PHYSICAL REVIEW A VOLUME 7, NUMBER 1 JANUARY 1973

Fully Renormalized Kinetic Theory. I. Self-Diffusion*

Gene F. Mazenko†
Department of Physics, Brandeis University, Waltham, Massachusetts 02194

(Received 15 June 1972)

In this paper a new fully renormalized kinetic theory for self-diffusion is described. The theory is developed in terms of time-dependent correlation functions, and the main effort is in deriving general microscopic expressions for the memory function associated with the phase-space fluctuation function. These general expressions are valid for all frequencies and wave numbers and are rearranged in a way such that approximations can be made at a microscopic level in a straightforward manner. The main idea in the rearrangement is the expression of the memory function in terms of an effective two-body problem where the dynamics are described by the two-particle Liouville operator and an effective source representing the effect of the other N-2 particles in the system on the colliding pair. An exact microscopic expression for the two-particle source is derived. It is shown that even the simplest approximation in this scheme leads to the nontrivial Boltzmann–Enskog approximation for the memory function.

I. INTRODUCTION

In this paper a new fully renormalized kinetic theory (FRKT) for self-diffusion in single-component monatomic fluids will be presented. This theory will be a microscopic theory and is designed to calculate time-correlation functions in realistic systems. The emphasis is on the calculation of time-correlation functions since all of the modern scattering techniques use these functions to interpret their experiments and these correlation functions are determined in molecular-dynamics experiments. In neutron scattering experiments[1] one can measure $S_s(\vec{k}, \omega)$, which is the Fourier transform in space and time of the correlation of the position of a tagged particle with its initial position

$$S_s(\vec{r}-\vec{r}'\, t-t') = \langle N\delta\,(\vec{r}-\vec{r}_1(t))\,\delta\,(\vec{r}'-\vec{r}_1(t'))\rangle \ , \qquad (1.1)$$

where N is the number of particles in the system. In molecular dynamics[2,3] one can calculate the velocity-autocorrelation function (VAF) $V_D(t)$, which is just the correlation of a tagged particle's velocity with its initial velocity

$$V_D(t) = \tfrac{1}{3}\,\langle N\vec{V}_1(t)\cdot\vec{V}_1(0)\rangle \ . \qquad (1.2)$$

One can show that the Fourier transforms of V_D and S_s are related by[1]

$$V_D(\omega) = \lim_{k\to 0}\,(\omega^2/k^2)\,S_s(\vec{k}, \omega) \ . \qquad (1.3)$$

Theoretically there has been a tremendous amount of effort to calculate $V_D(t)$. One fruitful approach is to write an equation of motion for $V_D(t)$ in terms of a single-component memory function as was done originally by Berne, Boon, and Rice[4] using Zwanzig's[5] projection-operator technique. Mori[6] has generalized this projection-operator technique to give general expressions for the memory functions associated with a wide class of time-correlation functions. This single-component description suffers from two basic computational difficulties which are related to the feasibility of calculating the memory functions from a microscopic point of view.

The first of these difficulties is related to the mathematical properties of the projection operator introduced by Mori[6] which projects onto a vector in Hilbert space that depends on the phase-space coordinates of N particles. Resibois and co-workers[7] have discussed the difficulties in making theoretical headway with the projection-operator expression for the single-component memory function. This is discussed further in Sec. IV of this paper.

The second difficulty is related to the fact that an explicit calculation can only be carried out after one has reduced the problem, through some series of approximations, to an equivalent few (one or two)-body problem. The obvious prototype of such a reduction is the Boltzmann equation, [8] where one describes an N-body system in terms of the two-body dynamics. Consequently, since one wants to derive expressions for the correlation functions in terms of the dynamics of a few particles, it is most natural to describe these events in terms of the phase-space coordinates of these particles. The single-component description, however, does not treat the momentum and spatial coordinates on an equal footing. It is, therefore, desirable to extend the description to the more general correlation function $C_s(12)$, defined in Sec. II, which is a matrix labeled by a continuous momentum index.

A complete theory for $C_s(12)$ for a low-density system has been developed[9–11] and a few results will be discussed in Secs. II B and V. In this paper, however, it is of primary interest to develop a microscopic theory valid beyond the low-density regime. In developing such a microscopic theory there are several possible approaches to writing down a "perturbation scheme." These depend on the choice of the fundamental units in the scheme. For example, in the mode-mode coupling formalism of Kawasaki[12] he writes a self-consistent scheme involving the correlation functions themselves and certain equal-time-correlation functions. Of course, this analysis considers only the contributions from fluctuating hydrodynamical modes and is, therefore, not intended to be a general microscopic theory. Forster[13] has developed a perturbation scheme involving the correlation function itself and the bare two-particle Liouville interaction operator. This theory is similar in approach to the diagrammatic analysis of the Prigogine school.[14] In these theories, it is quite difficult to make contact with the Enskog theory,[2,15,16] which is quite good up to moderate densities ($\eta = \frac{1}{6}\pi n r_0^3 \sim 0.3$, where r_0 is a hard-sphere diameter and n is the particle density). Another approach is the binary-collision expansion (BCE) approach due to Zwanzig,[17] where the basic units are the bare two-particle propagators. While one can make contact with the Enskog theory using this approach, it leads to unphysical divergences since the interaction of clusters of particles with the medium are not taken into account and it is quite difficult to include the statistically correlated events in the theory.

A major difference in these schemes is in the choice as to the relative importance of static or dynamic phenomena. In the FRKT one does not have to make this decision; instead the dynamics and statics are treated simultaneously. One major benefit of this approach is that the Enskog result, with its static effects, can be obtained in a very direct fashion (see Sec. V).

In developing a new theory of dense gases one will be confronted with the "divergence" problem encountered in the BCE approach. For three-dimensional systems these divergences[18-20] appear first in the four-body terms and presumably in all higher terms. Kawasaki and Oppenheim[18] proposed a remedy for this lowest-order divergence by resuming the most divergent terms in the density expansion. This resummation removed the lowest-order divergence and introduced logarithmic terms into the density expansion for the transport coefficients. This same renormalization technique—summing of ring diagrams—has recently been used by Dorfman and Cohen,[21] Pomeau,[22] and Dufty[23] in analyzing the very-long-time tail obtained by Alder and Wainwright[2,24] in their molecular-dynamics calculations of correlation functions for hard-sphere fluids. The long-time behavior obtained by Dorfman and Cohen seems to be correct at low densities and a good approximation at least up to half the close-packing density. Interestingly, a number of authors have obtained similar results using a mode-mode coupling or hydrodynamical approach.[25-29]

In the theory proposed here, the various one-, two-, and three-particle clusters are renormalized before one makes any type of expansion or approximation. Thus one never isolates the clusters that lead to the divergences in the BCE approach. Instead, each cluster of s particles is governed by the s-particle Liouville operator plus an effective external part to the Liouville operator representing the effect of the other N-s particles on the s-particle cluster. It will be shown in the second paper (II) in this series[30] how a full renormalization leads to an inclusion of the ring diagrams in the theory in a natural way. It will then be shown in II how these ring terms lead to the mode-mode coupling expressions for the memory functions.

Before going on to the basic formulation of this new theory, it is useful to comment on the relationship of this theory to some other fundamental theories. In Ref. 10 the calculation of memory functions via the method of thermodynamic Green's functions was discussed. It was pointed out there that the Green's-function method has the advantage that dynamic and static properties are calculated self-consistently. Unfortunately, as can be seen from the analysis in Ref. 10, this simultaneous treatment leads to extensive rearrangements if one is going to, for example, identify the pair-correlation function when it appears in the theory. To lowest order in the density, where $g(r) = e^{-\beta V(r)}$, this identification is relatively simple, but for higher orders in the density, where $g(r)$ will be given by something like the Percus–Yevick[31] equation, the coupling between the statics and dynamics will lead to untractable equations where, for example, the three-body scattering dynamics will be intimately connected with the static correlations between three particles. This same difficulty is inherent in the perturbation scheme due to Resibois and Deleener,[32] where they must eventually argue that the approximate static-correlation functions in their theory should be replaced by the "correct" ones when comparing with experiment. In the FRKT, as in the mode-mode coupling-type theories,[12,33] the exact static-correlation functions appear in the analysis and their calculation is deferred to a separate analysis.

There are some similarities between the work of Mori[6] and the FRKT in that projection operators are used in both and the resulting general expression for the memory functions "look" similar, but as will be discussed in Sec. IV C, there are some important differences which lead to a computational advantage for the FRKT.

While the theory described here has thus far been developed only for the case of a diffusing particle obeying classical mechanics, it is the author's opinion that the theory can be readily extended to the quantum case and the case of density fluctuations. In this first analysis the simplest realistic system is treated.

II. BASIC DEFINITIONS

A. Fundamental Fields

In the theory of self-diffusion a fundamental theoretical quantity is the phase-space density associated with a tagged particle (say particle 1) defined as

$$f_s(1)=\sqrt{N}\,\delta(1-q_1)\,, \tag{2.1}$$

where $q_1=(\vec{r}_1,\vec{p}_1)$ are the phase-space coordinates of particle 1, and there is a total (counting particle 1) of N particles in the system. One is also interested in the fields correlating particle 1 with the other particles

$$g(1\bar{1})=\sqrt{N}\,\delta(1-q_1)\sum_{j=2}^{N}\delta(\bar{1}-q_j) \tag{2.2}$$

and

$$g(1\,\bar{1}\,\bar{1}')=\sqrt{N}\,\delta(1-q_1)\sum_{i\neq j\neq 1}^{N}\delta(\bar{1}-q_j)\,\delta(\bar{1}'-q_i)\,. \tag{2.3}$$

It is very easy to calculate the thermodynamic averages of these fields:

$$\langle f_s(1)\rangle=\frac{\sqrt{N}}{N}\left\langle\sum_{i=1}^{N}\delta(1-q_i)\right\rangle=\frac{1}{\sqrt{N}}\,nf_0(p_1)\,, \tag{2.4}$$

where f_0 is the normalized Maxwell distribution

$$f_0(p_1)=\left(\frac{\beta}{2\pi m}\right)^{3/2}e^{-\beta p_1^2/2m}\,, \tag{2.5}$$

$$\begin{aligned}\langle g(1\bar{1})\rangle&=(1/\sqrt{N})\,n^2g(\vec{r}_1-\vec{r}_{\bar{1}})\,f_0(p_1)f_0(p_{\bar{1}})\\&\equiv(1/\sqrt{N})\,\omega_0(1\bar{1})\,,\end{aligned} \tag{2.6}$$

where

$$n^2g(\vec{r}_1-\vec{r}_{\bar{1}})=\left\langle\sum_{i\neq j}^{N}\delta(\vec{r}_1-\vec{r}_i)\,\delta(\vec{r}_{\bar{1}}-\vec{r}_j)\right\rangle \tag{2.7}$$

is the pair-distribution function, and

$$\begin{aligned}\langle g(1\,\bar{1}\,\bar{1}')\rangle&=(1/\sqrt{N})\;n^3g(\vec{r}_1,\vec{r}_{\bar{1}},\vec{r}_{\bar{1}'})\\&\qquad\times f_0(p_1)\,f_0(p_{\bar{1}})\,f_0(p_{\bar{1}'})\\&\equiv(1/\sqrt{N})\,\omega_0(1\,\bar{1}\,\bar{1}')\,,\end{aligned} \tag{2.8}$$

where

$$n^3g(\vec{r}_1,\vec{r}_{\bar{1}},\vec{r}_{\bar{1}'})=\left\langle\sum_{i\neq j\neq k}^{N}\delta(\vec{r}_1-\vec{r}_i)\,\delta(\vec{r}_{\bar{1}}-\vec{r}_j)\,\delta(\vec{r}_{\bar{1}'}-\vec{r}_k)\right\rangle \tag{2.9}$$

is the triplet-distribution function. It is clear that the equilibrium averages of these fields vanish in the thermodynamic limit N, $V\to\infty$ with $N/V=n$.

B. Static Correlations

One is also interested in the correlations between the fields defined above. In particular, one needs the static-correlation function

$$\begin{aligned}\tilde{C}_s(12)&=\langle\,\delta f_s(2)\,\delta f_s(1)\,\rangle\\&=n\,\delta(1-2)\,f_0(p_1)-(n^2/N)\,f_0(p_1)\,f_0(p_2)\,,\end{aligned} \tag{2.10}$$

where δf_s indicates the deviation of f_s from its average value. Note that static-correlation functions are denoted by a tilda. It should also be noted in the case of self-diffusion that the deviations of the fields from their equilibrium values are not important in the thermodynamic limit and can, therefore, be neglected. One also needs the results

$$\tilde{C}(1\,\bar{1}\,;2)=\langle f_s(2)g(1\bar{1})\rangle=\delta(1-2)\,\omega_0(1\bar{1})\,, \tag{2.11}$$

$$\begin{aligned}\tilde{C}(1\bar{1}\,;2\,\bar{2})&=\langle g(2\bar{2})\,g(1\bar{1})\rangle\\&=\delta(1-2)\,[\delta(\bar{1}-\bar{2})\,\omega_0(1\bar{1})+\omega_0(1\,\bar{1}\,\bar{2})]\,,\end{aligned} \tag{2.12}$$

and

$$\begin{aligned}\tilde{C}(1\,\bar{1}\,\bar{1}'\,;2\,\bar{2}\,\bar{2}')&=\langle g\,(2\,\bar{2}\,\bar{2}')\,g(1\,\bar{1}\,\bar{1}')\rangle\\&=\delta(12)\{[\delta(\bar{1}\,\bar{2})\,\delta(\bar{1}'\bar{2}')+\delta(\bar{1}'\bar{2})\,\delta(\bar{1}\,\bar{2}')]\\&\quad\times\omega_0(1\,\bar{1}\,\bar{1}')+[\delta(\bar{1}\,\bar{2})+\delta(\bar{1}'\bar{2})]\\&\quad\times\omega_0(1\,\bar{1}\,\bar{1}'\bar{2}')+[\delta(\bar{1}\,\bar{2}')+\delta(\bar{1}'\,\bar{2}')]\\&\quad\times\omega_0(1\,\bar{1}\,\bar{1}'\bar{2})+\omega_0(1\,\bar{1}\,\bar{1}'\bar{2}\,\bar{2}')\}\,.\end{aligned} \tag{2.13}$$

C. Time-Dependent Correlation Functions

The basic quantity of interest in the discussion will be the time-dependent correlation function

$$C_s(12;t-t')=\langle f_s(1,t)\,f_s(2,t')\rangle\,, \tag{2.14}$$

where the fundamental fields are displaced in time. One is also interested in the Fourier transform of this quantity

$$C_s(12;\omega)=\int_{-\infty}^{+\infty}d(t-t')\,e^{+i\omega(t-t')}\,C_s(12;t-t')\,, \tag{2.15}$$

and the Laplace transform

$$\begin{aligned}C_s(12)&=-i\int_0^{+\infty}d\,(t-t')\,e^{+iz(t-t')}\,C_s(12;t-t')\\&=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\,\frac{C_s(12;\omega)}{z-\omega}\,,\end{aligned} \tag{2.16}$$

where $\mathrm{Im}z>0$. One can deduce a useful representation of $C_s(12)$ if one notes the time propagation property of Koopman's operator[34]

$$f_s(1,t)=e^{+iLt}f_s(1)\,, \tag{2.17}$$

where L is the Liouville operator

$$L=L_0+L_I\,, \tag{2.18a}$$

with the free part

$$L_0 = -i \sum_{i=1}^{N} \frac{\vec{p}_i \cdot \nabla_{r_i}}{m} \tag{2.18b}$$

and the interaction part

$$L_I = i \sum_{i \neq j=1}^{N} \nabla_{r_i} V(r_i - r_j) \cdot \nabla_{p_i} . \tag{2.18c}$$

Using (2.17) together with the time-translational invariance of the equilibrium ensemble, (2.16) can be written as

$$\begin{aligned} C_s(12) &= -i \int_0^{+\infty} d(t-t') \langle f_s(2)\, e^{+i(z+L)(t-t')} f_s(1) \rangle \\ &= \langle f_s(2) [z+L]^{-1} f_s(1) \rangle . \end{aligned} \tag{2.19}$$

In the following discussion it will also be useful to consider the correlation functions

$$C(1\,\bar{1};2) = \langle f_s(2) [z+L]^{-1} g(1\,\bar{1}) \rangle , \tag{2.20}$$

$$C(1;2\,\bar{2}) = \langle g(2\,\bar{2}) [z+L]^{-1} f_s(1) \rangle , \tag{2.21}$$

$$C(1\,\bar{1};2\,\bar{2}) = \langle g(2\,\bar{2}) [z+L]^{-1} g(1\,\bar{1}) \rangle , \tag{2.22}$$

and, among other obvious generalizations,

$$C(1\,\bar{1}\,\bar{1}';2\,\bar{2}\,\bar{2}') = \langle g(2\,\bar{2}\,\bar{2}') [z+L]^{-1} g(1\,\bar{1}\,\bar{1}') \rangle . \tag{2.23}$$

III. EQUATIONS OF MOTION

A. Hierarchy

In developing techniques for calculating these correlation functions it will be useful to obtain the equations of motion they obey in Laplace transform space. First one needs to know the effect of the Liouville operator on the fundamental fields. It is shown in Appendix A that

$$L f_s(1) = -L_0(1) f_s(1) - \int d\bar{1}\, L_I(1\,\bar{1})\, g(1\,\bar{1}) , \tag{3.1}$$

where $L_0(1)$ is the single-particle Liouville operator

$$L_0(1) = -i \vec{p}_1 \cdot \nabla_{r_1}/m , \tag{3.2}$$

and $L_I(1\,\bar{1})$ is the interaction part of the two-particle Liouville operator[35]

$$L_I(1\,\bar{1}) = i \nabla_{r_1} V(\vec{r}_1 - \vec{r}_{\bar{1}}) \cdot (\nabla_{p_1} - \nabla_{p_{\bar{1}}}) . \tag{3.3}$$

It is also easy to show that the effect of the Liouville operator on $g(1\,\bar{1})$ is given by

$$\begin{aligned} L g(1\,\bar{1}) = &-L(1\,\bar{1})\, g(1\,\bar{1}) \\ &- \int d\bar{1}' [L_I(1\,\bar{1}') + L_I(\bar{1}\,\bar{1}')]\, g(1\,\bar{1}\,\bar{1}') . \end{aligned} \tag{3.4}$$

The effect of L in (3.1) and (3.4) is to introduce a field depending on the coordinates of one more particle. It is a simple matter to combine the definitions (2.20) through (2.23) with (3.1) and (3.4) and the operator identity

$$[A-B]^{-1} = A^{-1} + A^{-1} B [A-B]^{-1} \tag{3.5}$$

to find the equations of motion

$$[z - L_0(1)]\, C_s(12) - \int d\bar{1}\, L_I(1\,\bar{1})\, C(1\,\bar{1};2) = \tilde{C}_s(12) , \tag{3.6}$$

$$[z + L_0(2)]\, C(1\,\bar{1};2) + \int d\bar{2}\, L_I(2\,\bar{2})\, C(1\,\bar{1};2\,\bar{2}) = \tilde{C}(1\,\bar{1};2) , \tag{3.7}$$

and

$$\begin{aligned} &[z - L(1\,\bar{1})]\, C(1\,\bar{1};2\,\bar{2}) \\ &\quad - \int d\bar{1}' [L_I(1\,\bar{1}') + L_I(\bar{1}\,\bar{1}')]\, C(1\,\bar{1}\,\bar{1}';2\,\bar{2}) \\ &\quad = \tilde{C}(1\,\bar{1};2\,\bar{2}) . \end{aligned} \tag{3.8}$$

It should be clear that these equations are essentially equivalent to the lowest-order equations in the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy of equations familiar from conventional nonequilibrium statistical mechanics.[36]

B. Renormalization of Collisional Effects

It has been appreciated for some time that the efficient method for avoiding the unphysical secularities inherent in a direct expansion of a time-dependent correlation function is to make approximations for the inverse of the correlation function.[37] To lowest order in the density or for very large z one knows that the inverse operator for $C_s(12)$ is just the free-streaming operator $z - L_0(1)$, where $L_0(1) = -i \vec{p}_1 \cdot \nabla_{r_1}/m$ is the one-particle Liouville operator. It is then conceptually useful to define the full inverse as a sum of this free-streaming term and another function describing the collisional effects. This reasoning has led several authors[9–11,13,38–43] to investigate $C_s(12)$ via a generalized kinetic equation of the form

$$[z - L_0(1)]\, C_s(12) - \phi_s(1\,\bar{2})\, C_s(\bar{2}\,2) = \tilde{C}_s(12) , \tag{3.9}$$

where $\tilde{C}_s(12)$ is the static-correlation function given by (2.10). $\phi_s(12)$ is called the memory function and has a relatively simple physical interpretation. Since $z - L_0(1)$ is just the operator that describes the streaming of a single free particle, it is clear then that the memory function describes the effect of the other $N-1$ particles on this free-streaming particle. The memory function renormalizes the free-particle motion in the system. A physically fruitful interpretation is that the memory function is a nonlocal non-Markovian external source acting on a single free-streaming particle. Since the free motion is well understood and all of the N-particle dynamics are included in the memory function, one can switch one's attention from the correlation function to the memory function. This can be particularly useful in those cases where one expects the memory function to be a "less varied" function of its arguments than the correlation function.[44]

The relationship of the kinetic equation (3.9) to the Boltzmann equation can be made clear via linear-response theory. It can be shown[45] that the deviation from equilibrium of the singlet distribution function $f(1)$, for a system initially held in constrained equilibrium, is proportional to $C(1\,\bar{1})\,U(\bar{1})$, where U is the weak adiabatic external potential that set up the constrained initial state. Consequently, in the region where $f(1)$ satisfies the linearized Boltzmann equation, one expects $C(1\,\bar{1})$ will also obey the linearized Boltzmann equation. It can be shown, to lowest order in the density[46] and in the limit of long time and distances, that

$$\lim_{z\to i0^+}\ \lim_{k\to 0}\varphi_s(\vec{k},\vec{p}\,\vec{p}\,',z)=iK_B(p\,p')\ , \qquad (3.10)$$

where K_B is the linearized Boltzmann collision operator for a diffusing particle. Equation (3.9) is then essentially the Boltzmann equation. Expressions for the memory function have been found that are correct to lowest order in the density, that are valid for all frequencies and wavelengths, and which satisfy all the constraints that one knows to put on it.[10,11] It is very important to realize that an approximation to lowest order in the density for the memory function corresponds to keeping an infinite set of terms in the density expansion for the correlation function.

From the discussion above it is clear that one wants to use the equations developed in Sec. III A to investigate the renormalized kinetic equation (3.9). On comparing (3.9) and (3.6) it is easily seen that[47]

$$\varphi_s(1\,\bar{2})\,C_s(\bar{2}\,2)=\int d\bar{1}\,L_I(1\,\bar{1})\,C(1\,\bar{1};2)\ . \qquad (3.11)$$

Next, it is shown in Appendix B that C_s satisfies the adjoint equation

$$[z+L_0(2)]\,C_s(12)+C_s(1\,\bar{2})\,\varphi_s^T(\bar{2}\,2;-z)=\tilde{C}_s(12) \qquad (3.12)$$

and it follows, after integrating (3.7) over $\bar{1}$ and dividing by $N-1$, that

$$C_s(1\,\bar{2})\,\varphi^T(\bar{2}\,2;-z)=\int d\bar{2}\,L_I(2\,\bar{2})\,C(1;2\,\bar{2})\ . \qquad (3.13)$$

One can then apply the operator $z+L_0(2)$ to (3.11), and use (3.7) to obtain

$$\begin{aligned}\varphi_s(1\,\bar{2})\,\tilde{C}_s(\bar{2}\,2)&-\varphi_s(1\,\bar{2})\,C_s(\bar{2}\,\bar{3})\,\varphi_s^T(\bar{3}\,2;-z)\\&=\int d\bar{1}\,L_I(1\,\bar{1})\,\tilde{C}(1\,\bar{1};2)\\&\quad-\int d\bar{1}\,d\bar{2}\,L_I(1\,\bar{1})\,L_I(2\,\bar{2})\,C(1\,\bar{1};2\,\bar{2})\ . \qquad (3.14)\end{aligned}$$

It should be noted that the first term on the right-hand side of (3.14) vanishes since L_I is odd in $\vec{r}_1-\vec{r}_{\bar{1}}$ and $\tilde{C}(1\,\bar{1};2)$ depends on $\vec{r}_{\bar{1}}$ only through the difference $\vec{r}_1-\vec{r}_{\bar{1}}$. Equation (3.14) can then be written in a more useful form if (3.11) and (3.13) are used to eliminate the ϕ_s in the quadratic term. One then has the compact expression for the memory function

$$\varphi_s(12)\,nf_0(p_2)=-\int d\bar{1}\,d\bar{2}\,L_I(1\,\bar{1})\,L_I(2\,\bar{2})\,G(1\,\bar{1};2\,\bar{2})\ , \qquad (3.15)$$

where

$$G(1\,\bar{1};2\,\bar{2})=C(1\,\bar{1};2\,\bar{2})-C(1\,\bar{1};3)\,C_s^{-1}(34)\,C(4;2\,\bar{2})\ . \qquad (3.16)$$

Equations for the memory function similar to (3.14) have been known for some time,[4,6,48] but Eqs. (3.15) and (3.16) are a new result.[49]

The calculation of ϕ_s (and correspondingly C_s) has now been "reduced" to calculating the correlation function $C(1\,\bar{1};2\,\bar{2})$. It should be immediately clear that this is more difficult than calculating C_s since one now has a four-point function rather than a two-point function. It will be shown, however, that one can make simple approximations for $C(1\,\bar{1};2\,\bar{2})$ which lead to nontrivial results for ϕ_s. An important step in motivating these approximations is to realize that just as $C_s(12)$ satisfies a kinetic equation in terms of an effective one-body "source" so also $C(1\,\bar{1};2\,\bar{2})$ satisfies a kinetic equation in terms of an effective two-body "source":

$$[z-L(1\,\bar{1})]\,C(1\,\bar{1};2\,\bar{2})-M(1\,\bar{1};3\,\bar{3})\,C(3\,\bar{3};2\,\bar{2})=\tilde{C}(1\,\bar{1};2\,\bar{2})\ . \qquad (3.17)$$

It should be immediately clear from (3.8) that

$$M(1\,\bar{1};3\,\bar{3})\,C(3\,\bar{3};2\,\bar{2})=\int d\bar{1}'\,[L_I(1\,\bar{1}')+L_I(\bar{1}\,\bar{1}')]\,C(1\,\bar{1}\,\bar{1}';2\,\bar{2})\ . \qquad (3.18)$$

As one expects in a "hierarchy" approach, M is determined by an even-higher-order correlation function. One can follow the same method of attack that was used to obtain (3.15) to obtain the result

$$\begin{aligned}M(1\,\bar{1};3\,\bar{3})\,\tilde{C}(3\,\bar{3};2\,\bar{2})&=\int d\bar{1}'\,[L_I(1\,\bar{1}')+L_I(\bar{1}\,\bar{1}')]\,\tilde{C}(1\,\bar{1}\,\bar{1}';2\,\bar{2})\\&\quad-\int d\bar{1}'\,d\bar{2}'\,[L_I(1\,\bar{1}')+L_I(\bar{1}\,\bar{1}')]\\&\qquad\times[L_I(2\,\bar{2}')+L_I(\bar{2}\,\bar{2}')]\,G(1\,\bar{1}\,\bar{1}';2\,\bar{2}\,\bar{2}') \qquad (3.19)\end{aligned}$$

and

$$\begin{aligned}G(1\,\bar{1}\,\bar{1}';2\,\bar{2}\,\bar{2}')&=C(1\,\bar{1}\,\bar{1}';2\,\bar{2}\,\bar{2}')\\&\quad-C(1\,\bar{1}\,\bar{1}';3\,\bar{3})\,C^{-1}(3\,\bar{3};4\,\bar{4})\,C(4\,\bar{4};2\,\bar{2}\,\bar{2}')\ . \qquad (3.20)\end{aligned}$$

C. Properties of M

One can continue this process of introducing higher-order memory functions, but the usefulness is not transparent. It is more instructive to stop and consider the physical interpretation and properties of M. It can be seen from (3.17) that M serves as an effective external source which modifies the dynamics of a two-particle system. Clearly M is of first order in the density.

It can be seen from (3.19) that M has a static (independent of z) part

$$M^{(s)}(1\,\bar{1};3\,\bar{3})\,\tilde{C}(3\,\bar{3};2\,\bar{2})$$
$$=\int d\bar{1}'\,[L_I(1\,\bar{1}')+L_I(\bar{1}\,\bar{1}')]\,\tilde{C}(1\,\bar{1}\,\bar{1}';2\,\bar{2})\;. \quad (3.21)$$

Using (3.4) one can rewrite (3.21) as

$$M^{(s)}(1\,\bar{1};3\,\bar{3})\,\tilde{C}(3\,\bar{3};2\,\bar{2})$$
$$=-L_I(1\,\bar{1})\,\tilde{C}(1\,\bar{1};2\,\bar{2})-\langle g(2\,\bar{2})\,L_I\,g(1\,\bar{1})\rangle\;. \quad (3.22)$$

Consequently the "static" operator in (3.17) can be written

$$L(1\,\bar{1})\,\tilde{C}(1\,\bar{1};2\,\bar{2})+M^{(s)}(1\,\bar{1};3\,\bar{3})\,\tilde{C}(3\,\bar{3};2\,\bar{2})$$
$$\equiv\mathcal{L}(1\,\bar{1};3\,\bar{3})\,\tilde{C}(3\,\bar{3};2\,\bar{2})\;, \quad (3.23)$$

where

$$\mathcal{L}(1\,\bar{1};3\,\bar{3})\,\tilde{C}(3\,\bar{3};2\,\bar{2})=-\langle g(2\,\bar{2})\,L g(1\,\bar{1})\rangle\;. \quad (3.24)$$

It is clear from (3.24) that $\mathcal{L}$ satisfies the symmetry condition

$$\mathcal{L}(1\,\bar{1};3\,\bar{3})\,\tilde{C}(3\,\bar{3};2\,\bar{2})=-\tilde{C}(1\,\bar{1};3\,\bar{3})\,\mathcal{L}(2\,\bar{2};3\,\bar{3})\;. \quad (3.25)$$

While the right-hand side of (3.24) can be evaluated exactly in terms of $\omega_0(1\,\bar{1}\,\bar{2})$ and $\omega_0(1\,\bar{1})$ this result will not be needed here. If one ignores triplet correlation functions, then the interaction part of $\mathcal{L}$ can be written[50]

$$\mathcal{L}_I(1\,\bar{1};2\,\bar{2})$$
$$=-i\beta^{-1}\,\nabla_{r_1}\ln g(\vec{r}_1-\vec{r}_{\bar{1}})\cdot(\nabla_{p_1}-\nabla_{p_{\bar{1}}})\,\delta(12)\,\delta(\bar{1}\,\bar{2}) \quad (3.26)$$

and the interparticle force is replaced by the mean force.[51,52] If one further expands (3.26) to lowest order in the density, one finds

$$\mathcal{L}_I(1\,\bar{1};2\,\bar{2})=L_I(1\,\bar{1})\,\delta(12)\,\delta(\bar{1}\,\bar{2})\;. \quad (3.27)$$

On comparing (3.19) and (3.21) it can be seen that the "collisional" part of M is defined by

$$M_c(1\,\bar{1};3\,\bar{3})\,\tilde{C}(3\,\bar{3};2\,\bar{2})$$
$$=-\int d\bar{1}'\,d\bar{2}'\,[L_I(1\,\bar{1}')+L_I(\bar{1}\,\bar{1}')]$$
$$\times[L_I(2\,\bar{2}')+L_I(\bar{2}\,\bar{2}')]\,G(1\,\bar{1}\,\bar{1}';2\,\bar{2}\,\bar{2}')\;. \quad (3.28)$$

One sees immediately that (3.28) leads to a "conservation of particles" property

$$\int dp_1\,dp_{\bar{1}}\,M_c(1\,\bar{1};2\,\bar{2})=0\;, \quad (3.29)$$

and M_c satisfies the symmetry condition

$$M_c(1\,\bar{1};3\,\bar{3})\,\tilde{C}(3\,\bar{3};2\,\bar{2})=-\tilde{C}(1\,\bar{1};3\,\bar{3})\,M_c(2\,\bar{2};3\,\bar{3};-z)\;. \quad (3.30)$$

If one notes that

$$\int\frac{d\bar{1}}{(N-2)}\,G(1\,\bar{1}\,\bar{1}';2\,\bar{2}\,\bar{2}')=C(1\,\bar{1}';2\,\bar{2}\,\bar{2}')$$
$$-C(1\,\bar{1}';3\,\bar{3})\,C^{-1}(3\,\bar{3};4\,\bar{4})\,C(4\,\bar{4};2\,\bar{2}\,\bar{2}')=0\;, \quad (3.31)$$

one then has the very useful property

$$\int\frac{d\bar{1}}{(N-2)}\,M_c(1\,\bar{1};2\,\bar{2})=0\;. \quad (3.32)$$

There are a few interesting observations one can make in light of the properties of M just discussed. First, if one wants to derive (3.6) from (3.17), as is usual in the BBGKY hierarchy approach,[36] by integrating over the $\bar{1}$ index, then, owing to (3.32), it is only the static part of M that contributes. Next, it should be clear that M_s has the effect of replacing a bare interaction L_I with an average force between two particles. This effect could be quite important at high densities. A third observation is that these equations are exact and they can be used to generate phenomenological descriptions. For example, it is rather simple to extract the short-time, large-z behavior for these quantities. This could lead to an analysis of M similar to that carried out for ϕ by Duderstadt and Akcasu,[39] which led to good agreement with computer calculations for short times. On the other hand, of course, one can continue on with a first-principles approach.

IV. PLATEAU-VALUE PROBLEM AND PROJECTION OPERATORS

A. Plateau-Value Problem

In any first principle analysis of the microscopic expression for the memory function given by (3.14) or equivalently by (3.15), one is immediately faced with the so-called plateau-value problem. This problem has been discussed by Kirkwood,[53] Zwanzig,[54] Martin,[55] Mori,[6] Kubo,[56] and, in his original formulation of the mode-mode coupling theory, by Kawasaki.[57] The difficulty can easily be seen from (3.14):

$$\varphi_s(12)\,nf_0(p_2)$$
$$=\Phi(12)+\varphi_s(1\,\bar{3})\,C_s(\bar{3}\,3)\,\varphi_s^T(32;-z)\,nf_0(p_2)\;, \quad (4.1)$$

where Φ is the force-force correlation function (FFC) and is given by the last term on the right-hand side of (3.14). In terms of spatial Fourier transforms (4.1) can be rewritten as

$$\varphi_s(\vec{k},\vec{p}_1\vec{p}_2,z)\,nf_0(p_2)=\Phi(\vec{k},\vec{p}_1\vec{p}_2,z)$$
$$-\varphi_s(\vec{k},\vec{p}_1\vec{\bar{p}},z)\,C_s(\vec{k},\vec{\bar{p}}\vec{\bar{p}}_1',z)\,\varphi_s(\vec{k},\vec{\bar{p}}'\vec{p}_1',z)\,nf_0(p_2)\;. \quad (4.2)$$

One can then solve this equation for ϕ in terms of Φ. Then, schematically, neglecting the $\vec{k}\cdot\vec{p}/m$ terms for simplicity, one finds

$$\varphi_s=z\,\Phi\,[z+\Phi]^{-1}\;. \quad (4.3)$$

To lowest order in the density the memory function and the FFC are equal. If one wants to use (4.3) to go to higher densities and if one approximates Φ in (4.3) by its low-density value, which approaches a constant as $z \to 0$, one finds that the memory function vanishes as z goes to zero. This leads to the unphysical result that the associated transport coefficients vanish. The previously mentioned authors have "solved" this difficulty in the case where the memory function is that associated with the conserved quantities in the system. In that case they required that one take the limit of slowly varying spatial quantities before taking the $z \to i0^+$ limit. Then, in this case, where the FFC corresponds to the current associated with the conserved quantities, one has

$$\Phi_{\text{current}} \to k^2 \Delta(k, z) , \tag{4.4}$$

where Δ goes to a well-defined constant as k and z go to zero. Consequently, one has then

$$\lim_{k \to 0} \frac{1}{k^2} \varphi_{\text{conserved}} = \lim_{k \to 0} \frac{1}{k^2} z k^2 \Delta(\vec{k}_1 z) [z + k^2 \Delta(k, z)]^{-1}$$

$$= \Delta(\vec{0}, z) \tag{4.5}$$

and the transport coefficient associated with the memory function has a well-defined value as k, and then z, go to zero. Clearly this approach does not lead to a useful method for approximating ϕ for arbitrary k and z. Also, for our matrix memory function, there are momentum moments of Φ which do not go as k^2 for small k and, therefore, this limiting procedure is not useful. One must, in the final analysis, face up to the collective behavior in the FFC which arises for long times. These collective effects give rise to a long-time contribution such that the time integral over the FFC (or limit as $z \to 0$) is zero. It can be understood from the work of Mori[6] that the memory function itself should not involve these long-time processes.[58] It is for this reason that the memory function in the Mori formalism contains the modified time propagator $e^{i(1-P_m)Lt}$ which operates in the subspace orthogonal to the subspace of conserved variables. Since this "orthogonal" subspace, by definition, must contain only rapidly decaying quantities, the memory function will decay rapidly compared with the time-correlation functions.[59]

While the Mori formalism allows one to make qualitative statements about the "separation" of time scales, it is very difficult to make mathematical headway with the "thermodynamic projection operator" introduced by Mori. In some sense the Mori expression for the memory function is just a convenient way of writing (4.1). These expressions do not tell one how to combine the two pieces of $G(1\bar{1}; 2\bar{2})$ in (3.15) such that the collective behavior in the two pieces cancel. Thus, while one wants to avoid the mathematical difficulties presented by Mori's N-particle projection operator, one does need to remove that part of $C(1\bar{1}; 2\bar{2})$ in the FFC that has a component along $C_s(12)$ and which therefore contains the unwanted collective effects.

B. Two-Particle Vector Space

Before going on to further formal manipulations, it is convenient to introduce a linear vector space spanned by the complete and orthonormal set of vectors

$$|1\bar{1}\rangle = |1\rangle \otimes |\bar{1}\rangle ,$$

where

$$\langle 1\bar{1} | 2\bar{2}\rangle = \delta(12)\,\delta(\bar{1}\bar{2}) \tag{4.6}$$

and

$$1 = \int d1\, d\bar{1}\, |1\bar{1}\rangle\langle 1\bar{1}| . \tag{4.7}$$

One can then define the operators $C(z)$, $\tilde{C}$, and $M(z)$ such that

$$C(1\bar{1}; 2\bar{2}) = \langle 1\bar{1} | C(z) | 2\bar{2}\rangle , \tag{4.8}$$

$$\tilde{C}(1\bar{1}; 2\bar{2}) = \langle 1\bar{1} | \tilde{C} | 2\bar{2}\rangle , \tag{4.9}$$

$$M(1\bar{1}; 2\bar{2}) = \langle 1\bar{1} | M(z) | 2\bar{2}\rangle . \tag{4.10}$$

The two-particle Liouville operator is diagonal on these vectors:

$$\langle 1\bar{1} | L | 2\bar{2}\rangle = L(1\bar{1})\,\delta(12)\,\delta(\bar{1}\bar{2}) . \tag{4.11}$$

Using this notation and the completeness of the states, one can write the kinetic equation for $C(z)$ in the operator form

$$[z - L - M(z)]\, C(z) = \tilde{C} , \tag{4.12}$$

which one can formally invert to find

$$C(1\bar{1}; 2\bar{2}) = \langle 1\bar{1} | [z - V]^{-1} \tilde{C} | 2\bar{2}\rangle , \tag{4.13}$$

where $V = L + M$. Equation (4.13) will be used to great advantage in Sec. V. It is also quite useful to introduce "transpose" operators

$$\langle 1\bar{1} | A^T | 2\bar{2}\rangle \equiv \langle 2\bar{2} | A | 1\bar{1}\rangle . \tag{4.14}$$

Then, for example

$$\langle 1\bar{1} | L^T | 2\bar{2}\rangle = \langle 2\bar{2} | L | 1\bar{1}\rangle = L(2\bar{2})\,\delta(12)\,\delta(\bar{1}\bar{2}) \tag{4.15}$$

and

$$\langle 1\bar{1} | A L_I^T | 2\bar{2}\rangle = L_I(2\bar{2}) \langle 1\bar{1} | A | 2\bar{2}\rangle . \tag{4.16}$$

One can then write (3.25) and (3.30) in the compact forms

$$\mathcal{L} \tilde{C} = - \tilde{C} \mathcal{L}^T \tag{4.17}$$

and

$$M_c(z) \tilde{C} = - \tilde{C} M_c^T(-z) . \tag{4.18}$$

C. Useful Expression for the Memory Function

In order to write the expression (3.15) for the memory function in a more manageable form, it is convenient to introduce the projection operator

$$\langle 1\,\bar{1}|P|2\,\bar{2}\rangle = \tilde{C}(1\,\bar{1};3)\,\tilde{C}_s^{-1}(32)/(N-1) \qquad (4.19)$$

which, for the case of self-diffusion, can also be written

$$\langle 1\,\bar{1}|P|2\,\bar{2}\rangle = \omega_0(1\,\bar{1})\,(nf_0(p_1))^{-1}\,\delta(12)/(N-1)\,. \qquad (4.20)$$

The proof that this is a projection operator ($P^2 = P$) is straightforward. One can now use P and its complement $Q = 1 - P\,(PQ = 0)$ to rewrite the formal expression (4.13) for $C(1\,\bar{1};2\,\bar{2})$. Using the operator identity (3.5) one can write

$$\begin{aligned}\langle 1\,\bar{1}|[z-V]^{-1}\tilde{C}|2\,\bar{2}\rangle &= \langle 1\,\bar{1}|[z-(P+Q)V]^{-1}\tilde{C}|2\bar{2}\rangle \\ &= \langle 1\,\bar{1}|[z-QV]^{-1}\tilde{C}|2\,\bar{2}\rangle \\ &\quad + \langle 1\,\bar{1}|[z-V]^{-1}PV[z-QV]^{-1}\tilde{C}|2\,\bar{2}\rangle\,. \end{aligned} \qquad (4.21)$$

It is then easy to show that

$$\langle 1\,\bar{1}|[z-V]^{-1}P|2\,\bar{2}\rangle = C(1\,\bar{1};4)\,\tilde{C}_s^{-1}(42)/(N-1)\,, \qquad (4.22)$$

and with

$$C_Q(1\,\bar{1};2\,\bar{2}) \equiv \langle 1\,\bar{1}|[z-QV]^{-1}\tilde{C}|2\,\bar{2}\rangle$$

one has

$$\begin{aligned} C(1\,\bar{1};2\,\bar{2}) &= C_Q(1\,\bar{1};2\,\bar{2}) + C(1\,\bar{1};4)\,\tilde{C}_s^{-1}(43)(N-1)^{-1} \\ &\quad \times\langle 3\,\bar{3}|V[z-QV]^{-1}\tilde{C}|2\,\bar{2}\rangle\,. \end{aligned} \qquad (4.23)$$

It is shown in Appendix C that

$$\begin{aligned} &\tilde{C}_s^{-1}(43)(N-1)^{-1}\int d\bar{3}\langle 3\,\bar{3}|V\,[z-QV]^{-1}\tilde{C}|2\,\bar{2}\rangle \\ &\quad = C_s^{-1}(4\,\bar{3})\,C(\bar{3};2\,\bar{2}) - C_s^{-1}(42)\,\omega_0(2\,\bar{2})/z\,. \end{aligned} \qquad (4.24)$$

Combining this result with (4.23) one finds that

$$\begin{aligned} C(1\,\bar{1};2\,\bar{2}) &= C_Q(1\bar{1};2\,\bar{2}) + C(1\,\bar{1};4)\,C_s^{-1}(4\,\bar{4})\,C(\bar{4};2\,\bar{2}) \\ &\quad - C(1\,\bar{1};4)\,C_s^{-1}(42)\,\omega_0(2\,\bar{2})/z \end{aligned} \qquad (4.25)$$

and, using (3.16),

$$G(1\,\bar{1};2\,\bar{2}) = C_Q(1\,\bar{1};2\,\bar{2}) - C(1\,\bar{1};4)\,C_s^{-1}(42)\,\omega_0(2\,\bar{2})/z\,. \qquad (4.26)$$

It is clear from (4.26) that

$$\int d\bar{2}\,L_I(2\,\bar{2})\,G(1\,\bar{1};2\,\bar{2}) = \int d\bar{2}\,L_I(2\,\bar{2})\,C_Q(1\,\bar{1};2\,\bar{2})\,, \qquad (4.27)$$

since

$$\int d\bar{2}\,L_I(2\,\bar{2})\,\omega_0(2\,\bar{2}) = 0$$

due to the oddness of the spatial integration. One then has the compact expression for the memory function

$$\begin{aligned} \varphi_s(12)\,nf_0(p_2) &= -\int d\bar{1}\,d\bar{2} \\ &\quad \times\langle 1\,\bar{1}|L_I[z-QV]^{-1}\tilde{C}\,L_I^T|2\,\bar{2}\rangle\,, \end{aligned} \qquad (4.28)$$

which is very similar in form to the Mori expression. There are, however, some important differences. First, the projection operator introduced here acts only on a two-particle vector space. The Mori projection operator P_M projects onto an N-particle vector space. Next, since $V = \mathcal{L} + M_c$ and $PM_c = 0$, it follows that the projection operator defined by (4.19) acts only on $\mathcal{L}$ in (4.28). It can further be shown (see Appendix D) that the term $P\mathcal{L}_0$ does not contribute and can be neglected. Consequently the projection operator appears only in the form $P\mathcal{L}_I$, which can be evaluated more explicitly (see Appendix E) and is of first order in the density. In particular, to lowest order in the density, $Q\mathcal{L}_I = L_I$. In comparison, the form $P_M L$ that appears in the "modified time propagator" in the Mori formalism is not completely defined until one specifies the field on which it operates.

One can now use the identity (3.5) to iterate (4.28) and give

$$\begin{aligned} \varphi_s(12)\,nf_0(p_2) &= -\int d\bar{1}\,d\bar{2} \\ &\quad \times\langle 1\,\bar{1}|L_I[z-Q\mathcal{L}]^{-1}\tilde{C}\,L_I^T|2\,\bar{2}\rangle \\ &\quad -\int d\bar{1}\,d\bar{2}\langle 1\,\bar{1}|L_I[z-Q\mathcal{L}]^{-1} \\ &\quad \times M_c[z-Q\mathcal{L}-M_c]^{-1}\tilde{C}\,L_I^T|2\,\bar{2}\rangle\,. \end{aligned} \qquad (4.29)$$

The first term in (4.29),

$$\begin{aligned} \varphi_s^0(12)\,nf_0(p_2) &= -\int d\bar{1}\,d\bar{2} \\ &\quad \times\langle 1\,\bar{1}|L_I[z-Q\mathcal{L}]^{-1}\tilde{C}\,L_I^T|2\,\bar{2}\rangle\,, \end{aligned} \qquad (4.30)$$

contains the information that is found in the Boltzmann and Enskog equations. This is discussed in Sec. V. It is noted here that this leading term satisfies the symmetry condition

$$\varphi_s^0(12)\,nf_0(p_2) = -\varphi_s^0(21;-z)\,nf_0(p_1)\,. \qquad (4.31)$$

One can prove this by eliminating the projection operator and reintroducing the associated $G(M_c = 0)$ propagator.

One can now go on to discuss the second terms in (4.29). This term has a somewhat assymetric appearance, with the L_I on the left "shielded" by a generalized two-particle propagator but with a bare L_I^T on the right. One also wants to shield the L_I^T operator. To do this one must commute the full propagator with $\tilde{C}$. As a first step in doing this, one can use (4.27) and the fact that $G(z) = -G^T(-z)$ to find

$$\int d\bar{2}\,C_Q(z)\,L_I^T|2\,\bar{2}\rangle = \int d\bar{2}\,[-G^T(-z)]L_I^T|2\,\bar{2}\rangle.$$

Then, using (4.23), one finds that

$$\begin{aligned} \langle 1\,\bar{1}|G^T(-z)|2\,\bar{2}\rangle &= \langle 1\,\bar{1}|C_Q^T(-z)|2\,\bar{2}\rangle \\ &\quad - C(2\,\bar{2};4;-z)\,C_s^{-1}(43;-z)\,nf_0(3) \\ &\quad \times[-z\,\omega_0(3\,\bar{4})]^{-1}\langle 3\,\bar{4}|P\tilde{C}|1\,\bar{1}\rangle\,, \end{aligned}$$

which leads to a term in (4.29) proportional to

$$M_c(1\,\bar{1};3\,\bar{3})\langle 5\,\bar{5}|P\tilde{C}|3\,\bar{3}\rangle=\langle 1\,\bar{1}|M_c\tilde{C}P^T|5\,\bar{5}\rangle=0\,. \tag{4.32}$$

One has then that

$$\int d\bar{2}\,M_cC_Q(z)\,L_I^T|2\,\bar{2}\rangle=-\int d\bar{2}\,M_cC_Q^T(-z)\,L_I^T|2\,\bar{2}\rangle\,, \tag{4.33}$$

and the second term in (4.29) can be written as

$$\delta\varphi_s(12)nf_0(p_2)=-\int d\bar{1}\,d\bar{2}\langle 1\,\bar{1}|L_I[z-Q\mathcal{L}]^{-1}$$
$$\times M_c\tilde{C}[z+(Q\mathcal{L})^T+M_c^T(-z)]^{-1}L_I^T|2\,\bar{2}\rangle\,. \tag{4.34}$$

One can now iterate this expression once more using (3.5) to find

$$\delta\varphi_s(12)nf_0(p_2)=-\int d\bar{1}\,d\bar{2}\langle 1\,\bar{1}|L_I[z-Q\mathcal{L}]^{-1}$$
$$\times M_c\tilde{C}[z+(Q\mathcal{L})^T]^{-1}L_I^T|2\,\bar{2}\rangle$$
$$+\int d\bar{1}\,d\bar{2}\langle 1\,\bar{1}|L_I[z-Q\mathcal{L}]^{-1}$$
$$\times M_c\tilde{C}[z+(Q\mathcal{L})^T+M_c^T(-z)]^{-1}M_c^T(-z)$$
$$\times[z+(Q\mathcal{L})^T]^{-1}L_I^T|2\,\bar{2}\rangle\,. \tag{4.35}$$

One can show, using arguments like those below (4.31), that these two terms separately satisfy the symmetry condition (B5). One sees therefore that each of the three terms in the expression for the memory function satisfies this symmetry condition separately, and all of the L_I's are shielded.

It is useful to take one more step in the general formulation. First one defines the classical T matrix

$$\langle 1\,\bar{1}|T|2\,\bar{2}\rangle=\langle 1\,\bar{1}|L_I[z-Q\mathcal{L}]^{-1}[z-L_0]|2\,\bar{2}\rangle \tag{4.36}$$

and

$$T^T(z)=[z-L_0^T][z-(\varphi\mathcal{L})^T]^{-1}L_I^T\,. \tag{4.37}$$

Then, with the introduction of these T matrices into the exact expression for the memory function, one has

$$\varphi_s(12)nf_0(p_2)=-\int d\bar{1}\,d\bar{2}\langle 1\,\bar{1}|TG_0\tilde{C}L_I^T|2\,\bar{2}\rangle$$
$$+\int d\bar{1}\,d\bar{2}\langle 1\,\bar{1}|TG_0M_c\tilde{C}G_0^T(-z)\,T^T(-z)|2\,\bar{2}\rangle$$
$$-\int d\bar{1}\,d\bar{2}\langle 1\,\bar{1}|TG_0M_cC_Q(z)$$
$$\times M_c^T(-z)\,G_0^T(-z)\,T^T(-z)|2\,\bar{2}\rangle\,, \tag{4.38}$$

where

$$G_0(z)=[z-L_0]^{-1}\,, \tag{4.39}$$

$$G_0^T(-z)=-[z+L_0^T]^{-1}\,. \tag{4.40}$$

These exact expressions are useful only if one can make approximations in a natural way. In Sec. V it will be shown that even the simplest type of approximation leads to nontrivial and interesting results.

V. ENSKOG APPROXIMATION

It should be clear that M_c has the effect of changing two-particle collisions via dynamic shielding and by introducing recollision events. Consequently the approximation $M_c=0$ corresponds to neglecting these dynamical effects. One then has the approximation for the memory function

$$\varphi_s^0(12)nf_0(p_2)=-\int d\bar{1}\,d\bar{2}\langle 1\,\bar{1}|TG_0\tilde{C}L_I^T|2\,\bar{2}\rangle\,. \tag{5.1}$$

It should first be noted that (5.1) is not strictly a low-density approximation since $\tilde{C}$ and the $\mathcal{L}$ operator in T include the static effect due to the structure in the system. Second, it should be noted that (5.1) saturates the first sum rule (coefficient of z^{-1}) for the full $\phi_s(z)$. As a first approximation in analyzing (5.1) it is reasonable to assume that one can approximate $Q\mathcal{L}_I$ with its low-density value L_I.[60] The T matrix in (5.1) then reduces to the standard form introduced by Zwanzig.[17]

In order to go further one must introduce some form for the interparticle potential. In this paper and in II the case of a hard-sphere gas is treated. This is motivated by mathematical convenience and the desire to compare the results with the machine calculations of Alder, Gass, and Wainwright.[2] In applying the theory developed here to real gases it is important to add an attractive tail to the hard core. Rice and Allmatt[61] have argued that this tail has the important randomizing effect of destroying correlations between clusters of particles. This randomization involves adding a Fokker–Planck term to the hard-core expression for the memory function. It follows from the work of Forster and Martin[41] and Akcasu and Duderstadt[38] that the Fokker–Planck term follows from an expansion of the memory function to lowest order in the weak part of the potential. This tail is neglected in the following. Using (4.30) one can write

$$\varphi_s^0(12)nf_0(p_2)=-\int d\bar{1}\,d\bar{2}\,L_I(1\,\bar{1})$$
$$\times[z-L(1\,\bar{1})]^{-1}\langle 1\,\bar{1}|\tilde{C}L_I^T|2\,\bar{2}\rangle\,. \tag{5.2}$$

If one notes that

$$\int d\bar{2}\langle 1\,\bar{1}|\tilde{C}L_I^T|2\,\bar{2}\rangle=-\omega_0(1\,\bar{1})\,\tilde{L}_I(1\,\bar{1})\,\delta(12)\,, \tag{5.3}$$

where

$$\tilde{L}_I(1\,\bar{1})=-i\beta^{-1}[\nabla_{r_1}\ln g(\mathrm{r}_1-\mathrm{r}_{\bar{1}})]\cdot(\nabla_{p_1}-\nabla_{p_{\bar{1}}})\,, \tag{5.4}$$

one can write (5.2) as

$$\varphi_s^0(12)nf_0(p_2)=\int d\bar{1}\,L_I(1\,\bar{1})$$
$$\times[z-L(1\,\bar{1})]^{-1}\omega_0(1\,\bar{1})\,\tilde{L}_I(1\,\bar{1})\,\delta(12)\,. \tag{5.5}$$

To put this in a more convenient form one introduces the identity $1=\int d\bar{2}\,\delta(1-\bar{2})$ and Fourier transforms over the spatial variables $\vec{\mathrm{r}}_1$ and $\vec{\mathrm{r}}_2$ to obtain

$$\varphi_s^0(\vec{k}, \vec{p}_1\vec{p}_2, z)\, n f_0(p_2) = \int \frac{d\bar{1}\, d\bar{2}}{V}\, f_k(p_1, \bar{1})\, L_I(\bar{2}\bar{1}) \times [z - L(\bar{2}\bar{1})]^{-1}\, \omega_0(\bar{2}\bar{1})\, \tilde{L}_I(\bar{2}\bar{1})\, f_{-k}(p_2, \bar{1}) , \quad (5.6)$$

where

$$f_k(\vec{p}_1, \bar{1}) = e^{+i\vec{k}\cdot\vec{r}_{\bar{1}}}\, \delta(\vec{p}_1 - \vec{p}_{\bar{1}}) . \quad (5.7)$$

After integrating successively by parts one can write (5.6) in the form

$$\varphi_s^0(\vec{k}, \vec{p}_1\vec{p}_2, z)\, n f_0(p_2) = -\int \frac{d\bar{1}\, d\bar{2}}{V}\, \omega_0(\bar{1}\bar{2}) \times [\tilde{L}_I(\bar{2}\bar{1})\, f_{-k}(\vec{p}_2, \bar{1})]\, [z + L(\bar{2}\bar{1})]^{-1} \times L_I(\bar{2}\bar{1})\, f_k(\vec{p}_1, \bar{1}) . \quad (5.8)$$

It can easily be seen that this equation is the same as the memory function discussed in Ref. 62, where one replaces $g(r)$ in (5.8) by $e^{-\beta V(r)}$. One can use the results derived in Ref. 62 if one makes the approximation[63]

$$\nabla_{r_1} g(\mathrm{r}_1 - \mathrm{r}_{\bar{1}}) \approx \tilde{g}(r_0)\, \nabla_{r_1} e^{-\beta V(r_1 - r_{\bar{1}})} . \quad (5.9)$$

The corrections to this approximation in (5.8) have been investigated and for $k, z \to 0$ (where the correction should be the largest) the relative correction to (5.9) is $(0.29\eta + 0.21\eta^2)/\tilde{g}(r_0)$ to second order in η. This is a rather small correction. With this approximation and assuming a hard-core interaction, (5.8) is in a form evaluated in Ref. 62. One finds then

$$\varphi_s^E(\vec{k}, \vec{p}_1\vec{p}_2, z)\, n f_0(p_2) = i n^2 r_0^2 \tilde{g}(r_0)\, (\beta/\pi m)^3 \times \int d\Omega_{\hat{r}}\, d^3\bar{p}\, d^3\alpha\, e^{-\beta(\alpha^2+\bar{p}^2)/m}\, (2\hat{r}\cdot\bar{p}/m)\, \Theta_-(\hat{r}\cdot\bar{p}) \times \delta(\vec{p}_2 - \vec{\alpha} + \vec{\bar{p}})\, [\delta(\vec{p}_1 - \vec{\alpha} + \vec{\bar{p}}) - \delta(\vec{p}_1 - \vec{\alpha} + \vec{\bar{p}}^*)] , \quad (5.10)$$

where

$$\vec{\bar{p}}^* = \vec{\bar{p}} - 2\hat{r}(\hat{r}\cdot\vec{\bar{p}}) \quad (5.11)$$

and $\Theta_-(x)$ is the step function which is equal to one if x is less than zero and zero otherwise. The surprising simplicity of this result is discussed in Ref. 62. It is noted here that ϕ_s^E is independent of k and z in agreement with the long-maintained view that the "bare" transport coefficient is "essentially" local and Markovian. The expression for ϕ_s given by (5.10) will be referred to as the Enskog memory function for self-diffusion.

Given this Enskog memory function the question arises: How does one practically compute the diffusion constant and the momentum contracted correlation functions? This is discussed here since the analysis is simpler than it initially appears. From (3.9) it appears, to find $C_s(kz)$, that one must solve an integral equation due to the coupling between the momentum indices. Strictly speaking this is true but there is a vast literature available on approximation techniques for solving this "Boltzmann" equation. The general ideas discussed here have been treated elsewhere,[13,41] so the discussion will be brief. If one introduces a complete set of momentum states $|i\rangle$, as defined by Eqs. (3.9), and (6.1)–(6.5) in Ref. 10, which are complete and orthonormal, then one can formally invert the kinetic Eq. (3.9) to obtain

$$C_{ij}(\vec{k}, z) = \langle i|[z - \hat{\omega}_0(k) - \varphi_s(k, z)]^{-1}|j\rangle , \quad (5.12)$$

where

$$\langle p|\hat{\omega}_0(k)|p'\rangle = (\vec{k}\cdot\vec{p}/m)\, \delta(\vec{p} - \vec{p}') . \quad (5.13)$$

One has then immediately that

$$S_s(\vec{k}, \omega) = -2\,\mathrm{Im}\, C_{11}(\vec{k}, \omega + i0^+) \quad (5.14)$$

and it follows from (1.3) that

$$\tilde{V}_D(z) = -i \int_0^{+\infty} dt\, e^{+izt}\, V_D(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, \frac{V_D(\omega)}{z - \omega} = \lim_{k\to 0} C_{22}(\vec{k}, z) \quad (5.15)$$

and

$$V_D(\omega) = -2\,\mathrm{Im}\, \tilde{V}_D(\omega + i0^+) . \quad (5.16)$$

Consequently, one sees that the velocity-autocorrelation function is related to the memory function by

$$\tilde{V}_D(z) = V_0^2 \langle 2|[z - \varphi_s(0, z)]^{-1}|2\rangle, \quad V_0^2 \equiv (\beta m)^{-1} . \quad (5.17)$$

In many cases, one is interested in the hydrodynamic behavior in the system. This hydrodynamic behavior reflects the existence of conservation laws that hold in the small-wave-number and -frequency regimes. One can use the projection-operator technique due to Forster[13,41] to extract this collective behavior shown by $C_s(k, z)$. This method depends on projecting out those momentum states on which ϕ_s vanishes. These states are by definition the hydrodynamical states. In the case of self-diffusion there is only one such state, the state $|1\rangle$. It is therefore desirable to define the projection operator

$$P_H = |1\rangle\langle 1| \quad (5.18)$$

and its complement $Q_H = 1 - P_H$. One can then follow Forster to write the equation for C_s,

$$C_s(\vec{k}, z) = [z + ik^2 D(k, z)]^{-1} , \quad (5.19)$$

where

$$D(\vec{k}, z) = iV_0^2 \langle 2|[z - Q_H \bar{\varphi} Q_H]^{-1}|2\rangle \quad (5.20)$$

and

$$\bar{\varphi}(k, z) = \hat{\omega}_0(\vec{k}) + \varphi_s(\vec{k}, z) . \quad (5.21)$$

Hydrodynamics[64] then tells one that the diffusion constant is given by

$$D=\lim_{z\to i0^+}\lim_{k\to 0} D(\vec{k},z)$$

$$=-iV_0^2\langle 2|(Q_H\varphi_s(0,i0^+)Q_H)^{-1}|2\rangle\ . \qquad (5.22)$$

It is interesting to note that the Einstein[65] formula

$$D=\int_0^{+\infty} dt\, V_D(t) \qquad (5.23)$$

can be written as

$$D=\lim_{z\to i0^+} i\tilde{V}_D(z)\ . \qquad (5.24)$$

On combining this with (5.17) one sees that one obtains agreement with (5.22).

The set of equations from (5.12) to (5.24) are exact. One can now evaluate these various quantities using the Enskog expression for the memory function. It is very useful to note that to a good approximation ϕ_s^E is diagonal on the state[62] $|2\rangle$ and

$$\langle 2|\varphi_s^E|2\rangle=-i\tfrac{8}{3}r_0^2\tilde{g}(r_0)n(\pi/m\beta)^{1/2}\ . \qquad (5.25)$$

Since ϕ_s^E is essentially diagonal one has, using (5.22),

$$D_E=-i(\langle 2|\varphi_s^E|2\rangle)^{-1}V_0^2=3V_0[8nV_0^2\tilde{g}(r_0)\sqrt{\pi}]^{-1}\ . \qquad (5.26)$$

The assumption that ϕ_s^E is diagonal on $|2\rangle$ leads to an error of less than 2%.[66] If one now goes back to the expression (5.17) for $V_D(z)$ and uses the approximate diagonality of ϕ_s^E on $|2\rangle$ one finds

$$V_D^E(z)=V_0^2[z-\langle 2|\varphi_s^E|2\rangle]^{-1}=V_0^2[z+iV_0^2/D_E]^{-1}\ , \qquad (5.27)$$

which immediately leads to the result

$$V_D^E(t)=V_0^2e^{-V_0^2t/D_E}\ . \qquad (5.28)$$

If one introduces the mean-free time

$$\tau=(4\sqrt{\pi}nr_0^2V_0\tilde{g}(r_0))^{-1} \qquad (5.29)$$

and measures time in units of τ, $s=t/\tau$, one finds

$$V_D^E(t)=V_0^2e^{-2s/3}\ . \qquad (5.30)$$

One has then that $V_D(t)$, in this approximation, falls to 10% of its initial value after about four mean-free times. It is clear from the work of Alder, Gass, and Wainwright[2] that this approximation for the velocity-autocorrelation function serves as a very good zeroth approximation to the "observed" result even for rather dense systems.

The calculation of $C_s(\vec{k},z)$ or equivalently $D(\vec{k},z)$ given by (5.20) are nontrivial calculations even in the Enskog approximation. One can observe that a reasonable approximation for C_s is given by the so-called Gaussian approximation[67]

$$C_s(\vec{k},t)=e^{-k^2W(t)/2} \qquad (5.31)$$

or

$$C_s(\vec{r},t)=(\pi W^2(t))^{-3/2}e^{-[r^2/W^2(t)]}\ . \qquad (5.32)$$

The validity of this approximation has been discussed by Desai and Nelkin.[68] They show that the Boltzmann equation $\tilde{g}(r_0)=1$ shows deviations from the Gaussian model that are less than 6% for the lowest "spatial moment." The width function $W(t)$ can be determined from (1.3), (5.28), and the observations that

$$\lim_{t\to 0} W(t)=0 \qquad (5.33)$$

and

$$\lim_{t\to\infty} W(t)=2tD\ . \qquad (5.34)$$

Using these results one finds without further approximation that

$$W(t)=2D[t+(D/V_0^2)(e^{-V_0^2t/D}-1)]\ . \qquad (5.35)$$

Better approximations for $C_s(k,z)$ can be obtained by using the kinetic-modeling technique.[69] The results of such an analysis will be published elsewhere.[62]

VI. CONCLUSION

A new fully renormalized approach to the many-body problem has been described in this paper. The theory was developed without the use of any molecular chaos assumptions[16] or the use of the Bogliubov[36] functional assumption. The results are therefore not restricted to any time regime. At this point the only practical result derived—the Enskog memory function—has been available via the BCE[17] method for some time. However, this result has been obtained here via simple physical approximations and the treatment of the static correlations seems considerably more straightforward than in the BCE treatment.[70] This alone, however, does not justify the elaborate formalism described in this paper. Such a development can only be useful if it leads to new results or to new physical explanations of old results. As will be shown in II, simple approximations for the two-particle source M_c lead to new insights and results in an analysis of the dynamics of dense systems.

ACKNOWLEDGMENTS

I want to thank Professor E. P. Gross for his support and Professor Sidney Yip for many helpful discussions.

APPENDIX A

In this appendix (3.1) is proven. One has first, on applying L to f_s, that

$$Lf_s(1)=\left(-i\sum_{j=1}^{N}\frac{p_j\cdot\nabla_{r_j}}{m}+i\sum_{i\neq j}\nabla_{r_i}V(\vec{r}_i-\vec{r}_j)\cdot\nabla_{p_i}\right)\times\sqrt{N}\,\delta(1-q_1)$$

and

$$Lf_s(1)=-L_0(1)f_s(1)$$

$$+i \sum_{j\neq 1}^{N} \nabla_{r_1} V(\vec{\mathrm{r}}_i - \vec{\mathrm{r}}_j) \cdot \nabla_{p_1} \sqrt{N}\, \delta(1 - q_1) \, .$$

One can then introduce the identity $\int d\bar{1}\, \delta(\bar{1} - q_j)$ to obtain

$$Lf_s(1) = -L_0(1) f_s(1) + i \int d\bar{1} \sum_{j\neq 1}^{N} \delta(\bar{1} - q_j)$$

$$\times \nabla_{r_i} V(r_i - r_j) \cdot \nabla_{p_1} \sqrt{N}\, \delta(1 - q_1) \, ,$$

and finally

$$Lf_s(1) = -L_0(1) f_s(1) - \int d\bar{1}\, L_I(1\bar{1})\, g(1\bar{1}) \, ,$$

where

$$g(1\bar{1}) = \sum_{j\neq 1}^{N} \delta(\bar{1} - q_j) \sqrt{N}\, \delta(1 - q_1) \, .$$

APPENDIX B

In this appendix the symmetry properties of the correlation functions are considered. It should be noted from (2.19), that if one integrates successively by parts, one finds

$$C_s(12; z) = \langle f_s(1) [z - L]^{-1} f_s(2) \rangle = -C_s(21; -z) \, , \qquad \text{(B1)}$$

since the Liouville operator commutes with the canonical distribution function. The other correlation functions $C(1; 2\bar{2})$, $C(1\bar{1}; 2)$, and $C(1\bar{1}; 2\bar{2})$ satisfy similar symmetry properties. If one now investigates the equation of motion (3.9), letting $z \to -z$ and using (B1) one finds

$$[z + L_0(1)]\, C_s(21; z) + \varphi_s(1\bar{1}; -z)\, C_s(2\bar{1}; z) = \tilde{C}_s(21) \qquad \text{(B2)}$$

or, on defining

$$\varphi_s^T(1\bar{1}; z) = \varphi_s(1\bar{1}; z) \, ,$$

one obtains (3.12). One can next observe that the symmetry (B1) and the related symmetries observed by $C(1; 2\bar{2})$, $C(1\bar{1}; 2)$, and $C(1\bar{1}; 2\bar{2})$ imply, using (3.16), that

$$G(1\bar{1}; 2\bar{2}; z) = -G(2\bar{2}; 1\bar{1}; -z) \qquad \text{(B3)}$$

and, using (3.15), one has the symmetry condition

$$\varphi_s(1\bar{1})\, \tilde{C}_s(\bar{1}2) = -\varphi_s(2\bar{1}; -z)\, \tilde{C}_s(\bar{1}1) \qquad \text{(B4)}$$

or

$$\varphi_s(12)\, nf_0(p_2) = -\varphi_s(21; -z)\, nf_0(p_1) \, . \qquad \text{(B5)}$$

APPENDIX C

Here (4.24) is proven. First, since $PQ = 0$, one has

$$\langle 1\bar{1} | P[z - QV]^{-1} \tilde{C} | 2\bar{2} \rangle = z^{-1} \langle 1\bar{1} | P\tilde{C} | 2\bar{2} \rangle \, . \qquad \text{(C1)}$$

Next, one can write the left-hand side of (C1) in the form

$$\langle 1\bar{1} | P[z - (1-P)V]^{-1} \tilde{C} | 2\bar{2} \rangle = \langle 1\bar{1} | P[z - V]^{-1} \tilde{C} | 2\bar{2} \rangle$$

$$-\langle 1\bar{1} | P[z - V]^{-1} PV[z - QV]^{-1} \tilde{C} | 2\bar{2} \rangle$$

$$= \tilde{C}(1\bar{1}; 3)\, \tilde{C}_s^{-1}(34)\, C(4; 2\bar{2})$$

$$-\tilde{C}(1\bar{1}; 3)\, \tilde{C}_s^{-1}(35)\, C_s(57)\, \tilde{C}_s^{-1}(76)$$

$$\times \int \frac{d\bar{6}}{(N-1)} \langle 6\bar{6} | V[z - QV]^{-1} \tilde{C} | 2\bar{2} \rangle \, . \qquad \text{(C2)}$$

Combining (C2) and (C1) with (2.10) and (2.11), one has

$$C_s(14)\, \tilde{C}_s^{-1}(45) \int \frac{d\bar{5}}{(N-1)} \langle 5\bar{5} | V[z - QV]^{-1} \tilde{C} | 2\bar{2} \rangle$$

$$= C(1; 2\bar{2}) - \delta(12)\, z^{-1}\, \omega_0(2\bar{2}) \, . \qquad \text{(C3)}$$

After applying C_s^{-1} to the left-hand side of (C3), one obtains (4.24).

APPENDIX D

Here the effect of the PL_0 part of QV in (4.28) is investigated. First one notes that one can write

$$\langle 1\bar{1} | PL_0 | 2\bar{2} \rangle = -\langle 1\bar{1} | \omega_0 L_0 \omega_0^{-1} P | 2 2 \rangle$$

$$\equiv \langle 1\bar{1} | \delta L_0 P | 2\bar{2} \rangle \, . \qquad \text{(D1)}$$

Then, since

$$[z - QV][z - QV]^{-1} = 1 \qquad \text{(D2)}$$

or

$$[z - L_0 - Q(\mathcal{L}_I + M_c) - \delta L_0 P][z - QV]^{-1} = 1 \, ,$$

one can separate out the effect of $\delta L_0 P$ on the left-hand side to find

$$[z - L_0 - Q(\mathcal{L}_I + M_c)][z - QV]^{-1} - \delta L_0 P[z - QV]^{-1} = 1 \, ,$$

and since $PQ = 0$,

$$[z - L_0 - Q(\mathcal{L}_I + M_c)][z - QV]^{-1} - z^{-1} \delta L_0 P = 1 \, . \qquad \text{(D3)}$$

One can now invert this to obtain

$$[z - QV]^{-1} = [z - QV]^{-1}_{(PL_0=0)} + [z - QV]^{-1}_{(PL_0=0)}\, z^{-1} \delta L_0 P \, .$$

Since all of the “end states” on which this operates are orthogonal to P, one can neglect the PL_0 term.

APPENDIX E: PROPERTIES OF THE OPERATOR $P\mathcal{L}_I$

The operator $P\mathcal{L}_I$ is completely specified by its matrix element $\langle 1\bar{1} | P\mathcal{L}_I | 2\bar{2} \rangle$. Using the completeness of the two-particle vector space one can write

$$\langle 1\bar{1} | P\mathcal{L}_I | 2\bar{2} \rangle = \int d3\, d\bar{3} \langle 1\bar{1} | P | 3\bar{3} \rangle \langle 3\bar{3} | \mathcal{L}_I | 2\bar{2} \rangle \, . \qquad \text{(E1)}$$

The matrix element for P is given by (4.20) and $\mathcal{L}_I$ is given by (3.24). Combining these results one can write

$$\langle 1\bar{1} | P\mathcal{L}_I | 2\bar{2} \rangle = -\omega_0(1\bar{1})\, [nf_0(p_1)]^{-1}$$

$$\times\langle g(3\,\bar{3})\,L_I\,f_s(1)\rangle\,\tilde{C}^{-1}(3\,\bar{3};2\,\bar{2})\;. \qquad \text{(E2)}$$

If one uses the result $L_I\,f_s(1) = -\int d\,\bar{1}\,L_I(1\,\bar{1})\,g(1\,\bar{1})$ it is easy to show

$$\langle 1\,\bar{1}|P\mathcal{L}_I|2\,\bar{2}\rangle = -\,\omega_0(1\,\bar{1})\,[nf_0(p_1)]^{-1}\,L_I(2\,\bar{2})\,\delta(12)\,, \qquad \text{(E3)}$$

which is of first order in the density.

---

*Work supported by the National Science Foundation.

†Present address: Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Mass. and Department of Physics, Harvard University, Cambridge, Mass.

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

[2] B. J. Alder and T. E. Wainwright, Phys. Rev. Letters 18, 988 (1967); Phys. Rev. A 1, 18 (1970); B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970).

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

[4] B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. 45, 1086 (1966).

[5] R. Zwanzig, Phys. Rev. 124, 983 (1961).

[6] H. Mori, Progr. Theoret. Phys. (Kyoto) 33, 423 (1965).

[7] P. Resibois, J. Brocas, and G. Decan, J. Math. Phys. 10, 964 (1969).

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

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

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

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

[12] K. Kawasaki, Ann. Phys. (N.Y.) 61, 1 (1970).

[13] D. Forster, Ph.D. thesis (Harvard University, 1969) (unpublished).

[14] I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Wiley, New York, 1963), and other references cited therein.

[15] H. L. Frisch and E. McLaughlin, J. Chem. Phys. 55, 3706 (1971).

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

[17] R. Zwanzig, Phys. Rev. 129, 486 (1963).

[18] K. Kawasaki and I. Oppenheim, Phys. Rev. 136, A1519 (1964); 139, A649 (1965); 139, A1763 (1965); in *Statistical Mechanics*, edited by T. Bak (Benjamin, New York, 1967).

[19] M. H. Ernst, L. K. Haines, and J. R. Dorfman, Rev. Mod. Phys. 41, 296 (1969).

[20] The literature on the divergence and its historical development is discussed in Ref. 19.

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

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

[23] J. Dufty, Phys. Rev. A 5, 2247 (1972).

[24] T. E. Wainwright, B. J. Alder, and D. M. Gass, Phys. Rev. A 4, 233 (1971).

[25] K. Kawasaki, Phys. Letters 32A, 379 (1970).

[26] M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuween, Phys. Rev. Letters 25, 1254 (1970); Phys. Rev. A 4, 2055 (1971).

[27] A. Widom, Phys. Rev. A 3, 1394 (1971).

[28] R. Zwanzig, University of Maryland Institute for Fluid Dynamics and Applied Mathematics Technical Report No. 3N-695, 1971 (unpublished).

[29] R. Zwanzig and M. Bixon, Phys. Rev. A 2, 2005 (1970).

[30] G. F. Mazenko, following paper, Phys. Rev. A 7, 222 (1973).

[31] J. K. Percus, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).

[32] P. Resibois and M. Deleener, Phys. Rev. 178, 806 (1969); P. Resibois and G. Dewel, Ann. Phys. (N.Y.) 69, 299 (1972).

[33] L. P. Kananoff and J. Swift, Phys. Rev. 166, 89 (1968).

[34] R. Zwanzig, Phys. Rev. 144, 170 (1966).

[35] In labeling operators and fields one must make distinctions between "internal" and "external" variables. Internal variables are those phase-space coordinates labeling operators and fields that one averages over. External variables label the phase-space points not included in these averages. For example, in $f_s(1)$, given by (2.1), q_1 is the internal variable that one averages over, and 1 is an external variable. The convention will be used that the external variables are written explicitly and that the internal variables are suppressed. Consequently it is to be understood that the Liouville operator L is an N-particle operator operating on the internal N-particle phase-space, while $L(12\ldots M)$ is the M-particle Liouville operator that acts on the appropriate M-particle external space.

[36] R. L. Liboff, *Introduction to the Theory of Kinetic Equations* (Wiley, New York, 1969).

[37] This basic logic is behind the sum rule, dispersion-relation techniques developed by Martin. See Ref. 1.

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

[39] J. J. Duderstadt and A. Z. Akcasu, Phys. Rev. A 1, 905 (1970).

[40] R. C. Desai, Phys. Rev. A 3, 320 (1971).

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

[42] P. Ortelova and M. Nelkin, Phys. Rev. 181, 429 (1969); Phys. Rev. A 2, 187 (1970).

[43] J. L. Lebowitz, J. K. Percus, and J. Sykes, Phys. Rev. 188, 487 (1960).

[44] P. C. Martin and S. Yip, Phys. Rev. 170, 151 (1968).

[45] See Appendix D of Ref. 9.

[46] The analysis follows that in Ref. 10 [Boley (Ref. 11) has pointed out the corresponding form for ϕ_s].

[47] In a number of cases, like the left-hand side of (3.11) and in (3.9) the integration over the repeated variables is implied.

[48] N. Corngold and J. J. Duderstadt, Phys. Rev. A 2, 836 (1970).

[49] Steps similar to those used in going from (3.11) to (3.16) have been used by S. Ethofer and P. S. Schuck [Physik 288, 264 (1969)] in studying the mass operator associated with the single-particle Green's function.

[50] The free and interaction parts of L are determined by breaking L into its free and interaction parts in (3.24).

[51] P. A. Egelstaff, *An Introduction to the Liquid State*

(Academic, London, 1967), p. 53.

[52] E. P. Gross, Ann. Phys. (N.Y.) 69, 42 (1972).

[53] J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946).

[54] R. Zwanzig, J. Chem. Phys. 40, 2527 (1964).

[55] P. C. Martin, in *Statistical Mechanics of Equilibrium and Non-Equilibrium*, edited by J. Meixner (North-Holland, Amsterdam, 1965).

[56] R. Kubo, in *Many-Body Theory, Part I*, edited by R. Kubo (Benjamin, New York, 1966).

[57] K. Kawasaki, Phys. Rev. 150, 291 (1966).

[58] This idea has been challenged by the recently discovered "long-time tails." See Ref. 2.

[59] B. J. Berne and D. Forster, Ann. Rev. Phys. Chem. 20, 563 (1971).

[60] The corrections to the approximation $QL_I = L_I$ have not yet been evaluated, but it is anticipated that they could be quite important in very dense systems.

[61] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience, New York, 1965).

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

[63] $g(r_0)$ is the radial distribution function evaluated at $r = r_0 + 0^+$.

[64] L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) 24, 419 (1963).

[65] A. Einstein, *Investigations on the Theory of the Brownian Movement* (Dover, New York, 1956).

[66] C. L. Pekeris, Proc. U. S. Natl. Acad. Sci. 41, 661 (1955).

[67] G. H. Vineyard, Phys. Rev. 110, 999 (1958).

[68] R. Desai and M. Nelkin, Nucl. Sci. Eng. 24, 142 (1966).

[69] P. L. Bhatnagar, E. P. Gross, and M. Krook, Phys. Rev. 94, 511 (1954); L. Sirovich, New York University, Courant Institute of Mathematical Sciences, Report No. MF 17, 1961 (unpublished); A. Sugawara, S. Yip, and L. Sirovich, Phys. Rev. 168, 121 (1968); T. Wei, Masters thesis (MIT, 1972) (unpublished).

[70] J. R. Dorfman and E. G. D. Cohen, Phys. Letters 16, 124 (1965).

PHYSICAL REVIEW A VOLUME 7, NUMBER 1 JANUARY 1973

Fully Renormalized Kinetic Theory. II. Velocity Autocorrelation*

Gene F. Mazenko†

Department of Physics, Brandeis University, Waltham, Massachusetts 02194

(Received 15 June 1972)

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-