[17]P. Schofield, Proc. Phys. Soc. Lond. **88**, 149 (1966).

[18]J. Mc Donald and K. Singer (private communication).

[19]B. J. Alder and T. E. Wainwright, Phys. Rev. Lett. **18**, 988 (1967).

[20]M. Ross and P. Schofield, J. Phys. C **4**, L305 (1971).

[21]M. Wertheim, Phys. Rev. Lett. **10**, 321 (1963); E. J. Thiele , J. Chem. Phys. **38**, 1959 (1963).

[22]N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).

[23]A. Rahman, Phys. Rev. A **136**, 405 (1965).

[24]J. P. Boon, J. C. Legros, and G. Thomas, Physica (Utr.) **33**, 547 (1967).

[25]A. de Bock, W. Grevendonk, and W. Herreman, Physica (Utr.) **37**, 227 (1967).

[26]J. M. Luttinger, Phys. Rev. A **135**, 1505 (1964).

[27]P. G. de Gennes, Physica (Utr.) **25**, 825 (1959).

Kinetic Theory of a Dense Gas: Triple-Collision Memory Function[*]

C. D. Boley and Rashmi C. Desai

Department of Physics, University of Toronto, Toronto M5S 1A7, Ontario, Canada

(Received 3 November 1972; revised manuscript received 15 January 1973)

We study the phase-space density-correlation function $S(\vec{r}\,t;\vec{p}\,\vec{p}\,')$ for a dense classical gas with repulsive interaction using the language of memory functions. We derive the kinetic equation for S which is valid at all wavelengths and frequencies but limited to second order in the density (triple collisions). This model equation is, on the one hand, an extension of the earlier work of Mazenko to the next order in density and, on the other hand, an extension to arbitrary wavelengths and frequencies of some suggested generalizations of the linearized Boltzmann equation. The memory function for this kinetic equation is shown to be compatible with symmetry properties, sum rules, and the conservation laws. As an illustration of the hydrodynamics, we calculate the shear viscosity and show that the term linear in density agrees with an earlier calculation by Kawasaki and Oppenheim. We also give the analogous kinetic equation for the single-particle correlation function.

I. INTRODUCTION

A growing amount of attention has been focused on the time-dependent fluctuations of a classical many-body system. The principal object of interest is the correlation function

$$S(\vec{r} - \vec{r}\,', t - t\,'; \vec{p}\,\vec{p}\,')$$
$$= \langle (f(\vec{r}\,\vec{p}\,t) - \langle f(\vec{r}\,\vec{p}\,t) \rangle)(f(\vec{r}\,\vec{p}\,t) - \langle f(\vec{r}\,'\,\vec{p}\,'t\,') \rangle) \rangle ,$$

(1)

where $f(\vec{r}\,\vec{p}\,t)$ is the local density in phase space,

$$f(\vec{r}\,\vec{p}\,t) = \sum_{\alpha} \delta(\vec{r} - \vec{r}_{\alpha}(t)) \delta(\vec{p} - \vec{p}_{\alpha}(t)) ,$$

(2)

and the sum runs over the particles in the system, with the phase coordinates $(\vec{r}_{\alpha}, \vec{p}_{\alpha})$. The brackets denote a thermal-equilibrium average. Among the interesting quantities which can be determined from S are the neutron- and light-scattering spectra[1,2] and the transport properties. One of the most practical ways of calculating S consists in constructing and solving the appropriate kinetic equation. This equation contains S and the memory function Σ, which accounts for the effects of interparticle collisions. Approximations for S are phrased in terms of approximations to Σ, since the kinetic equation enables one to take into account the secular effects in S due to streaming in phase space. Among the useful approximations to Σ which have appeared recently are a weak-coupling expansion by Akcasu and Duderstadt[3] and Forster and

Martin,[4] an expansion to first order in the density n by Mazenko,[5-7] and also a renormalized theory for self-correlations by Mazenko.[8] One of the present authors has pointed out a simple derivation of the low-density memory function.[9]

The calculation of Refs. 3 – 6 and 9 are either implicitly or explicitly restricted to dilute systems, the weak-coupling memory function being a special case of the low-density memory function. A power-series expansion of Σ to each order in the density is not permissible for all wavelengths and frequencies, since divergent terms would arise from certain events involving four or more particles (in three dimensions).[10] The divergence would begin in the third-order term of Σ. This situation has led to the development of renormalized theories, in which clusters of particles are not isolated but are allowed to interact in an approximate way with the rest of the system. The associated memory functions contain contributions from all orders of the density expansion, and the transport coefficients are not analytic in the density. The early memory functions of this kind were appropriate to relatively dilute systems,[11,12] but that restriction has recently been removed.[8]

Although renormalized theories have the greatest current importance in the theory of dense gases, it is also of some interest to understand the remaining well-behaved terms in the density expansion of Σ. This paper is concerned with that term, which

depends on the dynamics of three particles and is the extension of the original Mazenko memory function to next order in density. In calculating it, we obtain the second term of a generalized linear Boltzmann equation, which is valid for all wave numbers and frequencies. No assumption of molecular chaos or of functional dependence is invoked. It is recalled that the Mazenko memory function constitutes an extension of the linearized Boltzmann collision kernel to arbitrary wave vectors and frequencies, thereby taking into account the spatial extent and nonzero duration of a binary collision. Some of the consequences are that the implied equation of state includes the second virial coefficient and that the transport coefficients include correlational corrections to the Chapman–Enskog results (these corrections start at first order in the density). Recently, some very interesting numerical results for the density-fluctuation spectrum of a hard-sphere gas have been obtained from this equation.[13] For this potential, the collision kernel is independent of frequency. However, because of the spatial extent of the particles, the spectrum can no longer be characterized only by the ratio of wavelength to mean free path.

Similarly, the present work serves as a wave-number–frequency generalization of the linearized kinetic equation at next order in density. The resulting equation is still consistent with the conservation laws and the known symmetry conditions. Proposed equations of this order have been worked out from the Bogoliubov prescription[14] by Choh and Uhlenbeck[15] and, from another starting point, by Green[16] and Cohen.[17] In the formulations of Refs. 14–17, which make use of the functional ansatz or similar hypothesis, the collision kernels are independent of frequency. This arises, of course, because time scales comparable to the duration of a collision are smoothed out. The kernels depend on wave number, although this dependence is not explicit in the original formulations since it occurs in the products of long-time streaming operators. We have investigated the kernel which follows from the Green–Cohen formulation and have found agreement with the second-order memory function only at $\vec{k} = 0$ and $z = i0^+$ (z is the Laplace-transform variable). We have not been able to carry through a similar analysis of the Choh–Uhlenbeck kernel, although the two kernels are generally thought to be equivalent. Since the calculations with these kernels are quite specialized, they are deferred to another paper.[18]

As $\vec{k} \rightarrow 0$ and $z \rightarrow i0^+$ the second-order memory function becomes equivalent to an operator introduced by Kawasaki and Oppenheim in their calculation of the first density correction to the shear viscosity.[19] We use this fact to verify that the model kinetic equation has the expected hydrodynamic

behavior, in that it leads to the known first-order shear viscosity.

As with Refs. 14–19, our results are restricted to force laws for which there are no bound states in two- and three-particle systems. (By "bound state" we mean a configuration at $t = 0$ such that at least two of the particles are still interacting at $t \rightarrow \infty$.) Therefore we deal with short-range monotonically repulsive forces. On account of the reasoning given after Eq. (20), we believe that the Mazenko memory function[5] is also restricted to this type of force law. Another way to verify this is to note that Mazenko's generalization of the Boltzmann equation predicts a bulk viscosity proportional to n^2, whereas it has been shown[20] that two-body bound states give a contribution proportional to n to the bulk viscosity.

We can get a rough idea of the range of densities for which the second-order kinetic equation is appropriate by referring to the density expansion of the pressure. A possible criterion is that the contribution of the third virial coefficient (the first to include three-body correlations) outweighs the contribution of the fourth by a factor of 100 or so. Referring for simplicity to a gas of hard spheres of diameter r_0, we obtain[21] $nr_0^3 \lesssim 0.010$. (If the ratio of the second and third virial coefficients is used to estimate the range of applicability of the first-order kinetic equation, the upper bound is $nr_0^3 \lesssim 0.0076$.) Both of these numbers will vary somewhat if other static quantities are used. Such estimates based on static properties like pressure are probably very conservative. If, on the other hand, we use a criterion involving a transport property, the result is different. Experimental measurements on the thermal conductivity of neon have been found[22] to fit a linear density dependence very well up to about 120 amagat, which gives a somewhat larger upper bound of $nr_0^3 \lesssim 0.065$ (r_0 is the Lennard-Jones parameter).

In Sec. II we calculate Σ through order n^2 and show that it fulfills the desired symmetry and sum-rule conditions. We also note the analogous memory function for self-correlations. In Sec. III we briefly indicate that the kinetic equation containing the approximate Σ is consistent with the conservation of number, momentum, and energy. Finally, in Sec. IV we consider the long-wavelength low-frequency behavior of this equation and show that it leads to the expected first density correction to the shear viscosity.

II. SECOND-ORDER EXPANSION

We first recall the basic kinetic equation for S, which has the form

$$(z - \vec{k} \cdot \vec{p}) S(\vec{k}z; \vec{p}\vec{p}') + \tilde{S}(\vec{k}; \vec{p}\vec{p}')$$

$$= \int d^3\vec{p} \, \Sigma(\vec{k}z; \vec{p}\vec{\bar{p}}) S(\vec{k}z; \vec{\bar{p}}\vec{p}'), \quad (3)$$

where the transforms are defined by

$$f(\vec{k}t) = \int d^3r \, e^{-i\vec{k}\cdot\vec{r}} f(\vec{r}t),$$

$$f(\vec{k}z) = i \int_0^\infty dt \, e^{izt} f(\vec{k}t) \qquad (\text{Im } z > 0), \qquad (4)$$

and for simplicity the particle mass is set to unity. The initial condition is

$$S(\vec{k};\vec{p}\vec{p}') = n\delta(\vec{p}-\vec{p}')\phi(\vec{p}) + n^2 h(\vec{k})\phi(\vec{p})\phi(\vec{p}'), \quad (5)$$

where $\phi(\vec{p})$ is the Maxwellian distribution,

$$\phi(\vec{p}) = (\beta/2\pi)^{3/2} e^{-\beta p^2/2}, \qquad (6)$$

and $h(\vec{r}) + 1 = g(\vec{r})$ is the radial distribution function. A large-z analysis of Eq. (3) shows that Σ consists of a static part which is independent of z, and a collisional part which vanishes as z^{-1} for large z:

$$\Sigma(\vec{k}z;\vec{p}\vec{p}') = \Sigma^{(s)}(\vec{k}\vec{p}) + \Sigma^{(c)}(\vec{k}z;\vec{p}\vec{p}'). \quad (7)$$

The static part is given by

$$\Sigma^{(s)}(\vec{k}\vec{p}) = -nc(\vec{k})\vec{k}\cdot\vec{p}\,\phi(\vec{p}), \qquad (8)$$

where $c(\vec{k}) = h(\vec{k})[1 + nh(\vec{k})]^{-1}$ is the direct correlation function.

A density expansion of the static part of Σ requires no attention since the expansion of $c(\vec{k})$ is well known. If the approximation scheme for $\Sigma^{(s)}$

were different from that used for $\Sigma^{(c)}$, ambiguities would arise in evaluation of the thermodynamic properties of the system, which can be calculated independently[4] from $\Sigma^{(s)}$ and $\Sigma^{(c)}$. The most practical way of obtaining the first two terms of the density expansion of $\Sigma^{(c)}$ is to expand each side of the kinetic equation and to collect terms of equal power in the density.[23] To do this we need the expansion of S through third order,

$$S = nS_1 + n^2 S_2 + n^3 S_3 + \cdots, \qquad (9)$$

which is unphysical except at short times and is used only for obtaining Σ. At this level it is not particularly obvious why the combinations of the S_i's which determine Σ_1 and Σ_2 should be well behaved. However, we know that if Σ does have a second-order expansion the coefficients must be given in terms of the S_i's.

The quantities S_i are most easily obtained in terms of the activity expansion, as was done in Ref. 9. Thus we use the grand-canonical prescription for averaging and eliminate the activity $y = e^{\beta\mu}(2\pi/\beta h^2)^{3/2}$ in terms of n by inverting the first few terms of the cluster expansion. Writing the activity expansion as $S = yS_1' + y^2 S_2' + y^3 S_3' + \cdots$, we obtain[24]

$$S_1'(\vec{r}t;\vec{p}\vec{p}') = \delta(\vec{r}-\vec{p}t)\delta(\vec{p}-\vec{p}')\phi(\vec{p}), \qquad (10a)$$

$$S_2'(\vec{r}t;\vec{p}\vec{p}') = \left(\frac{\beta}{2\pi}\right)^3 \int \frac{d1\,d2}{2!} \rho(x';\,12)[e^{-\beta H(12)+itL(12)} - e^{-\beta H_0(12)+itL_0(12)}]\rho(x;\,12), \qquad (10b)$$

$$S_3'(\vec{r}t,\vec{p}\vec{p}') = \left(\frac{\beta}{2\pi}\right)^{9/2} \int \frac{d1\,d2\,d3}{3!} \rho(x';\,123)[e^{-\beta H(123)+itL(123)} - e^{-\beta H(12)-\beta H(3)+itL(12)+itL(3)} - e^{-\beta H(23)-\beta H(1)+itL(23)+itL(1)}$$

$$- e^{-\beta H(13)-\beta H(2)+itL(13)+itL(2)} + 2e^{-\beta H_0(123)+itL_0(123)}]\rho(x;\,123), \qquad (10c)$$

where 1 stands for $(\vec{r}_1,\vec{p}_1)$, $H(1\ldots N)$ is the Hamiltonian of the N-particle system, and

$$\rho(x;\,1\ldots N) = \sum_{\alpha=1}^{N} \delta(\vec{r}-\vec{r}_\alpha)\delta(\vec{p}-\vec{p}_\alpha), \qquad (11)$$

with $x = (\vec{r},\vec{p})$ and $x' = (0,\vec{p}')$. Also, $L = L_0 + L_1$ is the Liouville operator, with

$$iL_0(1\ldots N) = \sum_{\alpha=1}^{N} \vec{p}_\alpha \cdot \vec{\nabla}_\alpha, \qquad (12a)$$

$$iL_1(1\ldots N) = -\sum_{\alpha<\beta}^{N} \vec{\nabla}v(\vec{r}_\alpha - \vec{r}_\beta)\cdot\left(\frac{\partial}{\partial\vec{p}_\alpha} - \frac{\partial}{\partial\vec{p}_\beta}\right). \qquad (12b)$$

In quantities like L_0 the interaction is turned off. The operators inside square brackets can be obtained in an obvious way from the Ursell functions. After expressing y in terms of n, we obtain the coefficients in the density expansion:

$$S_1 = S_1', \qquad (13a)$$

$$S_2 = S_2' - \beta_1 S_1', \qquad (13b)$$

$$S_3 = S_3' - 2\beta_1 S_2' + [\tfrac{1}{2}\beta_1^2 - \tfrac{1}{2}\int d^3r\, c_1(r)]S_1', \qquad (13c)$$

where β_1 is (minus) twice the second virial coefficient,

$$\beta_1 = \int d^3r\, f(r), \qquad (14)$$

with $f(r) = e^{-\beta v(r)} - 1$, and $c_1(r)$ is the first density correction to the direct correlation function,

$$c_1(\vec{r}) = f(\vec{r}) \int d^3r'\, f(\vec{r}-\vec{r}')f(\vec{r}'). \qquad (15)$$

Returning to the memory function, we take

$$\Sigma = n\Sigma_1 + n^2\Sigma_2 + \cdots, \qquad (16)$$

and by expansion of Eq. (3) express Σ_1 and Σ_2 in the terms of the S_i's:

$$\Sigma_1(\vec{k}z;\vec{p}\vec{p}')\phi(\vec{p}') = -(z - \vec{k}\cdot\vec{p}')$$

$$\times [(z - \vec{k}\cdot\vec{p})S_2(\vec{k}z;\vec{p}\vec{p}') + S_2(\vec{k};\vec{p}\vec{p}')], \qquad (17a)$$

$\Sigma_2(\vec{k}z;\vec{p}\vec{p}\,')\phi(\vec{p}\,')$

$= -(z-\vec{k}\cdot\vec{p}\,')[(z-\vec{k}\cdot\vec{p}\,)S_3(\vec{k}z;\vec{p}\vec{p}\,')+\tilde{S}_3(\vec{k};\vec{p}\vec{p}\,')$

$\qquad - \int d^3\vec{p}\,\Sigma_1(\vec{k}z;\vec{p}\vec{p})S_2(\vec{k}z;\vec{p}\vec{p}\,')]. \quad (17b)$

Equations (10), (13), and (17) completely determine the first two terms of the density expansion of Σ.

The first-order term is the Mazenko memory function,[5] the collisional part of which can be written in the form

$$\Sigma_1^{(c)}(\vec{k}z;\vec{p}\vec{p}\,')\phi(\vec{p}\,')=-\left(\frac{\beta}{2\pi}\right)^3\int \frac{d1\,d2}{V}\,e^{-\beta H(12)}$$

$$\Sigma_1^{(c)}(\vec{k}z;\vec{p}\vec{p}\,')\phi(\vec{p}\,')=\left(\frac{\beta}{2\pi}\right)^3\int \frac{d1\,d2}{V}\,e^{-\beta H(12)}[L_1(12)\rho_{kp'}^*(12)]\int_0^\infty dt\,e^{izt}\,\vec{\nabla}v[\,\vec{r}_1(t)-\vec{r}_2(t)]\cdot\frac{\partial}{\partial\vec{p}}\delta(\vec{p}-\vec{p}_1(t))e^{-i\vec{k}\cdot\vec{r}_1(t)}.$$

$$(20)$$

For this to exist in the limit $z\to i\epsilon$ (ϵ is the infinitesimal positive number), the factor following e^{izt} should vanish at $t\to\infty$. Thus the two particles, which were interacting at $t=0$ because of the operator $L_1(12)$, must be outside their mutual force range by then. This is guaranteed only if there are no bound states. All of the present discussion is therefore limited to the use of short-range monotonically repulsive potentials.[25]

The second-order term is more complicated than Σ_1 because a third particle enters into the dynamics. The details of the reduction of Σ_2 from Eqs. (17) to the form given below can be constructed in a straightforward manner and are omitted here. The collisional part can be written after some rearrangement as the sum of two terms, the first of which depends on the details of the three-body dynamics and the second of which is proportional to $\Sigma_1^{(c)}$, namely,

$$\Sigma_2^{(c)}=\Sigma_{2a}^{(c)}-2\beta_1\Sigma_1^{(c)}, \quad (21)$$

with

$$\Sigma_{2a}^{(c)}(\vec{k}z;\vec{p}\vec{p}\,')\phi(p')=\int \frac{d1\,d2\,d3}{2V}\,\phi(1)\phi(2)\phi(3)$$

$$\times \rho_{kp'}^*(123)M(\vec{k}z;\vec{p}\,';123)L_1(12)\rho_{kp}(12), \quad (22)$$

where M is the operator

$M(\vec{k}z;\vec{p}\,';123)=e^{-\beta v(123)}[\vec{k}\cdot\vec{p}\,'+L(123)]G_z(123)$

$-2e^{-\beta v(13)}[\vec{k}\cdot\vec{p}\,'+L(13)+L(2)]G_z(13)(z-\vec{k}\cdot\vec{p}_1)$

$\times e^{-\beta v(12)}G_z(12)-e^{-\beta v(12)}[\vec{k}\cdot\vec{p}\,'+L(12)]G_z(12), \quad (23)$

and $v(123)=v(12)+v(13)+v(23)$. Equations (21)–(23) are the primary result of this paper. In the second term of Eq. (21) the third particle serves only to modify the effective binary-collision frequency; this represents an enhancement rather than a

$$\times [L_1(12)\rho_{kp'}^*(12)]\,G_z(12)L_1(12)\rho_{kp}(1), \quad (18)$$

where

$$G_z(1\ldots N)=[z+L(1\ldots N)]^{-1}, \quad (19a)$$

$$\rho_{kp}(1\ldots N)=\sum_{\alpha=1}^N \delta(\vec{p}-\vec{p}_\alpha)e^{-i\vec{k}\cdot\vec{r}_\alpha}. \quad (19b)$$

The volume V is cancelled by integration over the position of the center of mass. We note here one aspect of the long-time behavior. If the particles are followed along their trajectories, via $\vec{r}_\alpha(t)=e^{itL(12)}\vec{r}_\alpha$, etc., then Eq. (18) becomes

shielding since $\beta_1<0$ for repulsive potentials. This effect is analogous to the phenomenological enhancement of the collision frequency in the Enskog theory of dense gases.[26]

It can now be verified that some general properties of the memory function hold in the case of $\Sigma_2^{(c)}$. By inserting the large-z expansion of S into the kinetic equation and matching powers of z, one can construct the large-z expansion of $\Sigma^{(c)}$, of which the term proportional to z^{-1} has been worked out.[4] It is automatic that $\Sigma_2^{(c)}$ will give these terms correctly to order n^2 (provided the potential is differentiable) and we have verified this for the coefficient of z^{-1}. The symmetry properties[4] of $\Sigma^{(c)}$ can also be directly verified in the case of $\Sigma_2^{(c)}$. It seems appropriate to comment on a few details connected with the symmetry under interchange of the momentum variables,

$$\Sigma^{(c)}(\vec{k}z;\vec{p}\vec{p}\,')\phi(\vec{p}\,')=\Sigma^{(c)}(\vec{k}z;\vec{p}\,'\vec{p})\phi(\vec{p}), \quad (24)$$

which follows for $\Sigma_2^{(c)}$ after an integration by parts. Another way to see that this holds in the density expansion is to recall that $\Sigma^{(c)}(\vec{k}z;\vec{p}\vec{p}\,')\phi(\vec{p}\,')$, considered as a matrix in $\vec{p}$, $\vec{p}\,'$, is essentially the inverse of the symmetric matrix $S(\vec{k}z;\vec{p}\vec{p}\,')$. Since each member of the density expansion of S maintains the symmetry under $\vec{p}\leftrightarrow\vec{p}\,'$, so will each approximation to the inverse. More explicitly, S^{-1} satisfies

$$\int d^3\vec{p}\,S(\vec{k}z;\vec{p}\vec{p})S^{-1}(\vec{k}z;\vec{p}\vec{p}\,')=\delta(\vec{p}-\vec{p}\,'), \quad (25)$$

and its large-z expansion follows readily from the large-z expansion of S. Inversion of the kinetic equation gives $\Sigma^{(c)}$ in terms of S^{-1} as

$$\Sigma^{(c)}(\vec{k}z;\,\vec{p}\vec{p}\,')\phi(\vec{p}\,')=n\phi(\vec{p})\phi(\vec{p}\,')\Big[S^{-1}(\vec{k}z;\vec{p}\vec{p}\,')$$

$$+\frac{(z-\vec{k}\cdot\vec{p})\delta(\vec{p}-\vec{p}\,')}{n\phi(\vec{p})}-zc(\vec{k})+c(\vec{k})\vec{k}\cdot(\vec{p}+\vec{p}\,')\Big]. \quad (26)$$

The last three terms in brackets serve to subtract off the terms in S^{-1} which go as z^0 or z^1 at large z. Aside from ensuring the symmetry of the density expansion of $\Sigma^{(c)}$, this relation has no further bearing on the present work.

To ensure that the solution of the approximate kinetic equation is symmetric under $\vec{p} \leftrightarrow \vec{p}\,'$, we must also specify the initial condition by using the consistent approximation to the radial distribution function. For the kinetic equation with the lth-order memory function, this approximation consists of first expressing $nh(\vec{k})$ in terms of $nc(\vec{k})$ and then expanding $nc(\vec{k})$ to order l. This choice is dictated by the fact that the direct correlation function is expanded in the static part of the memory function. [However, at moderately low gaseous densities there is not much difference if $nh(k)$ is truncated at order l in the initial condition.] The solution of the lth-order kinetic equation (denoted by $S^{(l)}$) is then the inverse of the truncation at order $l-1$ of the density expansion of S^{-1}, i.e.,

$$S^{(1)} = \left(\frac{1}{nS_1} - \frac{1}{S_1} S_2 \frac{1}{S_1} \right)^{-1}, \tag{27a}$$

$$S^{(2)} = \left[\frac{1}{nS_1} - \frac{1}{S_1} S_2 \frac{1}{S_1} + n\left(-\frac{1}{S_1} S_3 \frac{1}{S_1} + \frac{1}{S_1} S_2 \frac{1}{S_1} S_2 \frac{1}{S_1} \right) \right]^{-1}. \tag{27b}$$

These expressions, which are the solutions of the Mazenko equation and the equation of next order, illustrate concisely how the coefficients of the density expansion of S determine physically useful quantities. Of course the operation of matrix inversion amounts to solution of the kinetic equation.

In more traditional kinetic theory, the problem of the proper initial condition has been an unsettled one. Many proposed kinetic equations[14-17] are supposed to be valid only after some initial randomization time, and the degree to which the initial condition should contain the correlations is not clear. The correlation-function approach bypasses both this problem and the hypothesis of a succession of characteristic times,[14] by considering only a definite but representative class of irreversible phenomena.

The memory function describes a dynamically stable system if the imaginary part of $\Sigma^{(c)}$ satisfies[4]

$$\int d^3p \, d^3p' \, h^*(\vec{p})[\mathrm{Im}\,\Sigma^{(c)}(\vec{k}z; \vec{p}\vec{p}\,')] \phi(\vec{p}\,')h(\vec{p}\,') \leq 0 \tag{28}$$

when $\mathrm{Im}\,z > 0$ (h is an arbitrary function). This inequality guarantees, among other things, that the Van Hove scattering function is positive. Although it holds for the true $\Sigma^{(c)}$ and for the weakly coupled[4] and low-density[6] limits, we have not been able to prove it for the second-order approximation. The left-hand side is then the sum of two terms, of

which the first (containing the Mazenko memory function) is negative and the second can have either sign. Since the second term is smaller by a factor of nr_0^3 relative to the first (r_0 is the range of interparticle force), we can expect the sum to be negative at sufficiently low densities. Correspondingly, no general H theorem has yet been reported for the triple-collision operators in the kinetic theory of gases. This situation is reminiscent of a property encountered in the activity expansion of the pressure:

$$\beta p = \sum_{l=1}^{\infty} b_l y^l. \tag{29}$$

The first term and the sum are positive, but it has been shown[27] that the terms alternate in sign. However, for a given temperature and force law there is a range of activities for which Eq. (29) can be truncated at a particular l and remain positive.

We conclude this section by citing the corresponding memory function for the self-correlation function. The latter function, which we denote by $s(\vec{r}t; \vec{p}\vec{p}\,')$, describes the evolution of the distribution function for a test particle and contains the spectrum measured in incoherent-scattering experiments. It satisfies a kinetic equation of the form

$$(z - \vec{k} \cdot \vec{p})s(\vec{k}z; \vec{p}\vec{p}\,') + \tilde{s}(\vec{p}\vec{p}\,')$$

$$= \int d^3\bar{p} \, \sigma(\vec{k}z; \vec{p}\vec{\bar{p}})s(\vec{k}z; \vec{\bar{p}}\vec{p}\,') \tag{30}$$

with initial condition $\tilde{s}(\vec{p}\vec{p}\,') = n\delta(\vec{p} - \vec{p}\,')\phi(\vec{p})$. On account of the absence of radial correlations in the initial condition, the memory function[28] σ begins as z^{-1} for large z and has no static portion.

The method of expansion described earlier in this section applies equally well to self-correlations when one ignores dynamical correlations between different particles. Thus, for instance, the second term in the activity expansion of s has the form of Eq. (10b), except that the sums implied in $\rho(x'; 12)$ and $\rho(x; 12)$ run over a common index. One finds the first-order term[9,29] in the density expansion to be as in Eq. (18), with $\rho_{kp'}^*(12)$ replaced by $\rho_{kp'}^*(1)$. The second-order term requires more attention, and we eventually obtain

$$\sigma_2(\vec{k}z; \vec{p}\vec{p}\,')\phi(\vec{p}\,') = \int \frac{d1\,d2\,d3}{V} \phi(1)\phi(2)\phi(3)$$

$$\times \rho_{kp'}^*(1)m(\vec{k}z; \vec{p}\,'; 123) L_1(12)\rho_{kp}(1)$$

$$- 2\beta_1\sigma_1(\vec{k}z; \vec{p}\vec{p}\,')\phi(\vec{p}\,'), \tag{31}$$

where

$$m(\vec{k}z; \vec{p}\,'; 123) = e^{-\beta v(123)}[\vec{k} \cdot \vec{p}\,' + L(123)]G_z(123)$$

$$- e^{-\beta v(13)}[\vec{k} \cdot \vec{p}\,' + L(13)] G_z(13)(z - \vec{k} \cdot \vec{p}_1)$$

$$\times e^{-\beta v(12)} G_z(12) - e^{\beta v(12)}[\vec{k} \cdot \vec{p}\,' + L(12)]G_z(12). \tag{32}$$

The discussion of the properties of $\Sigma^{(c)}$ can be adapted without difficulty to σ, and we note in particular that $\sigma(\vec{k}z; \vec{p}\vec{p}')\phi(\vec{p}')$ and its various density approximations are symmetric in $\vec{p} \leftrightarrow \vec{p}'$. We do not discuss self-correlations further in this paper.

III. CONSERVATION LAWS

In this section we show why the second-order memory function is consistent with the conservation laws. A detailed discussion is unnecessary, since the procedure has been established and illustrated in the weakly coupled case[4] and also carried out in integral form at lowest order in the density.[6]

Conservation of number presents no problem, since one requires only that

$$\int d^3p\, \Sigma_2^{(c)}(\vec{k}z; \vec{p}\vec{p}') = 0 , \tag{33}$$

which is verified by a glance at $\Sigma_2^{(c)}$.

Verification of the conservation of momentum involves construction of the stress tensor of the system, which can be done if a factor of $\vec{k}$ can be extracted from the first moment of $\Sigma^{(c)}$ with respect to $\vec{p}$, with the balance well behaved as $k \to 0$. It suffices to do this for $\Sigma_{2a}^{(c)}$. Integrating Eq. (22) and focusing on the last two factors, we note that

$$L_1(12) \int d^3p\, p_i \rho_{kb}(12) = k_j\, \lambda_{ij}(\vec{k}; \vec{r}_1\vec{r}_2) \tag{34}$$

with

$$\lambda_{ij}(\vec{k}; \vec{r}_1\vec{r}_2) = -2e^{-i\vec{k}\cdot(\vec{r}_1+\vec{r}_2)/2}$$

$$\times \int d^3r\, \delta(\vec{r} - \vec{r}_1 + \vec{r}_2)\, \frac{r_i r_j}{r}\, \frac{dv(r)}{dr}\, \frac{\sin\frac{1}{2}\vec{k}\cdot\vec{r}}{\vec{k}\cdot\vec{r}} , \tag{35}$$

thus separating the desired factor. The rest of the term is finite as $k \to 0$ if the memory function itself is finite in that limit, essentially because the same collision operator appears in each expression. We assume that any singularities would show up in the additional limit of long times, or $z \to i\epsilon$ (Markovian limit). This limit is discussed in Appendix A, and one of the results is that $\Sigma_2^{(c)}$ remains finite. Therefore it can be concluded that the stress tensor is well defined.

This stress tensor is related to the density expansion of the true stress tensor $\tau_{ij}(\vec{r}t; \vec{p}')$ of the system (the latter quantity is as given in Ref. 4). When the second-order kinetic equation is used, the appropriate stress tensor $\tau_{ij}^{(2)}$ takes the form

$$\tau_{ij}^{(2)}(\vec{k}z; \vec{p}') = \int d^3p\, [p_i p_j + u_{ij}(\vec{k}z; \vec{p})]\, S^{(2)}(\vec{k}z; \vec{p}\vec{p}') , \tag{36}$$

where $S^{(2)}$ is the solution of the kinetic equation, and

$$u_{ij}(\vec{k}z; \vec{p}) = -\delta_{ij}\,\beta^{-1}[nf(\vec{k}) + n^2c_1(\vec{k})] + T_{ij}(\vec{k}z; \vec{p}) . \tag{37}$$

T_{ij} is obtained from the first moment of $n\Sigma_1^{(c)} + n^2\Sigma_2^{(c)}$, and the product $u_{ij}S^{(2)}$ accounts for the

two- and three-body correlations which occur in the potential part of the stress tensor. The point of interest in the present discussion is the relationship between u_{ij} and τ_{ij}, which is found to be

$$p_i' p_j' + u_{ij}(\vec{k}z; \vec{p}') = \int d^3p\, [\tau_{ij}(\vec{k}z; \vec{p})\, S^{-1}(\vec{k}z; \vec{p}\vec{p}')]_2 , \tag{38}$$

where $[\ldots]_2$ denotes the truncation of the density expansion at order n^2. Hence it is the expansion of $\tau_{ij}S^{-1}$ which enters explicitly into the present kinetic theory. Of course, Eq. (38) continues to hold formally at each higher order in the density, although the individual functions T_{ij} may then no longer exist as $k \to 0$, $z \to i\epsilon$.

Verification of the conservation of energy is less straightforward, since the correlation function $\epsilon(\vec{r}t; \vec{p}')$ for the energy density has both kinetic and potential contributions, and the latter part contains a three-body correlation function. This difficulty is overcome in the weakly coupled case by construction of a quantity which agrees with ϵ at least through order v^2, at all times, and which is conserved by the kinetic equation. The same method, with respect to n rather than v, also applies here, and we merely indicate the appropriate energy density and current. First, the exact ϵ and S are related as follows:

$$\epsilon(\vec{k}z; \vec{p}') = \int d^3p\, [\tfrac{1}{2}p^2 + E^{(s)}(\vec{k}\vec{p}) + E^{(c)}(\vec{k}z; \vec{p})]S(\vec{k}z; \vec{p}\vec{p}') , \tag{39}$$

and the separation of $E^{(s)}$ from $E^{(c)}$ follows from the large-z behavior of this equation ($E^{(c)} \sim z^{-1}$ at large z). These last two functions would be missing, of course, from a Boltzmann-like formulation which omits the potential contributions. When the memory function of order l is used, the appropriate conserved quantity is

$$\epsilon^{(l)}(\vec{k}z; \vec{p}') = \int d^3p\, \{\tfrac{1}{2}p^2 + [E^{(s)}(\vec{k}) + E^{(c)}(\vec{k}z; \vec{p})]_l\}$$

$$\times S^{(l)}(\vec{k}z; \vec{p}\vec{p}') \quad (l = 1, 2) , \tag{40}$$

which agrees with ϵ through order n^l but is not the same as a density truncation of ϵ. The second-order quantity $[E_s^{(s)} + E^{(c)}]_2$ can be calculated in straightforward fashion and will not be given here.

The equation of motion of $\epsilon^{(l)}$ follows directly from the kinetic equation and implies that $\epsilon^{(l)}$ is conserved if an explicit factor of $\vec{k}$ can be removed from the expansion to order l of $zE^{(c)}(\vec{k}z; \vec{p}')$ $+ \int d^3p\, \tfrac{1}{2}p^2\Sigma^{(c)}(\vec{k}z; \vec{p}\vec{p}')$ as $k \to 0$. We have verified that this is so for the functions in question again in the case $z \to i\epsilon$. The approximate current $\vec{j}^{(l)}$ is related to the true energy current of the system in the same way that the approximate and exact stress tensors are related. This means that $\vec{j}^{(l)}$ has the form

$$\vec{j}^{(1)}(\vec{k}z\,;\,\vec{p}') = \int d^3p\,[\,\vec{p}\tfrac{1}{2}p^2 + \vec{J}(\vec{k}z\,;\,\vec{p})\,]\,S^{(1)}(\vec{k}z\,;\,\vec{p}\vec{p}'),$$

$$(41)$$

where $\vec{J}(\vec{k}z\,;\,\vec{p}')$ is the density truncation of

$$\int d^3p\,\vec{j}^{\,\text{pot}}(\vec{k}z\,;\,\vec{p})\,S^{-1}(\vec{k}z\,;\,\vec{p}\vec{p}')\,,$$

with $\vec{j}^{\,\text{pot}}$ the potential part of the true energy current.

IV. TRANSPORT PROPERTIES: SHEAR VISCOSITY

In the limit of long wavelengths and low frequencies, the hydrodynamical contraction of the description is supposed to take place,[30] so that the kinetic equation becomes equivalent to the linearized Navier–Stokes equations. In this section we verify that the second-order kinetic equation has the expected hydrodynamic properties insofar as it leads to the known first-order shear viscosity (as first calculated by Kawasaki and Oppenheim[19]). Similar conclusions are expected in the case of the other hydrodynamic parameters. Only the essential reasoning is presented in this section, and computational details are relegated to the Appendixes.

It has been shown[4] that the transport coefficients can be expressed directly in terms of the memory function. In the case of the second-order kinetic equation, there are contributions at all orders in the density since the expressions involve, in part, essentially the inverse of the memory function. The terms of order n, which occur in the shear viscosity and thermal conductivity, are completely determined by Σ_1 and Σ_2. It is well known that at low order the shear viscosity takes the form η $= \eta_0 + n(\eta_{KK,1} + 2\eta_{KU,1}) + \cdots$, where η_0 is the Chapman–Enskog value, the kinetic term $\eta_{KK,1}$ is due to complete triple collisions and incomplete binary collisions, and $\eta_{KU,1}$ arises from the (instantaneous) transfer of momentum in a binary collision. In terms of the memory function, $\eta_{KK,1}$ is determined by the limit of $\Sigma_1^{(c)}$ and $\Sigma_2^{(c)}$ as $k \to 0$ and $z \to i\epsilon$, and $\eta_{KU,1}$ originates from terms of order k^0 and k^1 in $\Sigma_1^{(c)}$, again as $z \to i\epsilon$. The first of these limits will be denoted by

$$\lim_{\substack{k \to 0 \\ z \to i\epsilon}} \Sigma_l^{(c)}(\vec{k}z\,;\,\vec{p}\vec{p}') = iK_l(\vec{p}\vec{p}') \qquad (l = 1,\,2)\,. \qquad (42)$$

It has been shown[6] that nK_1 is the kernel of the linearized Boltzmann collision operator. In Appendix A we calculate K_2, which is real and has the same collisional invariants as K_1.

The shear viscosity will agree with the results of Ref. 19 if K_2 is equivalent to the appropriate collision operator used there and if the contributions from collisional transfer are equal (of course this second condition does not concern Σ_2). More specifically, application of the hydrodynamic analysis[4] to the second-order memory function shows

that the viscosity has the form $\eta = \eta' + \eta''$, where η' is determined by the solution of an integral equation with the same general properties as the one found in the Chapman–Enskog method, and η'' starts at order n^2 and is not needed here. Thus η' is given by

$$\eta' = \beta \int d^3p\,\phi(\vec{p})[\,p_x p_y + T_{xy}(\vec{p})\,]\,V(\vec{p})\,, \qquad (43)$$

where $T_{xy}(\vec{p})$ is the limit as $k \to 0$ and $z \to i\epsilon$ of the potential contribution to the stress tensor through second order [cf. Eq. (37)] and $V(\vec{p})$ satisfies

$$\int d^3p'\,[\,nK_1(\vec{p}\vec{p}') + n^2 K_2(\vec{p}\vec{p}')\,]\,\phi(\vec{p}')\,V(\vec{p}')$$

$$= -[\,p_x p_y + T_{xy}(\vec{p})\,]\,\phi(\vec{p})\,. \qquad (44)$$

We can identify $\eta_{KK,1}$ and $\eta_{KU,1}$ by expanding the solution and identifying the terms of first order. Doing this, we see that $\eta_{KK,1}$ is given in terms of an integral equation identical to the one found by Kawasaki and Oppenheim,[31] provided that K_2 serves as the kernel of one of their operators:

$$(t_+^r + t_{1+}\mathcal{L}_+)\phi(\vec{p})h(\vec{p}) = -\int d^3p'\,K_2(\vec{p}\vec{p}')\phi(\vec{p}')h(\vec{p}')$$

$$(45)$$

for arbitrary $h(p)$. We prove Eq. (45) in Appendix B and conclude that the kinetic part of the first-order viscosity is as expected.

Finally, the collisional-transfer term will be noted briefly. From the first-order expansion of Eqs. (43) and (44) it follows that $\eta_{KU,1}$ has the form

$$\eta_{KU,1} = \beta \int d^3p\,\phi(\vec{p})p_x p_y V_{KU}(\vec{p})\,, \qquad (46)$$

where V_{KU} satisfies

$$\int d^3p'\,K_1(\vec{p}_1\vec{p}')\phi(\vec{p}')V_{KU}(\vec{p}') = \int d^3p_2\,V^{-1}$$

$$\times \int d^3r_1 d^3r_2\,\phi(1)\phi(2)L_1(12)G_{i\epsilon}(12)\psi(12) \qquad (47)$$

and $\psi(12)$ is the potential part of the flux for shear viscosity:

$$\psi(12) = -\left(\frac{r_x r_y}{r}\,\frac{dv(r)}{dr}\right)_{\vec{r} = \vec{r}_1 - \vec{r}_2}\,. \qquad (48)$$

The right-hand side of Eq. (47) is (minus) the first-order contribution to $T_{xy}(\vec{p}_1)\phi(\vec{p}_1)$. By straightforward use of two-body dynamics, Eqs. (46) and (47) can be shown to be equivalent to the expressions found by Kawasaki and Oppenheim.

An extensive program of calculations has been carried out[32] for $\eta_{KK,1}$ in a gas of hard spheres. Because of the mathematical intractability of the three-body problem, this part of the shear viscosity is not well understood for more realistic potentials. In particular, it is known[33] that the attractive part of the potential and two-body bound states plays an important role in the temperature dependence of the first density correction $\eta_1(T)$. At intermediate reduced temperatures ($T^* \sim 10$, with $T^* = k_B T/\epsilon$ and ϵ the Lennard-Jones energy

parameter), repulsive potentials lead to a qualitatively incorrect temperature dependence. For understanding of such detailed transport behavior of real dense gases, the calculations of the memory function presented in this paper are only one step towards the ultimate goal. However, in a certain range of temperatures $(1 < T^* < 8)$, the transport coefficients[22] and the density-fluctuation spectrum[34] $S(\vec{k}\omega)$ are rather insensitive to the detailed nature of the intermolecular potential, and here the second-order memory function should be of use. Already, its comparison with the Bogoliubov-type kinetic equations yields[18] useful understanding of the limitations of the functional ansatz.[14]

APPENDIX A: LIMIT OF $\Sigma_2^{(c)}$ AS $k \to 0, z \to i\epsilon$

We reduce here the second-order memory function in the limit $k \to 0$ and $z \to i\epsilon$, in order to compare it with the work of Kawasaki and Oppenheim.[19] We first set $k = 0$ and find that $\Sigma_2^{(c)}$ becomes, after a little algebra,

$$\Sigma_2^{(c)}(0z; \vec{p}\vec{p}')\phi(\vec{p}') = - z \int \frac{d1\, d2\, d3}{2V} \phi(1)\phi(2)\phi(3) \rho_{p'}(123)$$

$$\times [e^{-\beta v(123)} G_z(123) - 2z\, e^{-\beta v(13)} G_z(13)$$

$$\times e^{-\beta v(12)} G_z(12) + e^{-\beta v(12)} G_z(12)] L_1(12) \rho_p(12) , \quad (A1)$$

where ρ_p is an abbreviation for ρ_{0p}. For convenience in comparison with Ref. 19, we split this into two terms by writing the first $e^{-\beta v(12)}$ as $1 + f(12)$ and the second $e^{-\beta v(12)}$ as $[e^{-\beta v(12)} - 2f(12) \times e^{-\beta v(13)}] + 2f(12)e^{-\beta v(13)}$, with the result

$$\Sigma_2^{(c)}(0z; \vec{p}\vec{p}') = \Sigma_2'(z; \vec{p}\vec{p}') + \Sigma_2''(z; \vec{p}\vec{p}') , \quad (A2)$$

where

$$\Sigma_2'(z; \vec{p}\vec{p}')\phi(\vec{p}') = - z \int \frac{d1\, d2\, d3}{2V} \phi(1)\, \phi(2)\, \phi(3)\, \rho_{p'}(123)$$

$$\times \{e^{-\beta v(123)} G_z(123) - 2z\, e^{-\beta v(13)}$$

$$\times G_z(13) G_z(12) + [e^{-\beta v(12)} - 2f(12)e^{-\beta v(13)}]$$

$$\times G_z(12)\} L_1(12)\rho_p(12) , \quad (A3)$$

$$\Sigma_2''(z; \vec{p}\vec{p}')\phi(\vec{p}') = z \int \frac{d1\, d2\, d3}{V} \phi(1)\phi(2)\phi(3)\, e^{-\beta v(13)}$$

$$\times [G_z^-(13)L_1(13)\rho_{p'}(13)] f(12)$$

$$\times G_z(12) L_1(12)\rho_p(12) . \quad (A4)$$

Although neither $\Sigma_2'(z; \vec{p}\vec{p}')\,\phi(\vec{p}')$ nor $\Sigma_2''(z; \vec{p}\vec{p}')\phi(\vec{p}')$ is symmetric in $\vec{p} \to \vec{p}'$, the sum is of course symmetric.

We note that Σ_2'' can be written as

$$\Sigma_2''(z; \vec{p}\vec{p}')\,\phi(\vec{p}') = z \int \frac{d1\, d2\, d3}{V} \phi(2) f(12)[G_z^-(13)L(13)$$

$$\times \phi(1)\phi(3)\, e^{-\beta v(13)}\rho_{p'}(13)]\, G_z(12)$$

$$\times L_1(12)\rho_p(12) , \quad (A5)$$

where $G_z^-(12) = [z - L(12)]^{-1}$, and as $z \to i\epsilon$ a familiar argument shows that the factor $e^{-\beta v(13)}$ can be dropped. Specifically,[19] $zG_z^-(13)$ then goes into $e^{-i\tau L(13)}$ with large τ, and the streaming operator separates particles 1 and 3 beyond their mutual force range. Hence we have in this limit $\Sigma_2''(z; \vec{p}\vec{p}') \to iK_2''(\vec{p}\vec{p}')$, with

$$K_2''(\vec{p}\vec{p}')\phi(\vec{p}') = \epsilon \int \frac{d1\, d2\, d3}{V} \phi(2) f(12)[G_{i\epsilon}^-(13)L_1(13)$$

$$\times \phi(1)\phi(3)\rho_{p'}(13)]\, G_{i\epsilon}(12) L_1(12)\rho_p(12) . \quad (A6)$$

This can be seen to be finite by the same reasoning which follows Eq. (20). As we show in Appendix B, $- K_2''(\vec{p}\vec{p}')$ is the kernel of an operator $t_{1+}\mathcal{L}_+$ introduced by Kawasaki and Oppenheim. Similar reasoning involving the streaming operators at large times show that in Σ_2' we can replace the factors of $e^{-\beta v(123)}$, $e^{-\beta v(13)}$ [preceding $G_z(13)$], and $e^{-\beta v(12)}$ with unity as $z \to i\epsilon$, with the result that $\Sigma_2'(z; \vec{p}\vec{p}') \to iK_2'(\vec{p}\vec{p}')$, with

$$K_2'(\vec{p}\vec{p}')\,\phi(\vec{p}') = - \epsilon \int \frac{d1\, d2\, d3}{V} \phi(1)\phi(2)\phi(3)\rho_{p'}(123)$$

$$\times [G_{i\epsilon}(123) - 2i\epsilon\, G_{i\epsilon}(13)G_{i\epsilon}(12)$$

$$+ G_{i\epsilon}(12)] L_1(12)\rho_p(12) . \quad (A7)$$

It is noted in Appendix B that $- K_2'$ is the kernel of Kawasaki and Oppenheim's operator t_+^r, which they show to be nonsingular.

Therefore we have

$$\lim_{\substack{k \to 0 \\ z \to i\epsilon}} \Sigma_2^{(c)}(\vec{k}z; \vec{p}\vec{p}') = iK_2(\vec{p}\vec{p}') , \quad (A8)$$

with $K_2 = K_2' + K_2''$ as given above. K_2 has collisional invariants corresponding to particle number, momentum, and kinetic energy. We forego the proof of this expected result, which is easy to believe since K_1 and also the full K have the same collisional invariants.

APPENDIX B: RELATION TO KAWASAKI-OPPENHEIM OPERATORS

In this appendix we give the details which were deferred in Sec. IV, dealing with the comparison of our work with that of Kawasaki and Oppenheim.[19] In particular, we demonstrate Eq. (45), which involves evaluation of the kernels of their operators $\mathcal{L}_+$, t_{1+}, and t_+^r. The first of these requires no effort since it is (minus) the linearized Boltzmann collision operator. We define for arbitrary $h(\vec{p})$

$$\mathcal{L}_+\phi(\vec{p})h(\vec{p}) = \int d^3p'\, K^{(\mathcal{L})}(\vec{p}\vec{p}')\phi(\vec{p}')h(\vec{p}') \quad (B1)$$

and the kernel $K^{(\mathcal{L})}$ is related to the limit of the

Mazenko memory function as $k \to 0$ and $z \to i\epsilon$ by $K^{(\mathcal{L})} = -K_1$, with[6]

$$K_1(\vec{p}\vec{p}')\phi(\vec{p}') = -i \int \frac{d1\,d2}{V} \phi(1)\,\phi(2)\,\rho_{p'}(12)$$

$$\times L_1(12)G_{i\epsilon}(12)L_1(12)\rho_p(1) \; . \quad (B2)$$

The operator t_{1_+} is given by

$$t_{1_+}(\vec{p}_1)\phi(\vec{p}_1)h(\vec{p}_1) = -\int d^3p_2\,V^{-1}\int d^3r_1\,d^3r_2\,L_1(12)G_{i\epsilon}^-(12)$$

$$\times f(12)\phi(1)\phi(2)[h(\vec{p}_1) + h(\vec{p}_2)] \; , \quad (B3)$$

and the kernel $K^{(t_1)}$, defined as in Eq. (B1), works out to be

$$K^{(t_1)}(\vec{p}\vec{p}')\phi(\vec{p}') = \int \frac{d1\,d2}{V} \phi(1)\phi(2)f(12)\rho_{p'}(1)$$

$$\times G_{i\epsilon}(12)L_1(12)\rho_p(12) \; . \quad (B4)$$

The combination needed in the discussion of the first density correction to the shear viscosity is $t_{1_+}\mathcal{L}_+$. In integral form, we have

$$t_{1_+}\mathcal{L}_+(\vec{p})\phi(\vec{p})h(\vec{p}) = \int d^3p'\,K^{(t_1\mathcal{L})}(\vec{p}\vec{p}')\phi(\vec{p}')h(\vec{p}') \; , \quad (B5)$$

and after some algebra involving Eqs. (B2) and (B4), the kernel becomes

$$K^{(t_1\mathcal{L})}(\vec{p}\vec{p}')\phi(\vec{p}') = -\epsilon \int \frac{d1\,d2\,d3}{V} \phi(2)f(12)$$

$$\times [G_{i\epsilon}^-(13)L_1(13)\phi(1)\phi(3)\rho_{p'}(13)]$$

$$\times G_{i\epsilon}(12)L_1(12)\rho_p(12) \; . \quad (B6)$$

Referring to Eq. (A6), we see that this is equivalent to one part of the second-order memory function, namely, $K^{(t_1\mathcal{L})}(\vec{p}\vec{p}') = -K_2''(\vec{p}\vec{p}')$.

Finally, we turn to the triple-collision operator defined by Eq. (6.6) of Ref. 19:

$$t_+^r(\vec{p}_1)\phi(\vec{p}_1)h(\vec{p}_1) = -\int d2\,d3\,L_1(12)\{G_{i\epsilon}^-(123)\,(\epsilon + iL_0)$$

$$- iG_{i\epsilon}^-(12)(\epsilon + iL_0)\,G_{i\epsilon}^-(13)\,(\epsilon + iL_0)$$

$$- iG_{i\epsilon}^-(12)\,(\epsilon + iL_0)G_{i\epsilon}^-(23)\,(\epsilon + iL_0) + G_{i\epsilon}^-(12)\,(\epsilon + iL_0)\}$$

$$\times \phi(1)\phi(2)\phi(3) \sum_{\alpha = 1}^{3} h(\vec{p}_\alpha) \; , \quad (B7)$$

where $L_0 = L_0(123)$. Since t_+^r is acting on a function of momentum only, all the explicit factors of L_0 can be shown to drop out. In the original form of this equation,[19] the G's contain free-streaming operators for all three particles; however, one can show that a free-streaming term in any G drops out unless an interaction term for that particle is also present, so that Eq. (B7) is correct. We define the kernel as in Eq. (B1) and find, after using translational invariance, permuting particles 1 and 2, and integrating by parts,

$$K^{(t^r)}(\vec{p}\vec{p}')\phi(\vec{p}') = \epsilon \int \frac{d1\,d2\,d3}{2V} \phi(1)\phi(2)\phi(3)\rho_{p'}(123)$$

$$\times [G_{i\epsilon}(123) - 2i\epsilon G_{i\epsilon}(13)G_{i\epsilon}(12)$$

$$+ G_{i\epsilon}(12)]L_1(12)\rho_p(12) \; . \quad (B8)$$

Reference to Eq. (A7) shows that this is related to the remaining part of K_2 by $K^{(t^r)}(\vec{p}\vec{p}') = -K_2'(\vec{p}\vec{p}')$. Combining this with the result stated at the end of the previous paragraph, we have

$$K^{(t^r)}(\vec{p}\vec{p}') + K^{(t_1\mathcal{L})}(\vec{p}\vec{p}') = -K_2(\vec{p}\vec{p}') \; , \quad (B9)$$

which demonstrates Eq. (45).

*Research supported by the National Research Council of Canada.

[1]L. Van Hove Phys. Rev. **95**, 240 (1954).

[2]P. C. Martin, in *Many-Body Physics*, edited by C. De Witt and R. Balian (Gordon and Breach, New York, 1968).

[3]A. Z. Akcasu and J. J. Duderstadt, Phys. Rev. **188**, 479 (1969).

[4]D. Forster and P. C. Martin, Phys. Rev. A **2**, 1575 (1970).

[5]G. F. Mazenko, Phys. Rev. A **3**, 2121 (1971).

[6]G. F. Mazenko, Phys. Rev. A **5**, 2545 (1972).

[7]A similar low-density memory function has been derived by L. Blum and J. L. Lebowitz [Phys. Rev. **185**, 273 (1969)] and the memory function for self-correlations is also given. In their analysis the static correlations are treated without approximation so that, in particular, the collisional part of the implied memory function contains the full radial distribution function instead of the factor $e^{-\beta v(|r_1 - r_2|)}$. As a result, this part of the memory function does not have the desired symmetry in the momentum indices, in the sense of our equation (24). It is an open question as to whether the inclusion of the full static correlations compensates in accuracy for the lack of symmetry.

[8]G. F. Mazenko, Phys. Rev. A **7**, 209 (1973); Phys. Rev. **7**, 222 (1973).

[9]C. D. Boley, Phys. Rev. A **5**, 986 (1972).

[10]J. R. Dorfman and E. G. D. Cohen, Phys. Lett. **16**, 124 (1965); K. Kawasaki and I. Oppenheim, Phys. Rev. **139**, A1763 (1965); J. V. Sengers, Phys. Rev. Lett. **15**, 515 (1965); and many other papers.

[11]Y. Pomeau, Phys. Rev. A **3**, 1174 (1971).

[12]J. R. Dorfman and E. G. D. Cohen, Phys. Rev. A **6**, 776 (1972).

[13]G. F. Mazenko, T. Y. C. Wei, and S. Yip, Phys. Rev. A **6**, 1981 (1972).

[14]N. N. Bogoliubov, in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (North-Holland, Amsterdam, 1962), Vol. I.

[15]S. T. Choh and G. E. Uhlenbeck, Navy Theoretical Physics, Contract No. Nonr 1224 (15) (1958) (unpublished).

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

[17]E. G. D. Cohen, Physica (Utr.) **28**, 1025 (1962); J. Math. Phys. **4**, 183 (1963).

[18]C. D. Boley and R. C. Desai, Phys. Rev. A (to be published).

[19]K. Kawasaki and I. Oppenheim, Phys. Rev. **136**, A1519 (1964).

[20]N. Hamer and I. Oppenheim, Phys. Rev. A **2**, 2153 (1970).

[21]The virial coefficients can be found in J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and*

Liquids (Wiley, New York, 1964).

[22]H. J. M. Hanley, R. D. McCarty, and J. V. Sengers, J. Chem. Phys. **50**, 857 (1969); also note the statement in this reference that the quadratic term does not contribute significantly till 200 amagat.

[23]This kind of approach was noted in passing in Ref. 4 (for the potential expansion) and used in Ref. 9.

[24]Similar formulas appear in R. Dashen and S.-K. Ma, Phys. Rev. A **4**, 700 (1971).

[25]The effects of bound states are discussed in detail by K. Kawasaki and I. Oppenheim [Phys. Rev. **139**, A649 (1965)].

[26]S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases,* 3rd ed. (Cambridge U. P., London, 1970).

[27]J. Groeneveld, Phys. Lett. **3**, 50 (1962).

[28]An expression for σ in terms of projection operators and the expansion to lowest order in the potential are given by A. Z. Akcasu, N. Corngold, and J. J. Duderstadt [Phys. Fluids **13**, 2213 (1970)].

[29]A. R. Altenberger and J. Stecki, J. Stat. Phys. **5**, 83

(1972).

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

[31]Reference 19, Eqs. (3.44) and (3.47).

[32]J. V. Sengers, Phys. Fluids **9**, 1333 (1966); J. V. Sengers, M. H. Ernst, and D. T. Gillespie, J. Chem. Phys. **56**, 5583 (1972).

[33]See S. K. Kim and J. Ross, J. Chem. Phys. **42**, 263 (1965), and the relevant references therein.

[34]The insensitivity of $S(k\omega)$ to the details of the repulsive potential at low densities was noted by A. Sugawara, S. Yip, and L. Sirovich [Phys. Fluids **11**, 925 (1968)]. Also, the comparison of these calculations (based on repulsive potentials) with experiments on gaseous xenon shows good agreement, indicating that the effect of the attractive part of the potential on $S(\vec{k}\omega)$ would not be great. For this comparison and a general review see S. Yip, J. Acoust. Soc. Am. **49**, 941 (1971).

Nuclear Magnetic Susceptibility of Solid He³ and of Dilute Solid Mixtures of He⁴ in He³ †

T. P. Bernat* and H. D. Cohen‡

Physics Department, Brandeis University, Waltham, Massachusetts 02154

(Received 11 December 1972)

Continuous-wave NMR was used to study the temperature dependence of the static nuclear magnetic susceptibility of solid He³ and solid mixtures of He⁴ in He³. Measurements were performed in the purest sample (3.7×10^{-5} He⁴ in He³) at four molar volumes (21, 22, 23, and 24 cm³/mole) in the bcc phase, and at several He⁴ concentrations ranging from 3.7×10^{-5} to 2.0×10^{-2} at 21 and 23 cm³/mole. The temperature range of the measurements was from 0.95 to 0.32 K. The data were fitted to a Curie–Weiss law with an rms deviation from best fit of less than 10^{-3} and best values of the Weiss constant θ were obtained. Susceptibilities and temperatures were measured to better than 0.1%. The temperature scale was based upon the susceptibility of the purest, most-dense sample. The desired accuracy in the susceptibility measurements necessitated a new method of data reduction. The accuracy in the extracted values of θ was better than ± 1 mk. The values of θ in the purest sample (-0.24 ± 0.82 mK at 21 cm³/mole, -1.03 ± 1.06 mK at 22 cm³/mole, -1.49 ± 0.27 mK at 23 cm³/mole, and -3.07 ± 0.78 mK at 24 cm³/mole) agreed within experimental uncertainty with those of earlier workers, operating at lower temperatures. They provide a high-temperature check on those measurements. The measured effects on θ of the He⁴ impurity are consistent with the work of Richards and Homer, but the measurements show an improved accuracy. The data, as a function of x, the atomic fraction of He⁴, have been fitted to the equation $\theta(x) = \theta_0(1 + Kx)$. Values of K of -430 ± 450 and -19 ± 10 were obtained at 21 and 23 cm³/mole, respectively.

I. INTRODUCTION

During the past decade there has been considerable theoretical[1-20] and experimental[21-48] interest in those properties of pure solid He³, as well as solid mixtures of He⁴ and He³, which depend upon the exchange interaction between He³ nuclei. Many of these properties have been described by means of a Heisenberg Hamiltonian

$$H_x^{3,3} = -2J \sum_{(nn)} \vec{S}_i \cdot \vec{S}_j \tag{1}$$

together with the usual dipole-dipole and Zeeman terms, where J is the exchange energy and the no-

tation (nn) indicates a sum over nearest-neighbor pairs only.[49] In the presence of He⁴ impurities, a second term[15,18] has been added to Eq. (1) in order to describe the exchange between a He³ and a He⁴ atom;

$$H_x^{3,4} = -2J'' \sum_{(nn),\sigma} D_{i\sigma}^+ D_{j\sigma}^- , \tag{2}$$

where we have used a notation similar to that of Balakrishnan and Lange.[18] It is possible that the presence of He⁴ in the He³ lattice also leads to modification of Eq. (1) by creating a local distortion around the He⁴ atom.[13] This distortion might produce an enhanced value of J.