New Approach to Transport Theory in Classical Gases*

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A new approach to transport theory in classical gases is described for a hard-sphere gas. The approach is designed to incorporate collective effects (sound waves, mean free path) at an early stage. A pseudopotential approximation to the N-body Liouville equation is given. By working only with symmetric distribution functions, a simple analogy to a quantum-mechanical many-body Hamiltonian is possible. The linearized Boltzmann equation is obtained as the "Hartree" solution to the single-particle states of this Hamiltonian. Sound waves appear as long-wavelength "single-particle" excitations. Collective excitations include the excluded volume correction to the velocity of sound. The "single-particle" solutions have the advantage of introducing the appropriate long-range space-time correlations into the basis functions for higher-order approximations. Because of the pseudopotential approximation in the present paper, there are *short-range* divergences in higher orders of perturbation theory, but no apparent long-wavelength divergences.

I. INTRODUCTION

DURING the last few years, considerable effort has been made to provide a theory of irreversible processes in classical gases. Basically, two proposals appeared: the theory of Prigogine and Resibois,[1] based on a resolvent solution of the Liouville equation, and the Bogoliubov method,[2] based on a time-synchronized solution of the BBGKY hierarchy. It has been shown recently[3] that in the thermodynamic limit and at the hydrodynamical stage, the latter is an exact consequence of the former theory, so there seems to be only one kind of theory.

Although one might have expected good results from both of these formulations, there are also strong arguments raising doubts about their validity. First of all, the fundamental synchronization assumption[2] of the Bogoliubov expansion is set in a concise mathematical form but has not been fully explained in a physical sense. Furthermore, all the formulations involve one or several power-series expansions, the convergence of which has never been proven. There are instead proofs that thermodynamic transport properties are not analytic at zero density.[4]

Collective modes have not so far been a part of the above theories and worse, there are some elementary results of collective effects that these theories will never yield. Consider a gas in three dimensions. The mean free path of long-wavelength phonons, which are damped by viscosity and thermal conductivity, is proportional to the square of the wavelength and to the gas density. The degree of nonadiabaticity is proportional to k^2. When the contribution to the thermal conductivity of these modes is summed[5] up to a wavelength cutoff at the mean free path, a contribution proportional to $(N/\Omega)^4$ to the thermal conductivity is obtained. The usual methods of approach to transport coefficients never obtain collective behavior—the dynamical problem solved is essentially the problem of a few atoms in an infinite box—so cannot yield this contribution. [*Note added in proof.* L. Kadanoff has helpfully pointed out the distinctions between transport of heat by elastic waves in gases and in solids.]

The divergence difficulties in transport-coefficient calculations ordinarily encountered[4] involve incorrect long-range space-time correlations. Physically, there will exist long-range correlations, but they are in fact due to collective modes (sound waves and entropy fluctuations). These collective modes fill in all time scales longer than the mean free time and prevent a division into "macroscopic times" and the mean free time. This is why even before going to such delicate problems as the three-body collisions and the high-frequency behavior, there is a need for a point of view which can properly provide collective behavior and collective excitations at low frequencies.

Our goal is to begin a theory which avoids the Bogoliubov synchronization assumption, which escapes power-series expansions of dynamical properties, which accounts for low-frequency sound waves, and which conceptually at least will insert the proper long-range space-time correlations into the next higher approximation.

In Sec. II, some useful properties of the linearized Boltzmann equation are recalled. One cannot, of course, find useful new results by assuming the validity of the Boltzmann equation. The structure of the collision term and of the solutions to this equation turn out, however, to be basic to the mathematics of our point of view. In Sec. III the collision pseudopotential and

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[1] I. Prigogine, *Non-Equilibrium Statistical Mechanics* (John Wiley & Sons. Inc., New York, 1962).
[2] N. Bogoliubov, *Problems of a Dynamical Theory in Statistical Physics* (State Publishing House of Theoretical-Technical Literature, Moscow, 1946). [English transl.: E. Gora, in *Studies in Mechanics*, edited by J. De Boer and G. Uhlenbeck (North-Holland Publishing Co., Amsterdam, 1952), Vol. I]; see also E. Cohen, *Fundamental Problems in Statistical Mechanics* (North-Holland Publishing Co., Amsterdam, 1962); An extensive bibliography will be found in: A. Kritz and G. Sandri, Phys. Today **19**, 57 (1966).
[3] J. Stecki and H. S. Taylor, Rev. Mod. Phys. **37**, 762 (1965).
[4] E. G. D. Cohen (to be published).
[5] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Inc., New York, 1958).

the equation of motion of the system are derived. Section IV sets up a useful formalism which converts the problem to a typical quantum-mechanical N-body problem. In Sec. V a well-defined approximation (which is in fact the exact analogous of the Hartree-Fock approximation in quantum mechanics) yields some expected results. The virtues and vices of the point of view are discussed in the conclusion.

II. BOLTZMANN EQUATION

Let us first briefly review some fundamental results on the Boltzmann equation which will be useful hereafter.

In the absence of any external field, this equation reads[6]

$$\frac{\partial f(1)}{\partial t}+\mathbf{v}\cdot\nabla f_{(1)}=\int d\mathbf{v}_1 d\Omega\, gI(g,\Omega)(f'f'_1-ff_1) \quad (1)$$

with traditional notations, or after a temporal Fourier transform:

$$i\omega f_{(1)}+\mathbf{v}.\nabla f_{(1)}=\int d\mathbf{v}_1 d\Omega g I(g,\Omega)(f'f'_1-ff_1). \quad (2)$$

Its equilibrium solution is the Maxwellian distribution function

$$f_0=n(2\pi kT/m)^{-3/2}\exp(-mv^2/2kT), \quad (3)$$

where n is the density of particles, m their mass. For simplicity we shall use a unit system such that

$$kT/m=1. \quad (4)$$

For small departures f from equilibrium f_0, one obtains the linearized Boltzmann equation

$$\frac{\partial f}{\partial t}+\mathbf{v}\cdot\nabla f=\int dv_1 d\Omega g I(g,\Omega) f_0(f'+f_1'-f-f_1), \quad (5)$$

which is an eigenvalue problem. The kernel $gI(g,\Omega)$ which appears in the right-hand side of (5) will be called the Boltzmann collision kernel and will be denoted by K_B.

It is well-known[5,6] that there are only five eigenfunctions of the collision operator belonging to the eigenvalue 0, namely, 1, v_x, v_y, v_z, $(v^2-\frac{3}{2})$ times f_0. This is a consequence of the five mechanical conservation laws during a collison (number of particles, energy, and three components of the momentum). All other eigenvalues are strictly negative. For hard spheres, the first nonzero eigenvalue is finite; there is a gap in the spectrum. If one considers the streaming term $\mathbf{v}\cdot\nabla$ as small compared to the collision operator (in other words, in the long-wavelength limit) one obtains sound waves[6] by a degenerate perturbation treatment on these eigenfunctions of zero frequency and gets the linear dispersion relationship for the velocity of sound:

$$c=(\tfrac{5}{3})^{1/2}. \quad (6)$$

If the solutions to (5) are computed to one higher order in powers of $(\mathbf{k}\cdot\mathbf{v})$, the damping of sound waves and of the entropy fluctuations will result. The transport coefficients can be identified from these damping coefficients. At this stage, it appears that (5) does not contain any effect of the finite size of the molecules because the collisions are local. The spatial structure of the solutions is not adequately general. While some collective properties (e.g., sound waves) result from these equations, the transport coefficients computed from this equation contain only single-particle properties. Most important, when higher-order calculations[1,2] of the transport coefficients have been attempted, they have not taken advantage of the solutions of (5) and, in particular, of the collective behavior of these solutions.

III. KINETIC EQUATION

As a first step, we derive the exact one-particle equation for a classical hard-sphere gas (the radius of the sphere will be denoted by r_0). We may hope it will be a good approximation for an actual monoatomic gas with a short-range repulsive potential and a cross section equivalent to that of a sphere. We shall take for granted, although this point has been considered as subject to discussion,[7] that the evolution (in time) of the one-particle distribution function has two separate causes: the flow of independent particles which correspond to the streaming term of traditional equations: $\{i\omega+\mathbf{v}\cdot\nabla\}f$, and the collisions which are described by the so-called "collision operator" as in the first equation of the BBGKY hierarchy.[4]

The collision term can be computed in the case of hard spheres. A collision can be described in the following way: the incoming particles have velocities $\mathbf{v}_1$ and $\mathbf{v}_2$; the contact point is located at $\mathbf{r}_1+\mathbf{r}_0 u$, and the particles at $\mathbf{r}_1$ and $\mathbf{r}_2=\mathbf{r}_1+2r_0\mathbf{u}$. The geometry is drawn in Fig. 1. The velocities after the collision are then $\mathbf{v}_1^*$ and $\mathbf{v}_2^*$. The effect of such a collision is to cancel a particle from the point $(\mathbf{r}_1,\mathbf{v}_1)$ of phase space and to introduce one at $(\mathbf{r}_1,\mathbf{v}_1^*)$, and similarly to cancel one at $(\mathbf{r}_2,\mathbf{v}_2)$ and to introduce one at $(\mathbf{r}_2,\mathbf{v}_2^*)$.

Given a particle at $(\mathbf{r}_1,\mathbf{v}_1)$, let us count the number dn of collisions it undergoes during the time interval

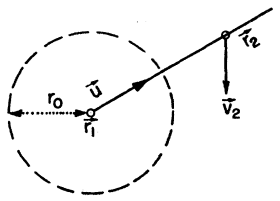

FIG. 1. The geometry of a two-particle hard-sphere collision.

[6] G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, R. I., 1963).

[7] I. Prigogine and J. Philippot, Physica **23**, 569 (1957).

dt. Separating contributions for given orientation of $\mathbf{u}$ (unit vector along the centers) and given value of $\mathbf{v}_2$, defining the angle ψ_2 as $(\mathbf{u},\mathbf{v}_2)$ and integrating, one finds

$$dn=-\int d\mathbf{v}_2 d\Omega\cdot r_0^2 v_2\cos\psi_2\cdot f_2(\mathbf{r}_1,\mathbf{v}_1;\,\mathbf{r}_1+2r_0\mathbf{u},\mathbf{v}_2)dt, \quad (7)$$

where $d\Omega$ is the element of solid angle and f_2 the standard two-particle distribution function. So the cancellation process contributes to the collision term by the amount

$$\int d\Omega d\mathbf{v}_2 r_0^2 v_2\cos\psi_2 f_2(\mathbf{r}_1,\mathbf{v}_1;\,\mathbf{r}_1+2r_0\mathbf{u},\mathbf{v}_2).$$

In the same fashion, the contribution for the creation process is

$$-\int d\Omega d\mathbf{v}_2 r_0^2 v_2\cos\psi_2 f_2(\mathbf{r}_1,\mathbf{v}_1^*;\,\mathbf{r}_1+2r_0\mathbf{u},\mathbf{v}_2^*).$$

By adding these up, the one-particle equation now can be written

$$(i\omega+\mathbf{v}\cdot\nabla)f_1=\int d\omega d\mathbf{v}_2 r_0^2 v_2\cos\psi_2[f_2(\mathbf{r}_1,\mathbf{v}_1,\mathbf{r}_1+2r_0\mathbf{u},\mathbf{v}_2)-f_2(\mathbf{r}_1,\mathbf{v}_1^*;\,\mathbf{r}_1-2r_0\mathbf{u},\mathbf{v}_2^*)]. \quad (8)$$

[*Note added in proof.* This equation has also been derived by a rigorous coarsegraining of the Liouville equation in S. A. Rice and P. Gray, *Statistical Mechanics of Simple Liquids* (Interscience Publishers, Inc., New York, 1965)].

An important difference from (2) comes from the spatial dependence of the f_2. If we neglect the variation of f_2 over the distance $2r_0\mathbf{u}$, and approximate it by a product of one-particle distribution functions (Kirkwood's principle), identifying $4\pi r_0^2$ with the total cross section we find exactly the Boltzmann equation. Equation (8), while exact, is, of course, insufficient to specify a solution for f_1 without a knowledge of f_2.

The next step is to write the N-particle kinetic equation which contains (8) as a particular case, i.e., the equation of motion which leads to (8) exactly as the Liouville equation leads to for the first BBGKY equation. Since the hard spheres interact only for infinitesimal times, the N-body Liouville equation can be integrated over the duration of a collision and the forces eliminated. One obtains

$$i\omega f_N+\sum_{j=1}^{N}\mathbf{v}_j\cdot\nabla_j f_N=\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i=1}^{N}K_{ij}f_N, \quad (9)$$

where f_N is the N-particle distribution function, $\nabla_i f_N$ its gradient with respect to the ith position and K_{ij} is defined as follows:

$$K_{ij}f_N(\cdots\mathbf{r}_i,\mathbf{v}_i\cdots\mathbf{r}_j,\mathbf{v}_j\cdots)=\frac{1}{2V}r_0^2 d\Omega[v_j\cos\psi_j\delta(\mathbf{r}_j-\mathbf{r}_i+2r_0\mathbf{u})f_N(\cdots\mathbf{r}_i,\mathbf{v}_i\cdots\mathbf{r}_j,\mathbf{v}_j\cdots)$$
$$-v_j\cos\psi_j\delta(\mathbf{r}_j-\mathbf{r}_i-2r_0\mathbf{u})f_N(\cdots\mathbf{r}_i\mathbf{v}_i^*\cdots\mathbf{r}_j\mathbf{v}_j^*\cdots)+v_i\cos\psi_i\delta(\mathbf{r}_j-\mathbf{r}_i+2r_0\mathbf{u})f_N(\cdots\mathbf{r}_i,\mathbf{v}_i\cdots\mathbf{r}_j,\mathbf{v}_j\cdots)$$
$$-v_i\cos\psi_i\delta(\mathbf{r}_j-\mathbf{r}_i-2r_0\mathbf{u})f_N(\cdots\mathbf{r}_i,\mathbf{v}_i^*\cdots\mathbf{r}_j,\mathbf{v}_j^*)], \quad (10)$$

where V is the volume of the system, $\mathbf{u}$ the unit vector along the line of the centers $(\mathbf{r}_i-\mathbf{r}_j)$, oriented from i to j, $\psi_i=(\mathbf{u},\mathbf{v}_i)$, $\psi_j=(\mathbf{u},\mathbf{v}_j)$. An intergration of the kinetic equation (10) over N-1 variables results in (8).

In the case of short-range but non-hard-sphere interactions, this time integration cannot be rigorously done. An additional parameter having to do with the duration of the collision will then enter the problem. A first approximation of the form of (9) to this case still seems physically reasonable (particularly so for studies of the origin of a "large time" divergence).

IV. QUANTUM FORMALISM

When the kinetic equation is expressed as in (9), K_{ij} is symmetrical with respect to the indices i and j. Thus (9) has exactly the same structure as an N-body Schrödinger equation, K_{ij} standing for the interaction between particles i and j, f_N standing for the wave function, and the $\mathbf{v}\cdot\nabla$ term being a single-particle "potential." The "coordinates" of the ith particle are the vectors $\mathbf{v}_i,\mathbf{r}_i$. All the formalisms connected with the mathematical structure of this N-body Schrödinger (but not with its interpretation) can be readily applied. First of all, provided we choose a complete basis in the Hilbert space of distribution functions, (9) can be usefully written in a second quantization formalism, namely,

$$i\omega f_N=Hf_N, \quad (11)$$

with

$$H=\sum_{k_\alpha}\sum_{k_\beta}\sum_{l_\alpha}\sum_{l_\beta}\times a_{k_\alpha,l_\alpha}^{\dagger}a_{k_\beta,l_\beta}\langle k_\alpha l_\alpha|-\mathbf{v}\cdot\nabla|k_\beta l_\beta\rangle$$
$$+\tfrac{1}{2}\sum_{k_\alpha}\sum_{k_\beta}\sum_{k_\gamma}\sum_{k_\delta}\sum_{l_\alpha}\sum_{l_\beta}\sum_{l_\gamma}\sum_{l_\delta}\times a_{k_\alpha l_\alpha}^{\dagger}a_{k_\beta l_\beta}^{\dagger}a_{k_\gamma l_\gamma}a_{k_\delta l_\delta}$$
$$\times\langle k_\alpha,l_\alpha;\,k_\beta l_\beta|K|k_\gamma,l_\gamma;\,k_\delta l_\delta\rangle. \quad (12)$$

$a_{k,l}^{\dagger}$ is the creation ("boson") operator corresponding to the one-particle state

$$f_{k,l}=(1/\sqrt{V})\phi_l(\mathbf{v})\exp(i\mathbf{k}\cdot\mathbf{r}). \quad (13)$$

When there is no ambiguity this state will be denoted in short by α.

This algebra will yield only symmetric distribution functions, but this is really no limitation. The choice of the spatial dependence of the basis functions offers no difficulty provided we enforce periodic boundary conditions in a system of volume V. For the $\phi_{l\alpha}(\mathbf{v})$ it will be convenient to take orthonormal [with weighting function $(2/\pi)^{1/4}\exp(v^2)$] eigenfunctions of the collision kernel K_B which appears in the right-hand side of (5). This choice for a weighting function makes the collision matrix symmetric. The corresponding eigenvalue will be denoted by ω_α. As we recalled previously, we know that the first five are proportional to f_0, $v_x f_0$, $v_y f_0$, $v_z f_0$, $(v^2-\frac{3}{2})f_0$, with eigenvalue 0. Moreover, although the spectrum of (5) is not explicitly known, it has been proven that all other eigenvalues are negative, from a dense spectrum for repulsive potentials decreasing faster than r^{-6}, and that there is a gap between the dense spectrum and zero.[8]

As far as the "matrix elements" are concerned, they display some selection rules. Those related to the velocity indices l_α, l_β $\cdots$ cannot be explicitly written down since most of the ϕ's are unknown. It is obvious that all matrix elements which violate wave-vector conservation are zero.

Written this way, our equation is no more soluble than the first one, so some kind of an approximation is needed. Instead of a systematic expansion procedure in powers of a suitable expansion parameter such as those which have been exclusively used recently,[4] we prefer a direct approximation on K. Thus, one escapes the problems concerning the convergence of the expansions and the physical meaning of the various terms, which are still subject to discussion.

We proceed as follows:

The two-particle part of H reads

$$H_2=\tfrac{1}{2}\sum_\alpha\sum_\beta\sum_\gamma\sum_\delta a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta\langle\alpha,\beta|K|\gamma\delta\rangle. \quad (14)$$

The matrix element exists in our basis only in a pseudopotential sense, and this limitation will be important in higher order. If we denote by $\psi^\dagger(\mathbf{r},\mathbf{v})$ and $\psi(\mathbf{r},\mathbf{v})$ the "field operators" defined by

$$\psi^\dagger(\mathbf{r},\mathbf{v})=\sum_k\sum_l a_{k,l}^\dagger f_{k,l}^*,$$
$$\psi(\mathbf{r},\mathbf{v})=\sum_k\sum_l a_{k,1}f_{k,l}, \quad (15)$$

we get

$$H_2=\tfrac{1}{2}\int d\mathbf{r}d\mathbf{v}d\mathbf{r}'d\mathbf{v}'\psi^\dagger(\mathbf{r},\mathbf{v})\psi^\dagger(\mathbf{r}',\mathbf{v}')K_{12}\psi(\mathbf{r},\mathbf{v})\psi(\mathbf{r}',\mathbf{v}').$$

Since K_{12} gives a nonzero contribution only where $|\mathbf{r}-\mathbf{r}'|=2r_0$ we may replace, in every term of H_2, $\psi^\dagger(\mathbf{r}')$ by $[\psi^\dagger(\mathbf{r})+2\mathbf{r}_0\mathbf{u}\cdot\nabla\psi^\dagger(\mathbf{r})]$, and so on. Our approximation consists in keeping only the leading term (which does not contain any gradient) and the terms which are linear in gradients. The validity of this scheme will be discussed in the last section.

As we noticed previously, replacing $\mathbf{r}'$ by $\mathbf{r}$ merely cancels the structure due to the size of the spheres. So, the leading term of our approximation is exactly that which would result from matrix elements of the Boltzmann collision kernel K_B. We write it

$$H_2^{(0)}=\tfrac{1}{2}\sum_\alpha\sum_\beta\sum_\gamma\sum_\delta a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta\langle\alpha,\beta|K_B|\gamma,\delta\rangle.$$

Keeping only this lowest-order term and using Kirkwood's principle would yield the ordinary Boltzman equation.

We next consider the first-order terms, which will be denoted by $H_2^{(1)}$. Since the latter will be relevant because of its spatial (or wave-vector) structure and not because of its velocity dependence, for simplicity we shall assume we can replace in it $\mathbf{v}^*$ by $\mathbf{v}'$ and $\mathbf{v}'^*$ by $\mathbf{v}$ (exchange of velocities). This is equivalent to a collision in the center-of-mass system. This procedure has been carried only in order to get reasonable computations but in principle it was not strictly needed. Once this has been done, expanding all the ψ's and $\psi^\dagger$'s, collecting terms, and replacing the field operators by their expression (15), one obtains

$$H_2^{(1)}=\tfrac{1}{2}\sum_\alpha\sum_\beta\sum_\gamma\sum_\delta a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta G(\alpha,\beta,\gamma,\delta), \quad (16)$$

where

$$G(k_\alpha l_\alpha\cdot k_\beta l_\beta\cdot k_\gamma l_{\gamma'}\cdot k_\delta l_\delta)$$
$$=\frac{2Nr_0^3}{V}(\mathbf{k}-\mathbf{k}_\beta)\delta(\mathbf{k}_\alpha+\mathbf{k}_\beta-\mathbf{k}_\gamma-\mathbf{k}_\delta)\int d\mathbf{u}dvdv'$$
$$\times(v\cos\psi-v'\cos\psi')\phi_\alpha(v)\phi_\beta(v')\phi_\gamma(v)\phi_\delta(v'). \quad (17)$$

We now will treat the N-body equation resulting,

$$i\omega f_N=\{H_1+H_2^{(0)}+H_2^{(1)}\}f_N, \quad (18)$$
$$H_1=\sum_\alpha\sum_\beta a_\alpha^\dagger a_\beta\langle\alpha|-\mathbf{v}\cdot\nabla|\beta\rangle,$$
$$H_2^{(0)}=\tfrac{1}{2}\sum_\alpha\sum_\beta\sum_\gamma\sum_\delta a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta\langle\alpha,\beta|K_B|\gamma,\delta\rangle, \quad (19)$$
$$H_2^{(1)}=\tfrac{1}{2}\sum_\alpha\sum_\beta\sum_\gamma\sum_\delta a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta G(\alpha,\beta,\gamma,\delta).$$

The higher-order gradient terms dropped in writing (18) are multiplied by higher powers of the parameter (particle size/particle separation).

V. HARTREE-FOCK TREATMENT

An approximate solution of (18) will be derived by a Hartree-Fock procedure. The ground state of the system is $(a_0^\dagger)^N|\phi\rangle$, where $|\phi\rangle$ is the vacuum and the $a_0^\dagger$

[8] H. Grad, in *Proceedings of the Third International Symposium on Rarified Gas Dynamics* (Academic Press Inc., New York, 1963, Vol. I, pp. 26 ff).

creates a particle in the one-particle ground state, namely a Maxwellian distribution function of velocity at some specified temperature and uniform in space. This is obviously an exact solution of (18) for $\omega=0$ (H_1 and $H_2^{(1)}$ contains spatial gradients, so they give zero when acting on the state and $H_2^{(0)}$ has the Maxwellian distribution as a zero eigenfunction).

We now look for the excitations of the system by examining the equation of motion of a creation operator $a_{k,l}^\dagger$. Since

$$\partial a_{k,l}^\dagger/\partial t=[a_{k,l}^\dagger H], \tag{20}$$

and H has already been expressed in (18) in boson operators a_α, some elementary algebra (and taking the wave-vector conservation into account) yields

$$[a_{k,l}^\dagger,H]=\sum_{l_\alpha} a_{k,l_\alpha}^\dagger\langle k,l_\alpha|\,\mathbf{v}\cdot\nabla\,|k,l\rangle-\tfrac{1}{2}\sum_{k_\alpha}\sum_{k_\beta}\sum_{k_\gamma}\sum_{l_\alpha}\sum_{l_\beta}\sum_{l_\gamma} a_{k_\alpha,l_\alpha}^\dagger a_{k_\beta,l_\beta}^\dagger a_{k_\alpha+k_\beta-k_\gamma,l_\gamma}$$
$$\times\{\langle\alpha,\beta|\,K_B\,|(k_\alpha+k_\beta-k),l_\gamma;k,l\rangle+\langle\alpha,\beta|\,K_B\,|k,l;(k_\alpha+k_\beta-k),l_\gamma\rangle$$
$$+G[\alpha;\beta;(k_\alpha+k_\beta-k)l_\gamma;k,l]+G[\alpha;\beta;k,l;(k_\alpha+k_\beta-k)l_\gamma]\}. \tag{21}$$

The Hartree-Fock approximation[9] consists in replacing the products $a^\dagger a$ occurring in the bilinear term by their expectation value in the ground state. We are then left with the following equation:

$$[a_{k,l}^\dagger,H]=\sum_m a_{k,m}^\dagger\langle k,m|\,\mathbf{v}\cdot\nabla\,|k,l\rangle-\omega_l a_{k,l}^\dagger. \tag{22}$$

This is exactly the equation which would have been obtained from the linearized Boltzmann equation by expanding the distribution function in terms of the eigenfunctions of the collision operator. So the Uhlenbeck theory of sound[6] is obtained as a lowest-order result.

The gradient terms of $H_2^{(1)}$, although they have been introduced in the theory, do not affect this one-particle picture. The point is that to improve the classical sound-wave theory, one should take into account the fact that sound is a collective mode of the system.

Collective Excitations

A typical excitation of wave vector q will be described by a linear combination of operators of the form $a_{k+q,l}^\dagger a_{k,m}$, so the equation of motion:

$$(\partial/\partial t)[a_{k+q,l}^\dagger a_{k,m}]=[a_{k+q,l}^\dagger a_{k,m},H] \tag{23}$$

is next investigated. Exactly as in the preceding treatment, H given by (19) is inserted into the commutation relation, wave-vector conservation is used. Quadrilinear terms are eliminated by taking expectation values in the ground state of all the products $a^\dagger a$ occurring in a quadrilinear term. The final result is:

$$[a_{k+q}^\dagger,a_{k,m},H]=\sum_{l_\alpha} a_{k+q,l}^\dagger a_{k,l_\alpha}\langle k,m|\,\mathbf{v}\cdot\nabla\,|k,l_\alpha\rangle-\sum_{l_\alpha} a_{k+q}^\dagger,a_{k,m}\langle(k+q),l_\alpha|\,\mathbf{v}\cdot\nabla\,|(k+q),l\rangle+\tfrac{1}{2}(\omega_m-\omega_l)a_{k+q,l}^\dagger a_{k,m}$$
$$+\tfrac{1}{2}\sum_{k_\alpha}\sum_{l_\alpha}\sum_{l_\beta} a_{k_\alpha+q,l_\beta}^\dagger a_{k_\alpha,l_\alpha}\{\delta(l)\delta(k+q)\langle(k_\alpha+q),l_\beta;k,m|\,K_B\,|k_\alpha,l_\alpha;0\rangle$$
$$-\delta(m)\delta(k)\langle(k_\alpha+q)l_\beta;0|\,K_B\,|(k+q),l;k_\alpha l_\alpha\rangle\}-\tfrac{1}{4}\sum_{l_\alpha} a_{k+q,l_\alpha}^\dagger a_{k,m}G[(k+q),l_\alpha;0;(k+q),l;0]$$
$$+\tfrac{1}{4}\sum_{l_\alpha} a_{k+q,l}^\dagger a_{k,l_\alpha}G(0;k,m;0;k,l_\alpha)+\tfrac{1}{4}\sum_{k_\alpha}\sum_{l_\alpha}\sum_{l_\beta} a_{k_\alpha}^\dagger,a_{k_\alpha-q,l_\beta}\{\delta(l)\delta(k+q)[G(k_\alpha,l_\alpha;k,m;(k_\alpha-k),l_\beta;0)$$
$$+G(k_\alpha,l_\alpha;k,m;0;(k_\alpha+k),l_\beta)]-\delta(m)\delta(k)[G(k_\alpha,l_\alpha;0;q,l;(k_\alpha-q),l_\beta)+G(0;k_\alpha,l_\alpha;q,l;(k_\alpha-q),l_\beta)]\}. \tag{24}$$

A feature of this equation is that it displays a coupling between excitations of different wave-vector indices. Also, the gradient terms appear in the "diagonal terms," that is to say between excitations of same wave-vector indices. This structure is exactly that which one gets when dealing with plasmons in an electron gas[9] and, as a matter of fact, our treatment of (24) is much like the standard theory of plasmons.

Most of the $a_{k+q}^\dagger a_k$ are coupled only to operators of same wave-vector indices. Only excitations of the type $a_q^\dagger a_0$ and $a_0^\dagger a_{-q}$ exhibit coupling with all others. So the eigenvalue problem is not changed by restricting consideration to these last two classes of operators and forgetting the others (RPA). We obtain:

$$[a_{q,l}^\dagger a_0,H]=\sum_{l_\alpha} a_{q,l_\alpha}^\dagger a_0\langle q,l_\alpha|\,-\mathbf{v}\cdot\nabla\,|q,l\rangle-\omega_l a_{q,l}^\dagger a_0-\tfrac{1}{2}\sum_{l_\alpha} a_{q,l_\alpha}^\dagger a_0 G(q,l_\alpha;0;q,l;0)$$
$$-\tfrac{1}{4}\sum_{l_\alpha} a_0^\dagger a_{-q,l_\alpha}G(0;0;q,l;-q,l_\alpha)[a_0^\dagger a_{-q,m},H]=\sum_{l_\alpha} a_0^\dagger a_{-q,l_\alpha}\langle q,m|\,\mathbf{v}\cdot\nabla\,|q,l_\alpha\rangle+\omega_m a_0^\dagger a_{-q,m}$$
$$+\tfrac{1}{2}\sum_{l_\alpha} a_0^\dagger a_{-q,l_\alpha}G(0;-q,m;0;-q,l_\alpha)+\tfrac{1}{4}\sum_{l_\alpha} a_{q,l_\alpha}^\dagger a_0 G(q,;-q,m;0;0). \tag{25}$$

In the long-wavelength limit, this system could be solved to any order of perturbation theory (provided the perturbation expansion converges—we shall come back to this particular point in the next section). Unfortunately the ω's and the ϕ's are now known, except for the first five of eigenvalue zero. The only thing which can be explicitly computed is the first-order result for the tenfold zero degeneracy (since there is a gap between 0 and the dense spectrum, a degenerate perturbation treatment is valid).

[9] D. Pines and P. Nozieres, *The Theory of Quantum Liquids* (W. A. Benjamin, Inc., New York, 1966).

If f_0, $v_x f_0$, $v_y f_0$, $v_z f_0$, $(v^2-\frac{3}{2})f_0$, are chosen respectively as ϕ_1, ϕ_2, ϕ_3, ϕ_4, ϕ_5, the matrix of the above system reads (after the matrix elements have been computed, and assuming $\mathbf{q}$ is parallel to the x axis):

$$\begin{bmatrix} 0 & A & 0 & 0 & 0 & 0 & -C & 0 & 0 & 0 \\ A & 0 & 0 & 0 & B & -C & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & B & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & C & 0 & 0 & 0 & 0 & A & 0 & 0 & 0 \\ C & 0 & 0 & 0 & 0 & A & 0 & 0 & 0 & C \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & B & 0 & 0 & 0 \end{bmatrix} \tag{26}$$

where

$$A = iq\left(1-\frac{4\pi N r_0^3}{3V}\right),$$

$$B = -iq\left(\frac{2}{3}\right)^{1/2}\left(1-\frac{4\pi N r_0^3}{3V}\right),$$

$$C = \tfrac{2}{3} iq \frac{\pi N r_0^3}{3V}.$$

The eigenmodes of the system are now some combinations of $a_q^\dagger a_0$ and $a_0^\dagger a_{-q}$. For the eigenvalues (eigenfrequencies) one finds:

$$0 \qquad \text{(sixfold)}$$

$$\pm i\left[\frac{5}{3}\left(1-\frac{4\pi N r_0^3}{3V}\right)\right]^{1/2} \qquad \text{(each twofold)}. \tag{27}$$

Reintroducing the dimension factor m/kT and denoting by V_b the volume of the particles (or covolume)

$$V_b = \tfrac{4}{3}\pi N r_0^3,$$

(28) is obtained for the dispersion relation of sound waves

$$\frac{\omega}{q} = \pm\left[\frac{5}{3}\frac{kT}{m}\left(1-\frac{V_b}{V}\right)\right]^{1/2}. \tag{28}$$

This is exactly what one would find by thermodynamic arguments, starting from an equation of state

$$P(V-V_b) = NkT$$

with a specific heat $c_v = \frac{3}{2}N_k$ and the classical formula for the velocity of sound $c = (\chi\rho)^{-1/2}$ (χ being the isentropic compressibility and ρ the density).

The usual solutions corresponding to zero eigenvalue are also obtained. They are the entropy fluctuations at constant pressure. As for the single-particle excitations, these collective excitations will be damped when calculations are made to one higher power of q.

VI. CONCLUSION

Let us briefly summarize what has been done. We have started from an N-particle equation of motion (9) and (10) which differs slightly from the Liouville equation for short-range potentials, but is equivalent to it for hard spheres. Taking matrix elements, we have replaced the exact interaction operator by a pseudopotential; the collision operator was then expanded in powers of spatial gradients times the particle size.

An approximate solution for the motion of "particles" and for some collective modes (sound waves) was found by applying well-known quantum methods (Hartree-Fock procedure). In particular, the classical thermodynamical results on sound waves were obtained, including the effect of the excluded volume. Already at this stage, this is an improvement with respect to former approaches insofar as a more precise result is here obtained in the long-wavelength limit, and as collective modes were included in the first approximation to many-body equations.

Some questions arise as to what the second approximation would be and about the convergence of the perturbation treatment. The first point is fairly clear. By going to second order of perturbation theory in the solution of (25), one would obtain the attenuation of sound and, assuming all summations over velocity indices converge, separate a term proportional to q, and another proportional to q^2. By identification with the hydrodynamics equations, the viscosity, and the thermal conductivity of the fluid can be defined. All the computations would be straightforward, except that the dense spectrum of K_B and the corresponding eigenfunctions are not known. Moreover, merely by looking at the structure of the matrix elements involved, one could tell which kind of interaction is responsible for which transport property. The second term in the Taylor expansion of $\psi(\mathbf{r}+2r_0\mathbf{u})$ could be taken into account but this would have given a contribution quadratic in wave vector and in density. This represents a small dispersion to the velocity of sound of little interest here. The Hartree-Fock solutions to (18) involve no fundamental problems.

The more fuudamental problem is the convergence of higher order than Hartree solutions to the many-body theory of Eq. (18). In fact, the first many-body perturbation correction to the eigenfrequencies of the Hartree solution diverges. This divergence arises from the lack of convergence of the perturbation sum for large wave vectors of "intermediate states." This divergence is completely expected. Our approximation consists in replacing spheres by geometrical points and adding corrections due to their size. The procedure is an excellent description of the effects on smooth functions (long-wavelength disturbances) but the method is drastically wrong in describing effects on the scale of the particle size. This problem is exactly the same as that which appears when, in quantum mechanics, a

hard-core scattering problem is replaced by a δ-function potential and Born approximation is used. First Born approximation is "correct;" second Born approximation diverges. [For considering multiple scattering due to several scattering centers, a cutoff higher-order Born approximation can still be useful; it is the (short-range) iteration on a single scattering center which causes difficulties].

If this divergence is for the moment removed by a physical cutoff at some k_c, there is no divergence in the first-order many-body correction to viscosity and thermal conductivity. There are no problems arising from the long-range correlations. A contribution to the damping of sound waves by sound waves can (and should) be seen as part of the perturbation-series structure.

The next step in this problem should be to investigate the effect of "three-body collisions," i.e., to treat the many-body equations in terms of an approximation better than the cutoff pseudopotential approximation. This is the point at which the virtue of the single-particle solutions to the Hartree equations will manifest itself. If three-body collisions of these Hartree "particles" are treated rather than three-body collisions of physical particles, all the correct long-range behavior will be built into the problem, and the nonphysical divergences of three real particles in an infinite box should not occur. The solution to this three Hartree-Fock particle scattering problem will not be trivial.

Note added in proof. Our approximate solution to Eq. (9) could have been presented in another fashion, which perhaps would have seemed more rigorous at first sight, but which is in fact entirely equivalent.

In the framework of a linearized theory, f_N stands for the difference between the actual and the equilibrium distribution functions, and has to be normalized (for obvious physical reasons) by $\int f_N = 0$. So it would be natural to take a basis $\{f_{k,l}\}$ of eigenfunctions such that $\int f_{k,l} = 0$. As a matter of fact, the functions defined by (13) satisfy this condition (but for the trivial maxwellian f_0). The average of A is then $\int A f_N = \langle A \rangle$. It is possible to define a whole algebra and second quantization operators consistent with the above normalization and averages.

But there is no objection to normalizing the same functions $f_{k,l}$ by a Hermitian scalar product (even if there is no physical reason for doing so). The standard second quantization algebra which has been used in this paper is precisely that one which is consistent with the Hermitian normalization. Provided $\langle f_N | A | f_N \rangle$ is equal to $\langle A \rangle$, both algebras are equivalent and both yield Eq. (25). The only difference lies in the choice of the basis of our functional vector space.

The only thing to be checked is whether $\langle A \rangle$ equals $\langle f_N | A | f_N \rangle$ or not. If f_N is the equilibrium distribution function (may we recall that we used only averages in the ground state), it is true.

If one intends to use average values in other states than the equilibrium state, $\langle A \rangle \neq \langle f_N | A | f_N \rangle$ and only one algebra yields exact results. But since we did not have to do so, we preferred the more usual boson second quantization algebra and the standard notations of the Hartree-Fock theory.