations

determines whether the transport equation is of the causal or the anticausal type.

It is natural to suppose, from the above results for the steady-state problem, that in the transient problem also, it is the phase of the off-diagonal density matrix elements that determines whether a nonequilibrium distribution will decay or grow; one can verify this directly by means of a theory of Van Hove.[3] This theory is expressed in very general terms so as to apply to a very great number of dynamic systems; it may readily be applied to conduction in an electron gas by specialization, provided the electric field is taken zero. We will not give the detailed exposition of Van Hove's theory, but will try to indicate a few of the main points. The problem of Van Hove, as specialized to our case, is to deduce the history of a distribution which is described at time zero by a density matrix that is exactly diagonal but has a nonzero current flow. By an ingenious method of approximate integration Van Hove demonstrated that the distribution approaches equilibrium both for positive and negative times, obeying, respectively, the Boltzmann and anti-Boltzmann equations for times sufficiently remote from zero. He found that for times very close to zero, i.e., times distinctly less than a mean free time, there is no decay of the current. Van Hove did not give formulas for the time dependence of the nondiagonal density matrix elements, but one can readily get such formulas from his theory. These formulas are (in our previous notation) for the weak scattering potential case

$$f_{kk'}(t)=iV_{kk'}\int_0^t d\tau\, e^{-id_{kk'}(t-\tau)}[f_k(\tau)-f_{k'}(\tau)], \qquad (t\gg 0), \quad (3.9)$$

$$f_{kk'}(t)=iV_{kk'}\int_0^t d\tau\, e^{-id_{kk'}^*(t-\tau)}[f_k(\tau)-f_{k'}(\tau)], \qquad (t\ll 0), \quad (3.10)$$

where $d_{kk'}^*$ is the complex conjugate of $d_{kk'}$, and the quantity s is to be set zero. Equations (3.9) and (3.10) show that for very small times the $f_{kk'}$ grow in each time direction away from time zero. If we neglect the time dependence of the f_k in the integrand, we find the same relation between $f_{kk'}$ and f_k found by Kohn and Luttinger with Eq. (3.9) corresponding to the causal, Eq. (3.10) corresponding to the anticausal, transport equation.

In view of these remarks we may consider that Van Hove's theory has application to a fluctuation with maximum deviation from equilibrium at time zero. We want to emphasize two features of his results:

(a) When the $f_{kk'}$ are very small there is no scattering.

(b) When the $f_{kk'}$ are significantly large there is scattering governed by the appropriate macroscopic transport equation—the Boltzmann equation when $\Gamma_{kk'}$ in $d_{kk'}$ is positive, the anti-Boltzmann equation when $\Gamma_{kk'}$ is negative.

Thus, Van Hove's theory provides support for the notion that the phase of the off-diagonal density matrix elements of nearly zero frequency is what determines which transport equation governs the nonequilibrium part of the distribution function.

The work of Van Hove toegther with that of Kohn and Luttinger suggests a point of view to replace the old condition[10] of "phase randomization between collisions," one which can be summarized in the phrase "phase persistence between collisions." Thus, in a system of distributed scatterers one may consider that a small amount of coherence remains from one collision to the next, expressing itself in the phase of the low frequency $f_{kk'}$, and it is this phase coherence that permits a steady course of the irreversible process.

IV. RELATION TO EXPERIMENT

The conditions under which most transport processes are observed do not permit the idealization that the observed system is isolated. However, it is possible in certain cases to approach the following idealization of isolation: (1) the system to be observed is isolated for a long time, after which (2) the system of interest is suddenly altered (we will consider that it is altered instantaneously) so that the experiment is initiated, (3) the altered system is again isolated and remains isolated while the course of the experiment is observed. We will take, as an example of this process, the diffusion of some gas molecules from a container under the conditions that the container was closed for a long period during negative times and opened suddenly at time zero.

We want to discuss the diffusion process in this example as though the observed system had always been isolated, whereas, in the physical system a very drastic change in the laws of motion has been made at the initial moment when the container is opened. Thus, we must consider that the *observed system is created at time zero* (as the term "system" is used in mechanics), and the behavior of the system for negative times is experimentally unknowable. We can, however, say something about the behavior of the system for negative times on the basis of theory: Theory tells us that with overwhelming probability the gas molecules moved into the container by an inverse diffusion process which obeys an "antidiffusion" equation. Under experimental circumstances such as "indiffusion" process is so overwhelmingly improbable as to be unobservable; however, *given that the container had been open for all time*, it would be overwhelmingly probable. Thus, viewed as a process in an isolated system, the diffusion process is just the regression of a fluctuation in concentration which reached its maximum very nearly at the zero of time.

From the above admittedly somewhat artificial point of view our idealized transport process is just the regression of a fluctuation: An experimental procedure to

[10] For a discussion of these requirements see, for example, R. E. Peierls, *The Quantum Theory of Solids* (Clarendon Press, Oxford, 1955), p. 140.

observe our transport process just creates a nonequilibrium situation corresponding to a fluctuation very near its maximum, so that it begins its regression almost as soon as the experiment is initiated. [The reason that the fluctuation is created so near maximum is to be found in the circumstance that a typical experimental procedure fixes the state of only a few of the many degrees of freedom of the gas (e.g., temperature, volume).] Our point of view, applicable to these special experiments, fits in very well with Van Hove's theory of irreversibility in all of its details if the time zero is identified (as is natural) with the moment of initiation of the experiment.

The problem discussed by Kohn and Luttinger cannot be treated merely by the application of the Van Hove theory because of the occurrence in the KL Hamiltonian of the (unbounded) electric potential. We have considered carefully the relation of the theory to experiment, and have found that the situation is surprisingly complex. We cannot give a definitive discussion at this time, but we will state our opinion since what is in question is relevant to the subject of this paper. We are presently of the opinion that: (a) There are two ohmic solutions of the equations of motion, formulated and solved by Kohn and Luttinger, the two solutions discussed in an earlier section. (b) The uniqueness of the direction of current flow in an experimental situation apparently similar to that discussed by Kohn and Luttinger is a consequence of a *time-directed* interaction of the electron system with some external system always present in experimental situations. In virtue of this interaction, which cannot conveniently be introduced into the Hamiltonian theory, the nature of the current flow and the density matrix describing it is largely independent of the initial conditions supposed at $t=-\infty$. (c) While the existence of such an external interaction is essential for understanding the irreversibility of the transport process, it is not essential for understanding what the transport equation is; we believe Kohn and Luttinger have deduced the correct higher order transport equation subject only to the limitations that they have stated. (d) We believe that similar remarks may be made concerning other theories in which the artifice of turning on an interaction is used to ensure the causal nature of a solution of some set of mechanical equations.

We will conclude by commenting on the applicability of the two transport equations for predicting the behavior of nonequilibrium distribution functions.

It seems feasible experimentally to observe motions governed by the anticausal transport equation. However, one can never use that equation for predicting the future experimental time variation of a nonequilibrium distribution function. The difficulty is that experiments do not provide the information necessary to infer the correlations which determine the nature of time variation. One can, at best, then, predict the likelihood of various future configurations on the basis of their relative *a priori* probabilities of occurrence. By definition, "equilibrium" configurations are just those of highest probability, and states near equilibrium are highly probable relative to those farther away; consequently, on an *a priori* basis and lacking information about the correlations, one can only predict that the system will approach equilibrium. Even though we may *observe* that a fluctuation is carrying the system ever further from an equilibrium state, we must *expect* at each moment that the trend will immediately turn back toward equilibrium. The proper application of the anti-Boltzmann equation is for retrodiction during the progression of a fluctuation, just as that of the Boltzmann equation is for prediction during the regression of a fluctuation. Prediction during the progression of a fluctuation is essentially impossible since the system is moving from configurations of more, to configurations of less, probability. It follows that *when the future course of a distribution function can be predicted* it is always the Boltzmann equation that must be used to predict it.

The above discussion follows conventional thinking as to the probabalistic elements of irreversibility. It is presented only to show why the theoretical idea that the correlations determine the manner of time variation of a distribution is not in conflict with the experimental fact that the upward course of a fluctuation is unpredictable. This paper is intended primarily as an *exposition* of ideas which are latent in the work of Kohn and Luttinger, Van Hove, and Brout and Prigogine which we believe did not get enough emphasis or discussion; thus, it is not intended to be in conflict with their results.

V. SUMMARY

1. There are two macroscopic equations that govern irreversible processes in an isolated system, the Boltzmann equation (causal), which describes the most probable mode of approach to equilibrium of a nonequilibrium distribution function, and an "anti-Boltzmann" equation (anticausal), which describes the most probable mode of motion away from equilibrium of a nonequilibrium distribution function: The problem of irreversibility is to determine which of these will govern a given nonequilibrium distribution function.

2. The decisive matter for determining whether a given nonequilibrium distribution function obeys a causal or anticausal transport equation is the phase of certain off-diagonal density matrix elements; in the theory of a classical electron gas these matrix elements describe position-velocity correlations.

3. In discussing irreversible processes in an isolated system it is the initial conditions which must guarantee the existence of the correct type of off-diagonal matrix elements. The solution density matrices are sometimes very sensitive to the details of these matrix elements are specified.

4. The analysis of how experimental procedures result in a specification of causal initial conditions is complex: Experimental conditions are not usually consistent with the notion that the system is isolated. However, in the

simple case that the observed process can be considered as a fluctuation in an isolated system, the theory of Van Hove can be related to the experimental situation in a natural way.

5. Ordinary probabalistic reasoning shows that in experimental situations the anti-Boltzmann is never useful for prediction of the future behavior of a non-equilibrium distribution function, even in cases for which the distribution function is changing according to that equation.

PHYSICAL REVIEW VOLUME 120, NUMBER 3 NOVEMBER 1, 1960

Temperature Dependence of the Low-Momentum Excitations in a Bose Gas of Hard Spheres*

F. Mohling
Department of Physics, Cornell University, Ithaca, New York

AND

M. Morita
Department of Physics, Columbia University, New York, New York

(Received June 24, 1960)

The pseudopotential method is used to calculate the temperature dependence of the low-momentum excitations in a Bose gas of hard spheres to an order beyond that previously known. The correction term is shown to be small compared to the leading term for all temperatures less than the critical temperature T_c. The excitations become poorly defined for temperatures slightly below T_c, however, since it is shown that in this region the excitation lifetimes are quite small.

INTRODUCTION

At any temperature T less than the critical temperature T_c, the low-lying excitation energies in a system of bosons are associated with unique wave numbers and, therefore, they exhibit particle-like properties. The (temperature-dependent) energy-momentum relation for these quasi-particles has been measured for liquid He II by neutron scattering experiments.[1] On the other hand, a theoretical calculation of quasi-particle energies has been made only for a Bose gas of hard spheres in the low-density limit. For this idealized model the leading term in the quasi-particle energy, as determined by Lee and Yang,[2] is

$$\omega_0(k)=(2M)^{-1}\hbar^2k(k^2+2k_0^2)^{\frac{1}{2}},$$

where $k_0^2=8\pi\rho aX$ (ρ=density, a=diameter of a hard sphere, and $X(T)$=fraction of bosons in zero-momentum state). The expression is valid for all $T<T_c$. Several calculations have been made of the leading correction to $\omega_0(k)$ at $T=0$ (where $X=1$).[3] On the other hand, the leading correction to $\omega_0(k)$ for $T\neq 0$ has not previously been published.

The problem of calculating the quasi-particle energies for the ground state ($T=0$) of a Bose gas of hard spheres possesses the simplifying feature that only two lengths characterize the system; namely, $l\equiv\rho^{-\frac{1}{3}}$ and a. The only dimensionless parameter which is encountered in the low-density case is found to be the small parameter $(\rho a^3)^{\frac{1}{2}}$.

When $T\neq 0$ another length occurs in the problem; namely, the thermal wavelength,

$$\lambda_T=(2\pi\hbar^2/kTM)^{\frac{1}{2}}.$$

The introduction of the thermal wavelength increases the number of dimensionless parameters which can be used to describe the Bose gas of hard spheres. Now, whereas the low-density Bose gas is certainly not the same system as real liquid He II, it is of value for orientation purposes to write down the lengths a, l, and λ_c ($=\lambda_T$ at $T_c=2.18$°K) of real He II,[4] together with various dimensionless combinations which are encountered in this paper. These are:

$$\begin{aligned} a&=2.30\text{ A}, & a/\lambda_c&=0.39,\\ l&=3.58\text{ A}, & (\rho a^3)^{\frac{1}{2}}&=0.515,\\ \lambda_c&=5.91\text{ A}, & \rho\lambda_c^3&=4.5,\\ && \rho a\lambda_c^2&=1.75. \end{aligned}$$

* This work was supported in part by the U. S. Atomic Energy Commission and in part by the Office of Naval Research. This research was started while the first author was at Columbia University.

[1] H. Palevsky, K. Otnes, and E. Larsson, Phys. Rev. **112**, 11 (1958); Y. L. Yarnell, G. P. Arnold, P. J. Bendt, and E. C. Kerr, Phys. Rev. **113**, 1379 (1959); D. G. Henshaw, Phys. Rev. Letters **1**, 127 (1958).

[2] T. D. Lee and C. N. Yang, Phys. Rev. **112**, 1419 (1958).

[3] S. T. Beliaev, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 433 (1958) [translation: Soviet Phys.—JETP **7**, 299 (1958)]; F. Mohling and A. Sirlin, Phys. Rev. **118**, 370 (1960), hereafter referred to as MS.

[4] See, e.g., F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1954), Vol. II.