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Fully Renormalized Kinetic Theory. II. Velocity Autocorrelation*

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In a previous paper a general formalism was developed for treating the time-dependent correlation functions that arise in the theory of self-diffusion. In this paper this formalism is used in conjunction with the approximation where the two-particle source is approximated by a sum of one-particle sources. This approximation follows from physical arguments and from an analysis of the exact equation for the two-particle source. The resulting expression for the memory function is similar to that found previously by Pomeau and is related to the ring terms studied by Kawasaki and Oppenheim. It is further shown that this correction to the Boltzmann–Enskog memory function can be written in terms of a product of phase-space correlation functions. This theory, to the extent that the hydrodynamical projection onto these correlation functions is dominant, provides a microscopic basis for the various mode-mode coupling theories. The associated long-time behavior of the velocity-autocorrelation function is shown to go as $t^{-3/2}$ and the coefficient agrees with that found by Dorfman and Cohen for low densities. For higher densities there are differences. It is further demonstrated how one can remove the wave-number cutoffs used in other theories, and the velocity-autocorrelation function is calculated, in a particular approximation, over the complete range of times with no adjustable parameters.

I. INTRODUCTION

In the preceeding paper[1] (I) a new approach to the theory of time-dependent correlation functions was described. This approach was specifically applied to the case of self-diffusion and some general expressions for the memory function $\phi_s(12)$ associated with the phase-space fluctuation $C_s(12)$ were derived. The notation here will be the same as in I. The expressions for the memory function derived in I are, of course, just a matter of rewriting the definition of $C_s(12)$ in what appears to be a more convenient form for making approximations. A crucial step in this rearrangement was a shifting of attention from the correlation function itself to the associated "external" one- and two-body sources ϕ_s and M. At the end of I it was shown that the simple approximation $M_c = 0$ leads, for moderate densities, to the Enskog result for the memory function, transport coefficients, and correlation functions. This paper will discuss how one can go beyond the Enskog result to find important new contributions to the memory function. This will necessarily entail a more sophisticated approximation for M_c.

The first half of this paper will be concerned with the determination of the first correction to the Enskog memory function. This analysis is com-

pleted in Sec. IV. While the resulting expression for the memory function suffices to determine $S_s(\vec{k}, \omega)$, the analysis here will be restricted to an investigation of the velocity-autocorrelation function (VAF), and the corrections to the Enskog result.

II. "DISCONNECTED" APPROXIMATION FOR M_c

In developing approximations one must deal with the general equation for ϕ_s. This expression has a rather simple structure as can best be seen from I (4.28). ϕ_s is determined by processes in the two-particle vector space $|1\bar{1}\rangle$, where the two-particles, labeled by the phase-space coordinates 1 and $\bar{1}$, first interact, and then propagate via C_Q to a new point in phase space, labeled by 2 and $\bar{2}$, where the two particles interact once more to terminate the disturbance. To obtain ϕ_s one simply integrates over the phase-space variables $\bar{1}$ and $\bar{2}$. In the analysis leading from I (4.28) to I (4.36) the bare L_I interactions were replaced with T matrices which describe complete scattering processes and can be treated for hard-core interactions. One can classify all of the contributions to ϕ_s in terms of the particles 1 and $\bar{1}$ and the processes they undergo as they propagate to the final state $1 \to 2$, $\bar{1} \to \bar{2}$. One notes from I (5.1) that the basic process in the Enskog approximation is that 1 and $\bar{1}$ collide and never come back together again. In looking at I (4.38) one sees that corrections to this process consist of recollision processes where 1 and $\bar{1}$ collide initially, and they propagate via some intermediate state until the particles recollide ending the process. These intermediate states consist of various complicated processes including static and dynamic shielding of intermediate scattering processes. From phase-space arguments one would expect that the most important intermediate process is where the initially colliding particles propagate independent of one another but interact with the medium. This interaction with the medium then leads to an eventual recollision. This will be the basic approximation made in this paper. It will be assumed that a major correction to the Enskog memory function is due to the process where the two initially colliding particles 1 and $\bar{1}$ are independent in the intermediate state. As will be indicated, this assumption can be given a solid mathematical basis and the corrections can be investigated systematically. Thus, using the formalism developed in I, one can make physical approximations in a controlled manner.

The basic physical assumption discussed above leads to two basic approximations in dealing with I (4.38). First one must consider the associated approximation for M_c, and then one must, in conjunction with this approximation for M_c, approximate $C_Q(z)$ in I (4.38).

Physically one knows that M_c represents the effect of the medium on the particles 1 and $\bar{1}$. These effects are of two primary types. One effect is a dynamical shielding that changes the two-particle scattering process. The other effect is to modify the single particle motion of the particles after their collision. One expects that this renormalization of the single-particle motion will be more important for moderately dense systems. Consequently one expects an important contribution to M_c will be a part that acts as a sum of one-body sources acting on 1 and $\bar{1}$ in the region where 1 and $\bar{1}$ are uncorrelated. Thus intuitively one could guess that the approximation

$$M_c(1\bar{1};\, 2\bar{2}) = \varphi_s^E(12)\delta(\bar{1}\,\bar{2}) + \varphi_E^{(c)}(\bar{1}\,\bar{2})\delta(12) \qquad (2.1)$$

represents the effects of the medium on the two uncorrelated particles 1 and $\bar{1}$. One should note that $\phi_E^{(c)}(12)$ is the Enskog approximation for the collisional part of the memory function associated with the density fluctuations in the system. This quantity has been studied by the author and others.[2,3]

While the approximation for M_c given by (2.1) makes good sense, one would like to show that it follows via a series of approximations from the general expression I (3.20) for M_c. This analysis has been carried out and while it is straightforward, it requires the development of more theoretical machinery. Since the result involves no intricate arguments or "leaps of faith" the method for obtaining this result will be described qualitatively. One follows a path quite similar to that used for the Enskog result. One assumes that the dynamics in I (3.20) can be evaluated using the scattering of the fewest number of particles. In this case this means that M_c depends on a minimum of three-particle scattering processes. The important idea is that these scattering processes involve connected and disconnected processes. Using Faddeev techniques[4] one can sort out the connected from the disconnected processes. Given the assumption that the particles 1 and $\bar{1}$ are uncorrelated or "disconnected" one can neglect the connected processes in this approximation. It is worth noting that this means neglecting processes where, for example, particle 1 collides with particle $\bar{1}'$ and then $\bar{1}'$ collides with particle $\bar{1}$. This process will lead to a dynamical correlation between particles 1 and $\bar{1}$ and will, therefore, be neglected in this analysis. It does seem plausible, however, that these terms could be important in dense systems and their importance should be investigated. One is now left with scattering processes where, for example, particles 1 and $\bar{1}'$ collide successively and $\bar{1}$ is a spectator. These events then lead, after some considerations of the static correlations between the three particles, to (2.1).

III. TREATMENT OF INTERMEDIATE PROPAGATOR

Given the approximation (2.1) for M_c one must still make some approximations for C_Q to be consistent with the assumed uncorrelated motion between collision processes. It is convenient to rewrite the expression for $\delta\phi_s$ [I (4.38)] by using the formal expression

$$C_Q(z) = (z - L_0 - Q\mathfrak{L}_I - M_c)^{-1}\tilde{C} ,$$

and Eqs. I (4.17) and I (4.18) in commuting $\tilde{C}$ with M_c and $[z + (Q\mathfrak{L})^T]^{-1}$ to obtain

$$\delta\varphi_s(12)f_0(2) = \int d\bar{1}\,d\bar{2}\,\langle 1\bar{1}|\,T(z)G_0(z)M_c(z) \times[1 + (z - L_0 - Q\mathfrak{L}_I - M_0)^{-1}M_c] \times G_0^T(-z)\tilde{T}^T(-z)|\,2\bar{2}\rangle , \quad (3.1)$$

where

$$\tilde{T}^T(-z) = (z + L_0^T)[z + (Q\mathfrak{L})^T]^{-1}\tilde{C}L_I^T . \quad (3.2)$$

This equation is still exact. One now expects that the $Q\mathfrak{L}_I$ that occurs in $(z - L_0 - Q\mathfrak{L}_I - M_c)^{-1}$ should be negligible in the region where the "colliding" particles are well separated. In the following analysis $Q\mathfrak{L}_I$ will be neglected in this intermediate propagator. It is straightforward to show that the correction to this approximation consists of a process where the particles 1 and $\bar{1}$ collide three times. One expects that the phase space available for such recollision processes will be small.

After neglecting $Q\mathfrak{L}_I$ in the intermediate propagator in (3.1) one has, on using the operator identity I (3.5) twice, that

$$\delta\varphi_s(12)f_0(2) = \int d\bar{1}\,d\bar{2}\,\langle 1\bar{1}|\,T(z) \times\{(z - L_0)^{-1} - [z - L_0 - M_c(z)]^{-1}\}\,\tilde{T}^T(-z)|\,2\bar{2}\rangle . \quad (3.3)$$

One can now write out the expression for $\delta\phi_s$ in a form that is more convenient for calculations. To do this one can introduce δ functions and change indices so that

$$\delta\varphi_s(12)f_0(2) = \int d\bar{1}\,d\bar{2}\,d5\,d\bar{5}\,\delta(1\bar{2})\langle\bar{2}\,\bar{1}|\,T(z)|\,3\bar{3}\rangle \times\langle 3\bar{3}|\{(z - L_0)^{-1} - [z - L_0 - M_c(z)]^{-1}\}|\,4\bar{4}\rangle \times\langle 4\bar{4}|\,\tilde{T}^T(-z)|\,5\bar{5}\rangle\,\delta(52) . \quad (3.4)$$

In the rest of the analysis the following approximations will be used:

$$\langle\bar{2}\,\bar{1}|\,T(z)|\,3\bar{3}\rangle \approx T_2(\bar{2}\,\bar{1})\delta(\bar{2}3)\delta(\bar{1}\,\bar{3}) , \quad (3.5)$$

$$\langle 4\bar{4}|\,\tilde{T}^T(-z)|\,5\bar{5}\rangle \approx f_0(p_4)f_0(p_{\bar{4}})T_2^T(4\bar{4};-z) \times\delta(45)\delta(\bar{4}\,\bar{5})\tilde{g}(r_0) , \quad (3.6)$$

where

$$T_2(\bar{2}\,\bar{1}) = L_I(\bar{2}\,\bar{1})[z - L(\bar{2}\,\bar{1})]^{-1}[z - L_0(\bar{2}\,\bar{1})] \quad (3.7)$$

is the usual two-particle T matrix. In arriving at (3.6) the approximations given by I (5.9) has been used. This is just the assumption that the pair-distribution function changes most rapidly at the point of discontinuity at the hard-core separation. The effects of this approximation have been checked in the case of the Enskog term and one is fairly confident in assuming these effects are small for moderate densities.

One can now rewrite (3.4) in the form

$$\delta\varphi_s(12)f_0(2) = \int d\bar{1}\,d\bar{2}\,d5\,d\bar{5}\,\delta(1\bar{2})\,T_2(\bar{2}\,\bar{1}) \times\langle\bar{2}\,\bar{1}|\{(z - L_0)^{-1} - [z - L_0 - M_c(z)]^{-1}\}|\,5\bar{5}\rangle \times f_0(p_5)f_0(p_{\bar{5}})T_2^T(5\bar{5};-z)\delta(52)\tilde{g}(r_0) . \quad (3.8)$$

One can then integrate by parts twice to find

$$\delta\varphi_s(12)f_0(2) = \int d\bar{1}\,d\bar{2}\,d5\,d\bar{5}\,[T_2(\bar{2}\,\bar{1};-z)\delta(1\bar{2})] \times\langle\bar{2}\,\bar{1}|\{(z - L_0)^{-1} - [z - L_0 - M_c(z)]^{-1}\}|\,5\bar{5}\rangle \times f_0(p_5)f_0(p_{\bar{5}})\tilde{g}(r_0)T_2(5\bar{5};z)\delta(52) . \quad (3.9)$$

It is then convenient to Fourier transform over $\vec{r}_1$ and $\vec{r}_2$ (Ref. 5),

$$\delta\varphi_s(\vec{k},\vec{p}_1\vec{p}_2,z)f_0(2) = \int\frac{d^3r_1d^3r_2}{V}\,e^{+i\vec{k}\cdot\vec{r}_1}e^{-i\vec{k}\cdot\vec{r}_2}\delta\varphi_s(12)f_0(2) \quad (3.10)$$

and introduce the field

$$f_k(\vec{p}_1,\bar{2}) = e^{+i\vec{k}\cdot\vec{r}_{\bar{2}}}\delta(\vec{p}_1 - \vec{p}_{\bar{2}}) \quad (3.11)$$

to find

$$\delta\varphi_s(\vec{k},\vec{p}_1\vec{p}_2,z)f_0(p_2) = \tilde{g}(r_0)\int\frac{d\bar{1}\,d\bar{2}\,d5\,d\bar{5}}{V}\,[T_2(\bar{2}\,\bar{1};-z)f_k(\vec{p}_1;\bar{2})] \times\langle\bar{2}\,\bar{1}|\,[(z - L_0)^{-1} - (z - L_0 - M_c)^{-1}]\,|\,5\bar{5}\rangle f_0(p_5) \times f_0(p_{\bar{5}})T_2(5\bar{5};z)f_{-k}(\vec{p}_2,\bar{2}) . \quad (3.12)$$

It is quite interesting to note that this expression for the correction to the Enskog memory function is quite similar to an expression found by Pomeau.[6] These expressions are in turn related to the "ring-collision" expressions studied by Dorfman and Cohen[7] and by Dufty.[8] One difference is that these last two sets of authors neglect the $(z - L_0)^{-1}$ term. While it is true that these "free" terms will not be dominant for long times they do play a role for short and intermediate times. This point is discussed further in Sec. V.

IV. MODE-MODE COUPLING FORM FOR $\delta\phi_s$

It is rather difficult to make mathematical headway with the expression (3.8) as it stands. This is, of course, because of the resolvent operator

$(z - L_0 - M_c)^{-1}$. An explicit calculation of this quantity would require solution of an integral equation with a coupling over two momentum variables. The problem can be reduced to the solution of two independent integral equations which are coupled by only one momentum variable and which are essentially equivalent to solving the Boltzmann equation. This reduction begins by considering the correlation function

$$\langle \bar{2}\,\bar{1}| \quad [z - L_0 - M_c(z)]^{-1} | 5\bar{5}\rangle f_0(p_5) f_0(p_{\bar{5}}). \tag{4.1}$$

This correlation function satisfies the "kinetic equation"

$$(z - L_0(\bar{1}\,\bar{2}))\, C_0(\bar{2}\,\bar{1}; 5\bar{5}) - \varphi_s^E(\bar{2}\,\bar{3})\, C_0(\bar{3}\,\bar{1}; 5\bar{5}) - \varphi_E(\bar{1}\,\bar{3}) C_0(\bar{2}\,\bar{3}; 5\bar{5}) = \delta(\bar{2}5)\delta(\bar{1}\,\bar{5}) f_0(p_5) f_0(p_{\bar{5}}), \tag{4.2}$$

where (2.1) has been used to approximate M_c.[9] Since, in the Enskog approximation ϕ_s and ϕ are independent of z, one finds in time space that (4.2) has the form

$$\frac{\partial}{\partial t} C_0(\bar{2}\,\bar{1};\ 5\bar{5};\ t) - iL_0(\bar{1}\,\bar{2}) C_0(\bar{2}\,\bar{1}; 5\bar{5}; t) - i\varphi_s^E(\bar{2}\,\bar{3}) C_0(\bar{3}\,\bar{1}; 5\bar{5}; t) - i\varphi_E(\bar{1}\,\bar{3}) C_0(\bar{2}\,\bar{3}; 5\bar{5}; t) = 0, \tag{4.3}$$

where

$$C_0(\bar{1}\,\bar{2};\ 5\bar{5};\ t=0) = \delta(\bar{2}5)\delta(\bar{1}\,\bar{5}) f_0(p_5) f_0(p_{\bar{5}}), \tag{4.4}$$

$$C_0(\bar{1}\,\bar{2}; 5\bar{5}; z) = -i\int_0^{+\infty} dt\, e^{+izt} C_0(\bar{1}\,\bar{2}; 5\bar{5}; t). \tag{4.5}$$

It is now convenient to define

$$G_s(\bar{1}5; t) = C_s^E(\bar{1}\,\bar{6}; t) \bar{C}_s^{-1}(\bar{6}5) f_0(5), \tag{4.6}$$

so that

$$G_s(\bar{1}5; t=0) = \delta(\bar{1}5) f_0(p_5) \tag{4.7}$$

and there is a similar normalized function for the full density-fluctuation function $C(12, z)$. Then C_0 can be written in the form

$$C_0(\bar{2}\,\bar{1}; 5\bar{5}; t) = G_s(\bar{2}5; t) G(\bar{1}\,\bar{5}; t), \tag{4.8}$$

since G_s and G satisfy the equations

$$\frac{\partial}{\partial t} G_s(\bar{2}\,5; t) - iL_0(\bar{2}) G_s(\bar{2}5; t) - i\varphi_s^E(\bar{2}\,\bar{3}) G_s(\bar{3}5; t) = 0, \tag{4.9}$$

$$\frac{\partial}{\partial t} G(\bar{1}\,\bar{5}; t) - iL_0(\bar{1}) G(\bar{1}\,\bar{5}; t) - i\varphi^E(\bar{1}\,\bar{3}) G(\bar{3}\,\bar{5}; t) = 0, \tag{4.10}$$

and

$$G_s(\bar{2}\,5; 0)\, G(\bar{1}\,\bar{5}; 0) = \delta(\bar{2}\,5)\delta(\bar{1}\,\bar{5}) f_0(p_5) f_0(p_{\bar{5}}). \tag{4.11}$$

It should be clear then that by setting $\phi_s^E = \phi^E = 0$ in Eq. (4.2) one finds that the term subtracted from C_0 in (3.12) is just the product of G's evaluated in the free-particle case. Then one has

$$\delta\varphi_s(\vec{k}, \vec{p}_1 \vec{p}_2, z) f_0(p_2) = i\tilde{g}(r_0) \int \frac{d\bar{1}\, d\bar{2}\, d5\, d\bar{5}}{V} \times [T(\bar{2}\,\bar{1}; -z) f_k(\vec{p}_1, \bar{2})] \int_0^{+\infty} dt\, e^{+izt} \times [G_s(\bar{2}5; t) G(\bar{1}\,\bar{5}; t) - G_s^0(\bar{2}5; t) G^0(\bar{1}\,\bar{5}; t)] T_2(\bar{5}5; z) f_{-k}(\vec{p}_2, 5), \tag{4.12}$$

and after introducing Fourier transforms for the internal quantities one finds

$$\delta\varphi_s(\vec{k}, \vec{p}_1 \vec{p}_2, z) f_0(p_2) = i\tilde{g}(r_0) \int d\vec{p}_{\bar{1}}\, d\vec{p}_{\bar{2}} dp_5 dp_{\bar{5}} \frac{d^3\bar{k}}{(2\pi)^3} \times t(\bar{k}, k, p_{\bar{1}} p_{\bar{2}}, p_1; -z) \int_0^{+\infty} dt\, e^{+izt} \times [G_s(\vec{\bar{k}}, \vec{p}_{\bar{2}} \vec{p}_5, t)\, G(\vec{k} - \vec{\bar{k}}, \vec{p}_{\bar{1}} \vec{p}_{\bar{5}}, t) - G_s^0(\vec{\bar{k}}, \vec{p}_{\bar{2}} \vec{p}_5, t) G_s^0(\vec{k} - \vec{\bar{k}}, \vec{p}_{\bar{1}} \vec{p}_{\bar{5}}, t)] \times t(-\vec{\bar{k}}, -\vec{k}, \vec{p}_5 \vec{p}_{\bar{5}}, \vec{p}_2; z), \tag{4.13}$$

where[10]

$$t(\vec{\bar{k}}, \vec{k}, \vec{p}_{\bar{1}} \vec{p}_{\bar{2}}, \vec{p}_1; -z) = \int d^3 r_{12}\, e^{+i(\vec{\bar{k}} - \vec{k}/2)\cdot \vec{r}_{12}} \times (z + L_0(\bar{1}\,\bar{2}))\, \theta(r_0^2 - |\vec{r}_{12}|^2) [z + L(\bar{1}\,\bar{2})]^{-1} \times L_I(\bar{1}\,\bar{2}) e^{+i\vec{k}\cdot\vec{r}_{12}/2} \delta(\vec{p}_{\bar{2}} - \vec{p}_1). \tag{4.14}$$

For hard cores one can evaluate the effect of the two-particle propagator in (4.14) to find[3]

$$t(\vec{\bar{k}}, \vec{k}, \vec{p}_{\bar{1}} \vec{p}_{\bar{2}}; \vec{p}_1; -z) = \int d^3 r\, e^{+i\vec{\bar{k}}\cdot\vec{r}} \times (-2i\vec{\bar{p}}\cdot\hat{r}/m) \delta(|\vec{r}| - r_0) \theta(-\hat{r}\cdot\vec{\bar{p}}) \times [\delta(\vec{p}_1 - \vec{\alpha} - \vec{\bar{p}}) - \delta(\vec{p}_1 - \vec{\alpha} - \vec{\bar{p}}^*)] = -t(-\vec{\bar{k}}, -\vec{k}, \vec{p}_{\bar{1}} \vec{p}_{\bar{2}}, \vec{p}_1; z), \tag{4.15}$$

$$\vec{\bar{p}} = \tfrac{1}{2}(\vec{p}_{\bar{1}} - \vec{p}_{\bar{2}}), \qquad \vec{\alpha} = \tfrac{1}{2}(\vec{p}_{\bar{1}} + \vec{p}_{\bar{2}}), \qquad \vec{\bar{p}}^* = \vec{\bar{p}} - 2\hat{r}(\hat{r}\cdot\vec{\bar{p}}).$$

The matrix correlation functions that appear in the integrand of (4.13) contain two distinct types of components according to the particular momentum "states" that are projected onto these matrices. In other words the matrix can be broken up into separate blocks if one transforms from a continuous space to a discrete space. These blocks are divided between the hydrodynamical states, and the nonhydrodynamical states. It can be shown that the hydrodynamical states predominate for long times. This is because they decay in time with a factor $e^{-k^2 D_E t}$ whereas the nonhydrodynamical states decay at least as fast as $e^{-V_0^2 t / D_E}$, where $V_0^2 = (\beta m)^{-1}$. Consequently as k becomes small the hy-

drodynamical states will persist for very long times compared to the nonhydrodynamical states.

With the above reasoning in hand, it is not difficult to see that for small k and z that the largest contribution to the integrand of (4.13) will come for small k and $\bar{k}$ and from those momentum components that project onto the hydrodynamical states. By writing the expression for $\delta\phi_s$ in terms of a product of matrix correlation functions one is able to pick out these hydrodynamical states in a straightforward manner and thereby circumvent the perturbation analysis used by Pomeau, Dorfman and Cohen, and Dufty in analyzing the intermediate "propagator" in (3.12). This observation that the hydrodynamical components give the largest contribution is essentially equivalent to the mode-mode coupling theories,[11] where it is assumed that such a product of hydrodynamical components are dominant. A big difference between the theory developed here and the mode-mode coupling theories is that the results here have been derived via a number of physically motivated microscopic approximations and one is free to go back and check the error made in making each approximation. Also, since the approximations have not been limited to any particular time or space regime, one does not have to introduce the wave-number cutoff used in the mode-mode coupling and "long-time" microscopic theories. One can in fact, investigate the legitimacy of using such a cutoff and the magnitude of such a cutoff if it exists.

The "divergences" of the density expansion for the transport coefficients can be easily understood from the mode-mode coupling expression (4.13) for $\delta\phi_s$. Clearly one cannot expand C and C_s in a power series in the density. This expansion would lead to secularities for small k and z. Thus such an expression of C and C_s in (4.13) would lead to similar secularities in the expression for $\delta\phi_s$ and, therefore, in the expression for the associated transport coefficients. Thus one should not expect that one can expand the transport coefficients in a power series in the density.

V. "LONG-TIME" APPROXIMATIONS FOR $\delta\phi_s$

In order to gain some understanding of the behavior of $\delta\phi_s$ it is worthwhile to consider first those terms in the integrand of (4.13) that determine the very long-time behavior of $\delta\phi_s$. Since $\delta\phi_s$ is given by (4.13) for all times, one can investigate the approach to this long-time behavior. In future work the terms which decay faster in time will be analyzed. In this work the analysis will be semiquantitative concerning the intermediate time regime. The long-time behavior will be treated quantitatively.

The analysis will focus on the velocity-autocorrelation function, and therefore, as discussed in Sec. V of I, one is most interested in the 2-2 matrix element of $\delta\phi_s$.[12] Consider now the contribution of the hydrodynamical states[13] in the integrand of (4.13). The only hydrodynamical state for G_s, $|1\rangle$, corresponds to conservation of particles. G has five hydrodynamical states $|i\rangle$, $i=1-5$, corresponding to conservation of particle number, momentum, and energy. After keeping only the projections onto these states, one is left with various matrix elements of the t operators of the form $\langle 2|t|1, i\rangle$. It is easy to show, using symmetry arguments, that all of these matrix elements go to zero as $k\to 0$ except for $i=2$. Consequently, the hydrodynamical coupling in $\delta\phi_s$ is between the self-diffusion mode and the current-current correlation function $G_{22}(\vec{k}, t)=\langle 2|G(\vec{k}, t)|2\rangle$. One has then

$$\delta\varphi_{22}(\vec{k}, z)=i\tilde{g}(r_0)\int\frac{d^3\bar{k}}{(2\pi)^3}\int_0^{+\infty}dt\, e^{+izt}\,|t_{22}(\bar{k})|^2 \times[G_s(\bar{k}, t)G_{22}(\vec{k}-\bar{\vec{k}}, t)-G_s^0(\bar{\vec{k}}, t)G_{22}^0(\vec{k}-\bar{\vec{k}}, t)], \tag{5.1}$$

where the free-particle term has been treated symmetrically with the full correlation functions. If one did otherwise, unphysical difficulties would result for short times. One can now note that the current correlation function that appears in (5.1) can be broken into a longitudinal and a transverse part:

$$G_{22}(\vec{k}, z)=\hat{k}_2^2G_l(\vec{k}, z)+(1-\hat{k}_2^2)\,G_t(\vec{k}, z)\,. \tag{5.2}$$

It is fairly easy to show that the longitudinal current correlation function does not contribute to the long-time behavior of $\delta\phi_{22}$. In the hydrodynamical region one has

$$G_l(\vec{k}, t)=\cos(Ckt)e^{-k^2D_Tt}\,, \tag{5.3}$$

where C is the adiabatic speed of sound and D_T is the thermal diffusivity. The presence of the collective mode leads to a long-time behavior that decays exponentially with a decay constant proportional to C. Therefore, one believes, if this reasoning is correct, that only the transverse state should contribute for long times. The analysis will, therefore, be restricted to what will be referred to as the long-time approximation for $\delta\phi_s$:

$$\delta\varphi_{22}(\vec{k}, z)=i\tilde{g}(r_0)\int\frac{d^3\bar{k}}{(2\pi)^3}\int_0^{+\infty}dt\, e^{+izt}\,|t_{22}(\bar{k})|^2 \times\left[1-\left(\frac{(\vec{k}-\bar{\vec{k}})_2}{|\vec{k}-\bar{\vec{k}}|}\right)^2\right][G_s(\bar{\vec{k}}, t)G_t(\vec{k}-\bar{\vec{k}}, t) - G_s^0(\bar{\vec{k}}, t)G_t^0(\vec{k}-\bar{\vec{k}}, t)]\,. \tag{5.4}$$

One can easily show from (4.15) that

$$t_{22}(\bar{\vec{k}})=-i\sqrt{\pi}\,V_0\tfrac{8}{3}r_0^2(\sin\bar{k}r_0/\bar{k}r_0)\,, \tag{5.5}$$

so that

$$\delta\varphi_{22}(\vec{k}, z) = i\tilde{g}(r_0)n(\sqrt{\pi}\, V_0 \tfrac{8}{3}r_0^2)^2 \int_0^{+\infty} dt\, e^{+izt}\Phi(\vec{k}, t)\,, \tag{5.6}$$

where

$$\Phi(\vec{k}, t) = \int \frac{d^3\bar{k}}{(2\pi)^3}\, \frac{\sin^2\bar{k}r_0}{(\bar{k}r_0)^2}\, \left[1 - \left(\frac{(\vec{k}-\vec{\bar{k}})_2}{|\vec{k}-\vec{\bar{k}}|}\right)^2\right] \times [G_s(\vec{\bar{k}}, t)G_t(\vec{k}-\vec{\bar{k}}, t) - G_s^0(\vec{\bar{k}}, t)\, G_t^0(\vec{k}-\vec{\bar{k}}, t)]\,. \tag{5.7}$$

The analysis here will be concerned with the velocity-autocorrelation function and consequently one can take k to zero. A finite-k calculation will lead to results for S_s similar to those found by Dufty. Since the analysis will be semiquantitative (given the previous approximation), V_D will be calculated using the "Born" approximation and the approximate diagonality of ϕ_s^E:

$$V_D(z) = V_0^2\langle 2|[z - \varphi_s(\vec{0}, z)]^{-1}|2\rangle \approx V_D^E(z) + V_0^E(z)\delta\varphi_{22}(z)V_D^E(z)\,. \tag{5.8}$$

One has, on inverting the Laplace transform,

$$V_D(t) = V_D^E(t) - \int_0^t d\bar{t}\; V_D^E(t-\bar{t}) \times \int_0^{\bar{t}} d\bar{t}'\, \delta\varphi_{22}(\bar{t}-\bar{t}')V_D^E(\bar{t}')\,. \tag{5.9}$$

This can be further simplified if one notes that the second term can be integrated by parts to give[14]

$$V_D(t) = V_D^E(t) - \int_0^t d\bar{t}\; (t-\bar{t})\delta\tilde{\varphi}_{22}(\bar{t})e^{-V_0^2(t-\bar{t})/D_E} \tag{5.10}$$

and

$$\delta\tilde{\varphi}_{22}(t) = -\tilde{g}(r_0)\,(\sqrt{\pi}\, V_0 \tfrac{8}{3}r_0^2)^2\Phi(\vec{0}, t)\,. \tag{5.11}$$

One can calculate the diffusion coefficient using the formula I(5.22) to find

$$D = D_E[1 + \delta\varphi_{22}(\vec{0}, z=0)/\varphi_{22}^E(\vec{0}, z=0)]^{-1}\,, \tag{5.12}$$

where it has been assumed, as a first approximation, that $\langle 2|\phi_2^{-1}|2\rangle = (\langle 2|\phi_s|2\rangle)^{-1}$ and

$$\delta\varphi_{22}(0, z=0) = i\tilde{g}(r_0)n(\sqrt{\pi}\, V_0 \tfrac{8}{3}r_0^2)^2 \int_0^{+\infty} dt\, \Phi(\vec{0}, t)\,. \tag{5.13}$$

The calculation of the velocity-autocorrelation function reduces to calculating $\Phi(\vec{0}, t)$. In order to evaluate this integral one must choose a form for the correlation functions that appear in the integrand. This is one advantage of this method over the small-$\bar{k}$ expansion developed by Pomeau and used by Dorfman and Cohen. By using the form (5.4), one can use all of the information that has been gathered over the past few years in evaluating correlation functions over the complete range of k and t. A reasonable approximation, valid for large and small k and t, is the Gaussian approximation for G_s. This approximation is discussed in I. While this approximation is usually used for G_s, it is convenient here to use a similar approximation for G_t. The justification for this lies in the observation that G_t possesses the same type of diffusive character as seen in G_s. This correspondence can be made closer with an investigation of certain kinetic models such as those discussed by Sirovich.[15] It is, therefore, reasonable to write

$$G_s(\vec{\bar{k}}, t) = e^{-\bar{k}^2 W_D(t)/2}\,, \tag{5.14}$$

$$G_t(\vec{\bar{k}}, t) = e^{-\bar{k}^2 W_\nu(t)/2}\,, \tag{5.15}$$

where

$$W_D(t) = 2D_E[t + D_E/V_0^2(e^{-V_0^2 t/D_E} - 1)]\,, \tag{5.16}$$

$$W_\nu(t) = 2\nu_E[t + \nu_E/V_0^2(e^{-V_0^2 t/\nu_E} - 1)]\,, \tag{5.17}$$

and the transport coefficients are given by the Enskog results. One has for the diffusion coefficient

$$D_E = 3V_0/8\sqrt{\pi}\, nr_0^2\tilde{g}(r_0) \tag{5.18}$$

and for the kinematic viscosity

$$\nu_E = 5V_0[16\sqrt{\pi}\, nr_0^2\tilde{g}(r_0)]^{-1} \times [1 + \tfrac{16}{5}\eta\tilde{g}(r_0) + 16(0.761)\eta^2\tilde{g}^2(r_0)]\,, \tag{5.19}$$

where $\eta = \frac{1}{6}\pi nr_0^3$.

One expects that this approximation for the correlation functions is good for large and small values of k and t. The error for the intermediate regions have been discussed by Desai and Nelkin.[16] The free-particle correlation functions are given by the well-known results[17]

$$G_s^0(\vec{\bar{k}}, t) = G_t^0(\vec{k}, t) = e^{-k^2V_0^2t^2/2}\,. \tag{5.20}$$

Using these results, noting that the correlation functions depend only on the magnitude of $\bar{k}$, one can easily do the angular integration over $\vec{\bar{k}}$ and use the identity

$$\sin^2\bar{k}r_0 = \tfrac{1}{2}(1 - \cos 2\bar{k}r_0) \tag{5.21}$$

to put $\Phi(\vec{0}, t)$ in a form where the $\bar{k}$ integration is in a tabulated form. One then finds that

$$\Phi(\vec{0}, t) = \frac{1}{12\pi^{3/2}r_0^2}\left[\frac{1}{[\alpha(t)]^{1/2}}\,(1 - e^{-r_0^2/\alpha(t)}) - \frac{1}{V_0 t}\,(1 - e^{-(r_0/V_0 t)^2})\right]\,, \tag{5.22}$$

where

$$\alpha(t) = \tfrac{1}{2}[W_D(t) + W_\nu(t)]\,. \tag{5.23}$$

For short times $\alpha(t)$ is given by

$$\alpha(t) = t^2V_0^2\left[1 - \tfrac{1}{6}tV_0^2\left(\frac{1}{D_E} + \frac{1}{\nu_E}\right) + O(t^2)\right]\,, \tag{5.24}$$

and consequently

$$\Phi(\vec{0}, 0) = \lim_{t\to 0}\Phi(\vec{0}, t) = \frac{V_0}{144\pi^{3/2}r_0^2}\left(\frac{1}{D_E} + \frac{1}{\nu_E}\right)\,, \tag{5.25}$$

which is positive and nonzero. It is also easy to see that for long times one has

$$\Phi(\vec{0}, t) \sim \frac{1}{12\pi^{3/2}} \{ [(\nu_E + D_E)t]^{-3/2} - (V_0 t)^{-3} \} , \tag{5.26}$$

and this clearly goes as $t^{-3/2}$ for large times. The quantity

$$\tilde{\Phi}(s) = 12\pi^{3/2} r_0^3 \eta^{-1} \tilde{g}(r_0)^{-1} \Phi(s) , \tag{5.27}$$

is plotted in Fig. 1 for several densities. It can be seen that the "width" of $\tilde{\Phi}(s)$ increases with density and since $\eta \tilde{g}(r_0)$ increases sharply with η, one sees that the area under $\Phi(s)$ increases rapidly with the density. Thus, as the density increases, $\delta\phi_s(s)$ is less and less of a perturbation on the Enskog result and the "Born" approximation formula given by (5.10) becomes less valid.

Given the expression (5.22) for $\Phi(t)$ one can now use the expression (5.10) to calculate $\delta V_D(t)$ numerically. The results of this calculation are plotted in Figs. 2 and 3 and are compared with the results of Alder, Gass, and Wainwright (AGW).[18] It can be observed first that the general shape of the curves are similar but the approximation of keeping only the long-time terms becomes, as expected, much less accurate at higher densities. Part of this discrepancy follows from the fact that the "Born" approximation becomes less accurate

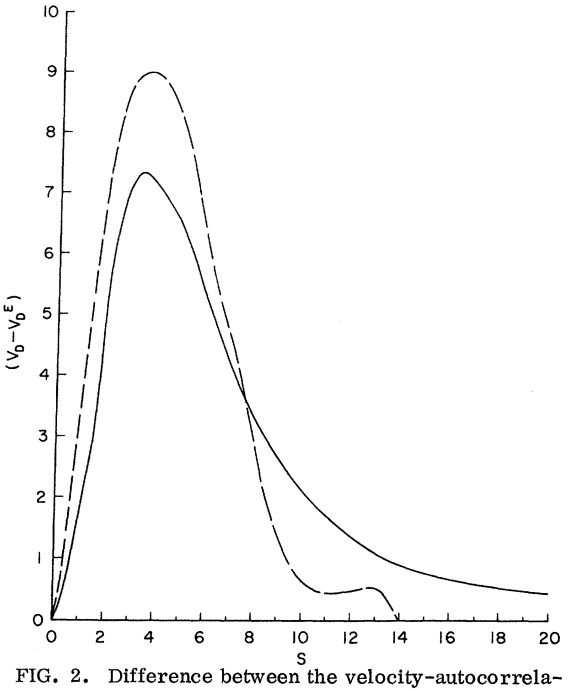

FIG. 2. Difference between the velocity-autocorrelation function and the simple exponential predicted by the Enskog theory, V_D^E, as a function of time s, measured in terms of mean-collision times at the density $\eta = 0.0741$. The solid line represents the results from Eqs. (5.10), (5.11), and (5.22). The dashed line represents the results of Alder, Gass, and Wainwright (Ref. 18). The magnitude of $V_D - V_D^E$ has been multiplied by 10^3.

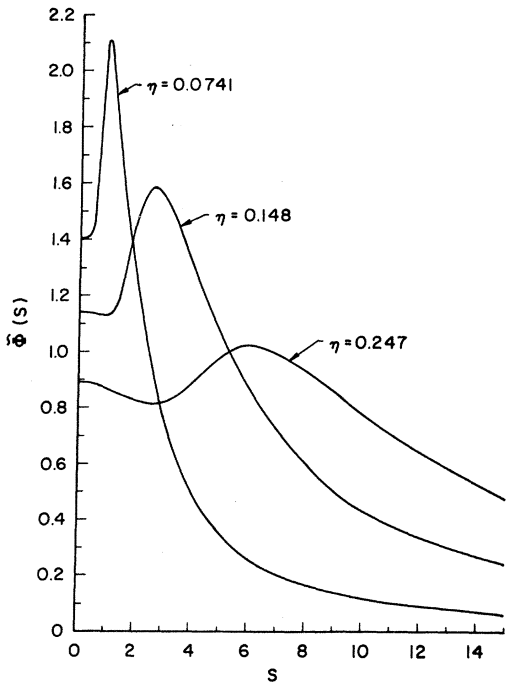

FIG. 1. Function $\tilde{\Phi}(s)$ defined by (5.27) as a function of the mean-free time at a series of densities indicated by $\eta = \frac{1}{6}\pi n r_0^3$.

at higher densities, but one also expects other momentum terms in (4.13) to become important for higher densities. For lower densities ($\eta \lesssim .07$) there is a rather remarkable agreement between

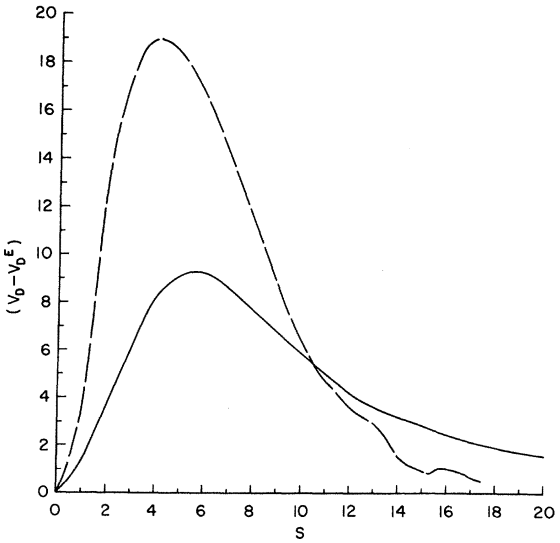

FIG. 3. Same as Fig. 2 except $\eta = 0.148$.

TABLE I. The ratio of calculated diffusion coefficient D to the Enskog value (see Ref. 20) at several densities.

$\eta = \frac{1}{6}\pi n r_0^3$	D/D_E[a]	D/D_E[b]
0.0741	1.07	1.05
0.148	1.16	1.11
0.247	1.34	1.16

[a]Calculated by Alder, Gass, and Wainwright (Ref. 18).
[b]Calculated using (5.12), (5.13), and (5.22).

the approximation $\delta V_D(t)$ and the results of AGW.

Both the peak position and the width of the intermediate peak are well described. It should be noted that the peak does move forward as the density increases as observed by Alder, Gass, and Wainwright. The long-time comparison in these figures should not be taken too seriously since AGW put an error of about 0.001 on their results, and this error is of the same order of magnitude as $V_D(t)$ in the long-time region. There are several difficulties in calculating $V_D(t)$ for long times using machines. These difficulties are discussed by AGW.

It can be seen from Figs. 1–3 that as the density increases the "microscopic" processes persist for a larger number of mean-free times. It appears that the asymptotic time region where $\delta V_D \sim s^{-3/2}$ occurs for mean-free times on the order of 20.

It does not seem likely from this analysis, that the long-time approximation can give rise to the negative structure observed by Rahman[19] and AGW. It is possible, however, that this negative structure could come from the other hydrodynamical states which do not contribute for very long times. This will be investigated in future work.

A better idea of the validity of the long-time approximation for $\delta\phi_s$ is given by the calculation of the diffusion coefficient since one does not have to solve an integral equation, and the "Born" approximation restriction is avoided. The results of this calculation are presented in Table I. It is apparent from the table that the hydrodynamical contribution essentially saturates the enhancement of the diffusion coefficient for $\eta \lesssim .07$.[20] Above these densities the contributions from the other momentum states become increasingly important.

VI. LONG-TIME ANALYSIS

The discussion of the long-time behavior of $V_D(t)$ can be made more quantitative than the discussion in Sec. V. This is because the asymptotic behavior of (5.1) is given by (5.11) and (5.26) without approximation. One finds then that

$$\delta\varphi_{22}(t) \sim - V_0^4 D_E^{-2} \tilde{g}^{-1}(r_0)\Phi(\vec{0}, t) .$$

Before evaluating the consequences of this result it is worthwhile to discuss the results of some other theories which make predictions about the long-time behavior of the velocity-autocorrelation function.

The various microscopic, hydrodynamical,[21] and machine calculations[22] are in agreement in predicting a long-time behavior for the VAF of the form

$$V_D(t)/V_D(0) \sim \alpha s^{-3/2} , \tag{6.1}$$

where $s = t/\tau$ and τ is the mean-free path given by I(5.29). To lowest order in the density there is agreement between these theories that

$$\alpha_0 = \tfrac{2}{3}[4\pi(D_0+\nu_0)\tau_0]^{-3/2} , \tag{6.2}$$

where the transport coefficients D_0 and ν_0 are the low-density values. This result also follows from (5.26) by using the Born-approximation form (5.10) and evaluating D, ν, and $\tilde{g}(r_0)$ to lowest order in the density.

There are a number of differences in these theories for higher densities. In the theory of Dorfman and Cohen (DC) one simply replaces the low-density transport coefficients with their Enskog values

$$\alpha_{DC} = \tfrac{2}{3}[4\pi(D_E+\nu_E)\tau]^{-3/2} . \tag{6.3}$$

In the hydrodynamical theories the low-density transport coefficients are replaced by the "full" transport coefficients to give

$$\alpha_H = \tfrac{2}{3}[4\pi(D+\nu)\tau]^{-3/2} . \tag{6.4}$$

Dufty has ignored Enskog-type corrections in his work, but he has included some renormalization effects not retained by Dorfman and Cohen to obtain

$$\alpha_{Du} = (D_R/D_0)^2 \alpha_0 , \tag{6.5}$$

where $D_R = D_0 + \Delta D$ and ΔD is the contribution of the ring terms to the diffusion coefficient. This will lead to an initial enhancement of α over the Dorfman and Cohen result for moderate densities. It is shown in the Appendix that in Born approximation (5.26) leads to the expression

$$\alpha_B = \tilde{g}^{-1}(r_0)\alpha_{DC} , \tag{6.6}$$

which leads to an over-all decrease in α from the Dorfman and Cohen result. The difference in the factor of $\tilde{g}^{-1}(r_0)$ from the DC results comes from the full expression (4.13). DC obtain another factor of $\tilde{g}(r_0)$ in a manner that has not yet been described in the literature. It is not at all obvious how this extra factor of $\tilde{g}(r_0)$ could be obtained in the analysis leading to (4.13). It certainly does not follow from a straightforward use of approximations like I(5.9), which led to the Enskog memory function. It is further shown in Appendix A that corrections essentially equivalent to those found by Dufty correspond to keeping higher terms in the Neumann series for $\delta V_D(t)$. This analysis leads to the result

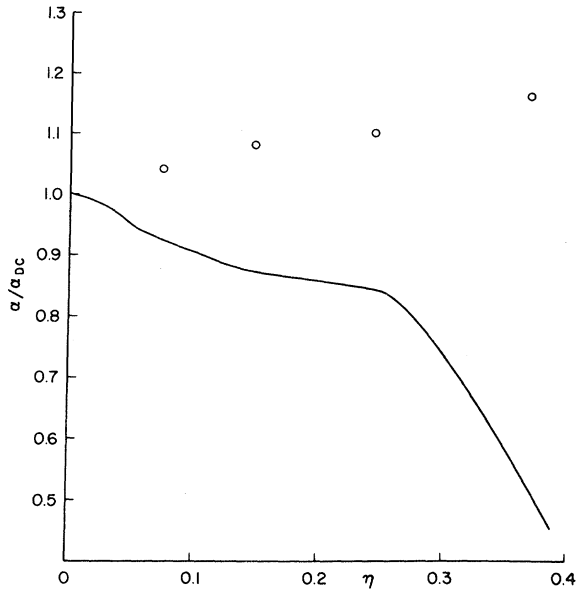

FIG. 4. Various expressions for the coefficient α [defined by (6.1)] relative to the value of α_{DC} obtained by Dorfman and Cohen, (6.3), as a function of the density. The solid line represents the ratio of α_{fr} [given by (6.7)] to α_{DC}. The circled points represent the ratio of α_H given by (6.4) to α_{DC}. The transport coefficients in α_H have been evaluated using the results in Ref. 18.

$$\alpha_{fr} = \xi(\eta)\alpha_{DC} , \tag{6.7}$$

where

$$\xi(\eta) = (D/D_E)^2 \tilde{g}^{-1}(r_0) , \tag{6.8}$$

and fr is an abbreviation for "fully renormalized." $\xi(\eta)$ is plotted as a function of η in Fig. 4. It is easily seen that there is fair agreement between α_{fr} and α_{DC} up to $\eta \sim 0.25$. For larger values of η there is essential disagreement. A few values of α as given by the hydrodynamical theory are also plotted in Fig. 4. The hydrodynamical form leads to an enhancement over the DC result and this enhancement increases with the density.

In Fig. 5 the absolute values of α are plotted for the present theory given by (6.7) and for the DC theory. It can be seen that α vanishes as η^3 for small η and then increases rather rapidly with increase in density. It should be noted that both the fr and DC theories predict a maximum value for α. The difference is that DC find this maximum at $\eta = 0.436$ whereas the fr gives a value of $\eta = 0.29$. The magnitude of α^{max} also differs considerably with $\alpha_{DC}^{max} = 0.6$ and $\alpha_{fr}^{max} = 0.37$. A major reason for the difference is the disagreement in the $\tilde{g}(r_0)$ factors in the asymptotic expression for $\delta\phi_s$.

VII. DISCUSSION

In this paper an attempt has been made to calculate the velocity-autocorrelation function for dense systems using a first-principles approach. Explicit numerical results have been obtained from a set of exact equations via a series of well-defined and controlled approximations. It has been demonstrated that in this way one can calculate time-correlation functions and transport coefficients to a realtively high degree of accuracy and with no adjustable parameters. This has been demonstrated by the calculation of the diffusion coefficient for moderate densities. It should also be apparent that the present theory poses no divergence problems.

The theory is, however, not yet complete since not all of the various approximations used in arriving at the final numerical results have been fully tested. It should be pointed out that these approximations can be divided into two separate types. Those which lead to the expression (4.13) for the correction to the Enskog memory function and the approximations one makes in analyzing this expression.

The approximations made in arriving at (4.13) were generally of a physical nature, and were motivated by one's intuition as to what processes should be important in a dense system. The first major approximation made was that the important intermediate state in a recollision process is where two particles travel independently, but under the influence of the medium. It is worth noting that it is this approximation that allows one to bypass the difficult three-body problem.

The second major approximation that was made was that the basic structure in the system does not radically change the dynamics of two-particle collisions. This approximation was enforced when $Q\mathcal{L}_I$ was set equal to L_I. This approximation clearly breaks down as one approaches the solid state since the structure of the system will play an increasingly important role in determining the effective interparticle potential. Consequently,

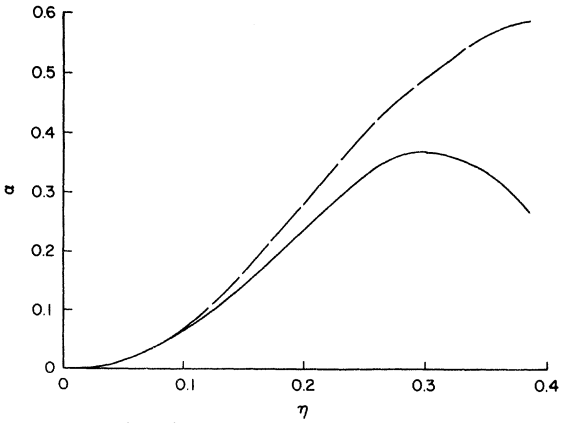

FIG. 5. Plot of the absolute values of α_{DC} (dashed line) and α_{fr} (solid line) as a function of the density.

this effect could be very important in very dense systems.

It will of course be important to investigate the regimes of validity of these approximations, and such an investigation seems to be quite possible within the framework of the FRKT. However, it would be of more immediate interest to remove the restrictions on the final results introduced by the second type of approximations. These approximations were those which allowed one to start with the expression (4.13) for the memory function and then arrive at the results presented in Sec. V. These approximations included the assumed diagonality of the various pieces of the memory function. This assumption allows one to avoid the solution of various integral equations. One also needs a better mathematical model for handling the product of matrix correlation functions. This can probably be accomplished by using the generalized modeling techniques due to Sirovich,[15] which gives one a practical method for solving the Boltzman equation over the complete range of frequencies and wave numbers.

ACKNOWLEDGMENTS

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APPENDIX

The equation of motion for the VAF in the case of hard cores can be written in the form

$$\frac{dV_D(t)}{dt} = -\frac{V_0^2}{D_E} V_D(t) - \int_0^t d\bar{t}\, \delta\varphi_{22}(t-\bar{t}) V_D(\bar{t}) \,. \tag{A1}$$

This equation can be partially integrated to give

$$V_D(t) = V_D^E(t) - \int_0^t d\bar{t}\, V_D^E(t-\bar{t}) \times \int_0^t d\bar{t}'\, \delta\varphi_{22}(\bar{t}-\bar{t}') V_D(\bar{t}') \,, \tag{A2}$$

where $V_D^E(t) = e^{-V_0^2 t/D_E}$. If one defines the deviation from the Enskog result as

$$v(t) = V_D(t) - V_D^E(t) \,, \tag{A3}$$

then

$$v(t) = -\int_0^t d\bar{t}\, V_D^E(t-\bar{t}) \int_0^{\bar{t}} d\bar{t}'\, \delta\varphi_{22}(\bar{t}-\bar{t}') V_D^E(\bar{t}') - \int_0^t d\bar{t}\, V_D^E(t-\bar{t}) \int_0^{\bar{t}} d\bar{t}'\, \delta\varphi_{22}(\bar{t}-\bar{t}') v(\bar{t}') \,. \tag{A4}$$

It will be assumed that this equation can be solved by iteration. The conditions under which one expects this iteration process to converge will be discussed later. This iteration process consists of taking

$$v_0(t) = -\int_0^t d\bar{t}\, V_D^E(t-\bar{t}) \int_0^{\bar{t}} d\bar{t}'\, \delta\varphi_{22}(\bar{t}-\bar{t}') V_D^E(\bar{t}') \,, \tag{A5}$$

and the nth iteration is of the form

$$v_n(t) = v_0(t) - \int_0^t d\bar{t}\, V_D^E(t-\bar{t}) \int_0^{\bar{t}} d\bar{t}'\, \delta\varphi_{22}(\bar{t}-\bar{t}') v_{n-1}(\bar{t}') \,. \tag{A6}$$

This analysis will investigate only the long-time solution to (A4). It is important to realize that the large time contributions come from the region where the argument of V_D^E is small. Outside this region one has exponential decay. Consequently, these equations can be approximated by

$$v_0(t) = -\delta\varphi_{22}(t) \int_0^t d\bar{t}\, V_D^E(t-\bar{t}) \times \int_0^t d\bar{t}'\, V_D^E(\bar{t}') + O(e^{-V_0^2 t/D_E}) \,, \tag{A7}$$

$$v_n(t) = v_0(t) - \int_0^t d\bar{t}\, V_D^E(t-\bar{t}) \times \int_0^t d\bar{t}'\, \delta\varphi_{22}(t-\bar{t}') v_{n-1}(\bar{t}') + O(e^{-V_0^2 t/D_E}) \,. \tag{A8}$$

One finds, after doing the integrations over the V_D^E's and keeping the terms that do not decay exponentially, that

$$v_0(t) \sim -\delta\varphi_{22}(t) (D_E/V_0^2)^2 \,, \tag{A9}$$

$$v_n(t) \sim v_0(t) - (D_E/V_0^2) f(t) \,, \tag{A10}$$

where

$$f(t) = -\int_0^t d\bar{t}'\, \delta\varphi_{22}(t-\bar{t}') v_{n-1}(\bar{t}') \,. \tag{A11}$$

In analyzing $f(t)$ one can make the scale transformation $y = \bar{t}'/t$ and then break f up into three integrals,

$$f(t) = -t \int_{1-\epsilon}^1 dy\, v_{n-1}(ty) \delta\varphi_{22}(t(1-y)) - t \int_{\epsilon'}^{1-\epsilon} dy\, v_{n-1}(ty) \delta\varphi_{22}(t(1-y)) - \int_0^{\epsilon'} dy\, v_{n-1}(ty) \delta\varphi_{22}(t(1-y)) \,, \tag{A12}$$

where ϵ and ϵ' are small positive constants.

In the middle integral in (A12) one sees that both v_{n-1} and $\delta\phi$ should be replaced by their long-time expressions

$$v_{n-1} \sim \alpha_{n-1} t^{-3/2}, \quad \delta\varphi_s \sim -\alpha_B D_E^{-2} t^{-3/2} \,,$$

in units where $V_0 = 1$. Consequently, the middle term in (A12) goes as t^{-2}, which can be neglected compared to the $t^{-3/2}$ behavior shown by the other two terms. It is easily seen that the other two terms lead to the long-time result

$$f(t) = [-\alpha_{n-1} \int_0^{+\infty} d\tau\, \delta\varphi_{22}(\tau) + \alpha_B D_E^{-2} \int_0^{+\infty} d\tau\, v_{n-1}(\tau)] t^{-3/2} \,. \tag{A13}$$

Combining (A13) with (A9) and (A10) one can identify

$$\alpha_n = \alpha_B + [-\alpha_{n-1} D_E \int_0^{+\infty} d\tau\, \delta\varphi_{22}(\tau) + \alpha_B D_E^{-1} \int_0^{+\infty} d\tau\, v_{n-1}(\tau)] \,. \quad \text{(A14)}$$

One can see from (5.12) that

$$D_E \int_0^{+\infty} d\tau\, \delta\varphi_{22}(\tau) = -1 + D_E/D = -D_E \Delta D/D^2 \,. \quad \text{(A15)}$$

It is also a reasonable approximation to take

$$\Delta D = \int_0^{+\infty} d\tau\, v_{n-1}(\tau) \quad \text{(A16)}$$

if one assumes that the Born approximation gives a reasonable estimate for ΔD. This approximation should be investigated for higher densities. One has then that

$$\alpha_n = \alpha_B (1 + \Delta D/D_E) + \alpha_{n-1} D_E \Delta D/D^2 \quad \text{(A17)}$$

or

$$\alpha_n = \alpha_B (1 + \Delta D/D_E) \sum_{s=0}^{n} (D_E \Delta D/D^2)^s + \alpha_B (D_E \Delta D/D^2)^n \quad \text{(A18)}$$

$$= \frac{\alpha_B (1 + \Delta D/D_E)}{1 - D_E \Delta D/D^2} (1 - [D_E \Delta D/D^2]^{n+1}) + \alpha_B (D_E \Delta D/D^2)^n \,. \quad \text{(A19)}$$

One eventually wants to take the limit as $n \to \infty$. It is clear from (A19) that this iteration approach will be successful only if

$$|D_E \Delta D/D^2| < 1 \,. \quad \text{(A20)}$$

This in turn requires that $|\Delta D/D_E| > 0.38$ or $D/D_E > 0.62$. From the data of AGW one sees that this iteration analysis can be valid only for densities up to $\eta \sim 0.48$. In the case where (A20) holds one has

$$\alpha_{tr} = \lim_{n \to \infty} \alpha_n = \frac{\alpha_B (1 + \Delta D/D_E)}{1 - D_E \Delta D/D^2} = \alpha_B (D/D_E)^2 \,, \quad \text{(A21)}$$

which is similar to the result obtained by Dufty.

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[1]G. F. Mazenko, preceding paper, Phys. Rev. A 7, 209 (1973). This paper will be referred to as I.

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

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

[4]The Faddeev approach to scattering in the quantum-mechanical three-body problem has led to tremendous progress. See, for example, K. M. Watson and J. Nuttall, *Topics in Several Particle Dynamics* (Holden-Day, San Francisco, 1967). These same ideas can be used in the classical scattering problem if one recognizes the formal relationship between the quantum-mechanical resolvent which contains the N-particle Hamiltonian and the classical resolvent which contains the N-particle Liouville operator. This correspondence was used by Zwanzig [Phys. Rev. 129, 486 (1963)] in transcribing the quantum-mechanical binary collision expansion [developed by A. J. F. Siegert and E. Teramoto, Phys. Rev. 110, 1232 (1958)] into the classical regime. Eu [J. Chem. Phys. 55, 4613 (1971)] has already used these ideas to rewrite the density expansion for the self-diffusion coefficient in terms of irreducible cluster functions. In the work here these ideas have been used to analyze the three-particle resolvent $[Z + L(1\bar{1}1')]^{-1}$.

[5]The volume V is introduced in (3.10) as a mathematical convenience since $\delta\phi_s(12)$ depends only on the difference $\vec{r}_1 - \vec{r}_2 = \vec{r}_{12}$.

[6]Y. Pomeau, Phys. Rev. A 3, 1174 (1971). See, in particular, Eqs. (2.23) and (3.2).

[7]J. R. Dorfman and E. G. D. Cohen, Phys. Rev. Letters 25, 1257 (1970); Phys. Rev. A 6, 776 (1972).

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[9]While M_c contains only the collisional part of ϕ (see Ref. 2), a more sophisticated treatment of the propagator QL_I, using the same "disconnected" arguments as used in Sec. II, leads to the replacement $L_I \to L_I + \phi^{(s)}$ and in turn $\phi^{(c)} \to \phi$.

[10]r_0 is the hard-sphere diameter and $\theta(x)$ is the unit step function which is equal to one for x greater than zero and zero for x less than zero. These factors of $\theta(r_0^2 - |r_{12}|)$ must appear in t in the case of hard spheres because of the initial condition where there were no overlapping particles. This point can be traced back to equation (I 3.1). If one does not include this factor, one cannot preserve conservation of particles.

[11]K. Kawasaki, Ann. Phys. (N.Y.) 61, 1 (1970); Phys. Letters 32A, 379 (1970); L. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968); R. Zwanzig, University of Maryland Institute for Fluid Dynamics and applied Mathematics Technical Note No. 3N-695, 1971 (unpublished).

[12]This assumption is valid only if $\delta\phi_s$ is a perturbation on ϕ_s^E or if $\delta\phi_s$ is also "almost" diagonal on the state $|2\rangle$.

[13]The five hydrodynamical momentum states associated with the density fluctuations in the system are discussed in Ref. 2. Here, it will be noted that $\langle p/1\rangle = 1$, $\langle p/2\rangle = p_l$, $\langle p/3\rangle = (1/\sqrt{6})(P^2 - 3)$, $\langle p/4\rangle = p_t$, $\langle p/5\rangle = p_{t'}$, where p_l is the longitudinal component of the momentum and p_t and $p_{t'}$ are the two transverse components of the momentum. Consequently, in an expression like $\langle 2|A|2\rangle$, one means $\int d^3p\, d^3p'\, \vec{p}_l \vec{p}_l'\, A(p, p')$.

[14]The author wishes to thank Professor M. Grisaru for pointing out this simplification.

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[19]A. Rahman, Phys. Rev. 136, A405 (1964).

[20]One should note that the value of D_E used in computing D/D_E does not include the "Sonine polynomial corrections." These corrections (see Ref. 15) will increase D_E by about 1.5% and, therefore, decrease the corresponding

value of D/D_E. This leads to better agreement than appears in Table I.

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Liquid Structure Function for Dilute He^3-He^4 Solutions*

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We present semitheoretical estimates for the liquid structure function $S_k(x)$ of He^3-He^4 solutions at low-He^3 concentrations x. Our calculation makes use of a perturbation theory in the representation of correlated basis functions, a variational procedure for intermediate- and high-momentum transfers, experimental data on the concentration dependence of the velocity of sound, and an interpolation between $k \approx 0.6$ and 1.2 $Å^{-1}$. For a 6% solution, the entire $S_k(0.06)$ curve is obtained. Experimental measurements, presumably by x-ray scattering, are not yet available.

I. INTRODUCTION

Several recent papers[1-3] have dealt with the experimental determination of the liquid structure function of He^4. For liquid He^3, neutron-scattering experiments are not feasible, on account of the high efficiency with which neutrons are absorbed by He^3 nuclei. X-ray scattering, however, does not face such difficulties: Reliable experiments have been carried out by Achter and Meyer[1] and Hallock,[4] who determined the He^3 liquid structure function at low temperatures over a wide range of momenta. In spite of the active interest in He^3-He^4 solutions over the last decade, there is as yet no information available on how the liquid structure function S_k changes when a small concentration of He^3 is added to superfluid He^4. The extension of x-ray-scattering experiments to dilute He^3-He^4 solutions does not appear to involve any technical difficulty.[5]

We present in this paper a first-order semitheoretical estimate of the concentration dependence of S_k in dilute He^3-He^4 solutions. The application of a microscopic theory reported in earlier publications[6] leads to reliable information on S_k at intermediate- and large-momentum transfers, say for $k \gtrsim 1.2$ $Å^{-1}$. However, the theory as it now stands makes use of a variational calculation which is not sensitive to the long-range behavior of the wave function. Thus the liquid structure function obtained is not accurate for small wave numbers. In that region we must supplement the microscopic calculation with an alternate procedure. The main body of this paper deals with such a procedure, which we outline below.

Denoting the He^3 concentration by x, with $x \equiv \rho_3/(\rho_3+\rho_4)$, where ρ_3 and ρ_4 denote partial number densities of He^3 and He^4, respectively, the liquid structure function at small x may be written as follows:

$$S_k(x) = S_k(0)\,(1+\xi_k x)\,, \tag{1}$$

where $S_k(0)$ is the liquid structure function for pure He^4. In the limit $k \to 0$, we find

$$S_k(x) \to \frac{\hbar k}{2m_4 c(0)}\,(1+\xi x)\,, \tag{2}$$

where $c(x)$ denotes the velocity of sound. It is our goal to determine the coefficient ξ.

First we carry out a perturbative expansion in the correlated representation and derive a relation between the phonon branch of the excitation spectrum, $\omega_k(x)$, and the liquid structure function $S_k(x)$. The result may be expressed as

$$\omega_k(x) = \omega_k^0(x) + \Delta\omega_k(x)\,, \tag{3}$$

where $\omega_k^0(x)$ is the "Feynman spectrum"

$$\omega_k^0(x) = \hbar^2 k^2/2m(x)S_k(x) \tag{4}$$

generated by the density fluctuation

$$\rho_{\vec{k}} = \rho_{\vec{k}}^{(3)} + \rho_{\vec{k}}^{(4)}\,, \tag{5}$$

with

$$\rho_{\vec{k}}^{(3)} = \sum_{i=1}^{N_3} e^{i\vec{k}\cdot\vec{r}_i} \tag{6}$$