Kinetic theory of single-particle motion in a fluid

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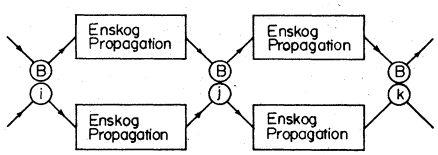
A repeated-ring kinetic theory is derived to describe the thermal motion of a tagged particle of arbitrary size and mass immersed in a fluid. In the spirit of the fully renormalized kinetic theory developed by Mazenko, systematic approximations are made in the exact equations of motion for the tagged-particle phase-space correlation function to cast the dynamics of the system in terms of the two-body Enskog collision operator. In addition to Enskog (uncorrelated collisions) and ring (two correlated collisions) events, we include repeated-ring (3,4,...correlated collisions) events. The theory is applied to the calculation of the velocity autocorrelation function and diffusion coefficient of a large hard sphere immersed in a dense fluid of smaller hard spheres. The accepted long-time behavior of the velocity auto-correlation function $t^{-3/2}$ is obtained and the diffusion coefficient is found to have the same functional form as in the Stokes-Einstein law of hydrodynamics. It is suggested that the theory be applied to study self-diffusion in a dense hard-sphere fluid.

I. INTRODUCTION

In this article, we present a new kinetic theory to describe the thermal motion of a tagged particle of arbitrary size and mass immersed in a fluid.[1] We follow the spirit of fully renormalized kinetic theory (FRKT), developed by Mazenko[2-5] for simple fluids, to approximate the dynamics of the system in terms of effective two-body interactions. Our theory differs from FRKT in that it includes, in addition to the contributions from Enskog and correlated collisions (ring events) found in FRKT, contributions from multiple-correlated collisions (repeated ring events). When the effective diameter σ_B of the tagged particle is much larger than the mean free path l_b of the bath particles, one must include contributions from events in which a typical bath particle experiences a large number of correlated collisions with the tagged particle. We stress that the condition $\sigma_B \gg l_b$ alone determines that multiple-correlated collisions are important. Even when the tagged particle is mechanically equivalent to the bath particles, if the density is high enough such that $\sigma_B \gg l_b$, the repeated ring events must be included to obtain a successful theory of self-diffusion.

It is well established[6] that the Enskog kinetic theory[7] provides a good description of self-diffusion in simple fluids at low and moderate densities. Although equilibrium correlations are incorporated in the collision frequency, all dynamical correlations are neglected in the Enskog theory; that is, a tagged particle only collides with particles chosen from an equilibrium spatial and momentum distribution. At higher densities, other dynamical events referred to as ring events become probable. In a ring event first the tagged particle and another particle i undergo a collision. They then travel independently of one another interacting with the rest of the particles via Enskog collisions. After some time the tagged particle (labeled particle B) again collides with particle i, or with some particle j dynamically correlated with i subsequent to the Bi collision. In this fashion a noninstantaneous (non-Markovian) response to a disturbance is introduced into the kinetic theory. Theories which include, in addition to the Enskog term, these ring events are known as ring kinetic theories.[3,5,8] They have been used to obtain the long-time tail[3,5,8] of the velocity autocorrelation function discovered by the computer molecular-dynamics experiments of Alder *et al.*[9] Subsequently, they were used to calculate the full-time course of the linear velocity[10,11] and angular velocity[12] autocorrelation functions and the self-diffusion coefficient.[10,11] The ring theory shows reasonable agreement with the computer molecular-dynamics simulations[6] and represents a first step in the inclusion of collective effects of tagged-particle motion in liquids.

At sufficiently high fluid density, the mean free path is considerably smaller than a particle's effective diameter. This suggests that a much larger class of dynamical events than just the ring events contribute to the collective effects on tagged-particle motion. The additional events that we include in our kinetic theory are easiest to understand with the aid of the following diagram:



Note that the Bj collision has not terminated the

initial correlation between B and i (as it would have in the ring theory) but, rather, initiates a new Enskog propagation of tagged and fluid particles. The initial correlation in the diagram is finally terminated by the Bk collision. (In the above diagram particle j is either particle i or another particle dynamically correlated with i since the Bi collision. Similarly, particle k is either particle j or another particle dynamically correlated with j since the Bj collision.) All alternating sequences of "correlating collisions" followed by "intermediate propagations" are to be included in the theory. We refer to the collection of these dynamical events as multiple rings and the kinetic theory including Enskog, ring, and multiple-ring events as repeated-ring kinetic theory.

Repeated-ring kinetic theories, but with the neglect of equilibrium correlations, were first presented by Ernst and Dorfman[13] to study the dispersion relation in gases and by Dorfman, van Beijeren, and McClure[14] to study Stokes law for an infinitely massive large particle. In our theory, though, all collisions are expressed in terms of the Enskog binary-collision operator in which the static structure of the fluid is incorporated through the radial distribution function. This is the first repeated-ring kinetic theory in which the equilibrium structure of the fluid renormalizes the bare two-body interactions. While the Mazenko formalism is rather complicated, its great utility is demonstrated by its ability to be cast in a form where systematic approximations lead to this result. Since, even at the Enskog level, incorporating the equilibrium structure of the fluid is vital, we expect that it is also crucial to include it in the repeated-ring kinetic theory.

The many-body problem in fluids is so complicated that, to our knowledge, there exists no truly systematic procedure for obtaining a kinetic equation with a proper estimate of the effect of what has been left out. Thus, while we provide here a careful derivation of the repeated-ring kinetic theory, its validity can only be established by its predictive ability.

Of course, the solution of a kinetic equation can be difficult to obtain: often more difficult than the derivation of the kinetic equation itself. However, when a large tagged particle is immersed in a dense fluid of bath particles (with effective diameter σ_B), the solutions of the ring and repeated-ring kinetic theories for the velocity autocorrelation function $\psi_v^B(t)$ and the diffusion coefficient D^B are greatly simplified. Also, in such a system, the necessity of utilizing repeated-ring kinetic theory over previous ring kinetic theories is most pronounced. In this limit, where $\sigma_B \gg \sigma_b \gtrsim l_b$, the essential simplifying feature in both the ring and repeated-ring theories is that, during the intermediate propagations between successive correlated collisions, the coupling of the tagged-particle motion to the collective motion of the bath is dominated by the hydrodynamic (long-time) form of the transverse bath current (shear-viscosity mode). One might expect that the complexity of the various contributions to the repeated-ring theory would increase as the number of correlated collisions increases. We demonstrate though, that (independently of the condition $\sigma_B \gg \sigma_b \gtrsim l_b$) we can express, without approximation, the terms appearing in the repeated-ring theory corresponding to increasing numbers of correlated collisions in terms of the ring and Enskog contributions. Hence, in practice, the repeated-ring theory is no more difficult to analyze than the ring theory!

In this paper we solve both the ring and repeated-ring kinetic theories for D^B and $\psi_v^B(t)$ under the simplifying conditions $\sigma_B \gg \sigma_b \gtrsim l_b$ and compare their predictions. In this large-particle limit, we find that the repeated-ring kinetic theory gives far superior predictions for D^B and $\psi_v^B(t)$ than does the ring kinetic theory. In particular, in the ring theory we find that the diffusion coefficient has the form

$$D^B = D_E^B (1-a)^{-1} , \tag{1.1}$$

where D_E^B is the Enskog diffusion coefficient and $a \propto n_b \sigma_b^3 (\sigma_B/\sigma_b)$ with n_b the bath number density. This result is clearly catastrophic, for as σ_B/σ_b increases D^B increases without limit until, at some value of σ_B/σ_b, it turns negative. In contrast, the repeated-ring kinetic theory predicts a finite positive diffusion coefficient which is similar to the Stokes-Einstein form.[15] That is,

$$D^B = k_B T/5\pi\eta_E R_B , \tag{1.2}$$

where k_B is the Boltzmann constant, T and η_E are, respectively, the fluid temperature and Enskog shear viscosity and R_B is the tagged-particle radius. As for the long-time behavior of $\psi_v^B(t)$, whereas both the ring and repeated-ring kinetic theories are found to predict the $t^{-3/2}$ tail, only the repeated-ring coefficient of $t^{-3/2}$ is found to agree with the prediction of fluctuating hydrodynamics.[16]

In Sec. II A, we introduce the basic definitions required in our kinetic theory. Here the general case is treated in which the tagged particle is assumed to be a member of any of the species present in a multicomponent fluid. The formally exact kinetic equation for the tagged-particle phase-space density is presented in terms of its memory function in Sec. II B. The memory function, which describes the effects of the bath particles on the tag-

ged particle, is expressed in terms of higher-order correlation functions. Approximations are made at this stage to express the dynamics of the system in terms of effective two-body interactions. The equilibrium structure of the fluid influences two-particle collisions via the excluded-volume effect and shielding. Hence the collision frequency in the fluid is given by its Enskog form rather than the dilute-gas Boltzmann form. In Sec. IIC, we present the Enskog approximation to the memory function in which only contributions from uncorrelated effective collisions are retained. Following FRKT, in Sec. IID, we show how the ring approximation can be extracted from the exact memory-function expression. Finally in Sec. IIF, we present our derivation of the repeated-ring memory function.

In Sec. III, we solve the kinetic equation for the tagged-particle velocity autocorrelation function and diffusion coefficient in the limit where the tagged particle is a large sphere immersed in a dense fluid of smaller spheres. The Enskog approximation is shown, in Sec. IIIB, to lead to an exponentially decaying velocity autocorrelation function and a diffusion coefficient varying inversely as the cross section of the tagged particle. These results are not in agreement with hydrodynamic theories or experiments. We continue in Sec. IIIC to evaluate $\psi_v^B(t)$ and D^B in the ring approximation. Here it is found that during the intermediate propagation between correlated collisions, when $\sigma_B \gg \sigma_b \gtrsim l_b$, the coupling of the tagged-particle motion to the bath is dominated by the transverse current. The ring-theory results for $\psi_v^B(t)$ and D^B are then shown to be unsatisfactory. In Sec. IIID, we evaluate $\psi_v^B(t)$ and D^B in the repeated-ring approximation. We demonstrate how one handles the contributions from 3, 4, ... correlated collisions. Analytic expressions for D^B and the long-time behavior of $\psi_v^B(t)$ are derived.

A summary of our results and comparison with those of other investigators is given in Sec. IV. We also discuss the range of utility of our theory with regard to fluid density and tagged-particle mass and size.

II. KINETIC EQUATION

A. Definitions

We consider a classical fluid which is in equilibrium at temperature $T = 1/k_B\beta$, enclosed in a volume Ω, and comprised of N_a particles of species a, N_b particles of species b, etc. The total number of particles is $N = \sum_\alpha N_\alpha$. The center-of-mass position and momentum of the ith particle are denoted by $\vec{r}_i$ and $\vec{p}_i$, respectively. To simplify our notation, the operator O_i^α is introduced to determine whether the ith particle is of species α or not.

$$O_i^\alpha = \begin{cases} 1 & \text{if } i \in \alpha \\ 0 & \text{if } i \notin \alpha \end{cases} . \tag{2.1}$$

The species-dependent intermolecular potential $V^{\alpha\beta}(|\vec{r}_i - \vec{r}_j|)$ is assumed to be pairwise additive. As a consequence, the Hamiltonian of our system has the form

$$H = \sum_\alpha \sum_{i=1} \frac{O_i^\alpha p_i^2}{2m_\alpha} + \frac{1}{2} \sum_{\alpha,\beta} \sum_{i \neq j = 1} O_i^\alpha O_j^\beta V^{\alpha\beta}(r_{ij}) , \tag{2.2}$$

where m_α is the mass of a particle of species α and $r_{ij} \equiv |\vec{r}_i - \vec{r}_j|$.

Our goal is to describe the thermal fluctuations of a *tagged*-particle's motion in a fluid mixture. Our description is expressed in terms of the species-dependent tagged-particle phase-space density, f_s^α, defined as

$$f_s^\alpha(1, t_1) = \sqrt{N}\, O_s^\alpha \delta[1 - q_s(t_1)] , \tag{2.3}$$

where $q_s(t_1) = [\vec{r}_s(t_1), \vec{p}_s(t_1)]$ represents the phase-space coordinates of the tagged particle, at time t_1, whereas $1 = (\vec{r}_1, \vec{p}_1)$ represents field points. The field points serve to label fixed points in phase space; they are *not* dynamical variables. Unbarred and unprimed field points (integers) will only be used when referring to tagged-particle quantities. The motion of the tagged particle is, of course, coupled to the thermal fluctuations of the entire fluid. Such fluctuations can be expressed in terms of the species-dependent phase-space density

$$f^\gamma(\bar{1}, t_1) = \sum_{i=1}^{N} O_i^\gamma \delta[\bar{1} - q_i(t_1)] . \tag{2.4}$$

We shall use only barred and barred-primed integers to denote field points of the fluid.

In the thermodynamic limit ($N_\alpha \to \infty$, for all α, and $\Omega \to \infty$, such that $n_\alpha = N_\alpha/\Omega$, for all α, and $n = N/\Omega$ are constant) the thermal averages, denoted by $\langle \cdots \rangle_0$, of the phase-space densities defined above are

$$\langle f_s^\alpha(1, t_1) \rangle_0 = 0$$

and (2.5)

$$\langle f^\gamma(\bar{1}, t_1) \rangle_0 = n_\gamma f_0^\gamma(p_{\bar{1}}) ,$$

where $f_0^\gamma(p_{\bar{1}})$ is the Maxwellian momentum distribution function

$$f_0^\gamma(p_{\bar{1}}) = (\beta/2\pi m_\gamma)^{3/2} \exp(-\beta p_{\bar{1}}^2/2m_\gamma) . \tag{2.6}$$

As the density increases, the equilibrium structure becomes important in the kinetic theory of

the fluid. For this reason we introduce the equilibrium correlation functions

$$\omega_0^{\alpha_1\alpha_2\cdots\alpha_k}(\bar{1}\,\bar{2}\cdots\bar{k}) \equiv \Big\langle \sum_{i_1\neq i_2\neq\cdots i_k=1} O_{i_1}^{\alpha_1}\delta(\bar{1}-q_{i_1})O_{i_2}^{\alpha_2}\delta(\bar{2}-q_{i_2})\cdots O_{i_k}^{\alpha_k}\delta(\bar{k}-q_{i_k})\Big\rangle_0$$

$$= n_{\alpha_1}n_{\alpha_2}\cdots n_{\alpha_k} f_0^{\alpha_1}(p_{\bar{1}})f_0^{\alpha_2}(p_{\bar{2}})\cdots f_0^{\alpha_k}(p_{\bar{k}})\, g_k^{\alpha_1\alpha_2\cdots\alpha_k}(\vec{r}_{\bar{1}},\vec{r}_{\bar{2}}\cdots\vec{r}_{\bar{k}}), \tag{2.7}$$

where $g_k^{\alpha_1\alpha_2\cdots\alpha_k}$ is the species-dependent k-particle static distribution function. We also will use the cumulants (connected parts) $g_{kc}^{\alpha_1\alpha_2\cdots\alpha_k}(\vec{r}_{\bar{1}},\vec{r}_{\bar{2}},\cdots,\vec{r}_{\bar{k}})$ of these distribution functions defined such that $g_{kc}=0$ when any set of coordinates become independent of the others.[17] For example, $g_{2c}^{\alpha\beta}(\vec{r}_{\bar{1}},\vec{r}_{\bar{2}}) = g_2^{\alpha\beta}(\vec{r}_{\bar{1}},\vec{r}_{\bar{2}}) - 1$.

B. Formal kinetic theory

We use the method developed by Mazenko[2-5] in FRKT for simple fluids to derive a hierarchy of correlation functions. The equations presented in this section are exact and serve to write the hierarchy in a form suitable to approximate. In subsequent sections, we approximate the dynamical events in terms of effective two-body collisions.

We derive a kinetic equation for the Laplace transform of the time-dependent tagged-particle phase-space density correlation function $C_s^{\alpha\alpha}$ which is defined as

$$C_s^{\alpha\alpha}(12) \equiv -i\int_0^\infty e^{iz(t_1-t_2)}\, C_s^{\alpha\alpha}(12;t_1-t_2)\,d(t_1-t_2)$$

$$= -i\int_0^\infty e^{iz(t_1-t_2)}\langle f_s^\alpha(1,t_1)f_s^\alpha(2,t_2)\rangle\!\rangle_0 \times d(t_1-t_2), \tag{2.8a}$$

with $t_1 > t_2$ and $\mathrm{Im}(z) > 0$. The van Hove self-correlation function and the tagged-particle velocity autocorrelation function (and, hence, the diffusion coefficient) are simple momentum moments of $C_s^{\alpha\alpha}$. Since the tagged-particle motion is coupled to the fluid fluctuations we shall also require the Laplace transform of the time-dependent phase-space density correlation function, $C^{\nu\mu}$, defined as

$$C^{\nu\mu}(\bar{3}\,\bar{4};t_3-t_4) = \langle [f^\nu(\bar{3},t_3) - \langle f^\nu(\bar{3},t_3)\rangle\!\rangle_0] \times [f^\mu(\bar{4},t_4) - \langle f^\mu(\bar{4},t_4)\rangle\!\rangle_0]\rangle_0 . \tag{2.8b}$$

The generalization of the hierarchy to mixtures is straightforward,[18] so that we will not present the details of the calculations; but instead, present the results of some involved manipulations.

The first member of the hierarchy is the kinetic equation for $C_s^{\alpha\alpha}$. It has the form

$$[z - L_0^\alpha(1)]\, C_s^{\alpha\alpha}(12) - \int d3\,\phi_s^{\alpha\alpha}(13)C_s^{\alpha\alpha}(32) = \tilde{C}_s^{\alpha\alpha}(12). \tag{2.9}$$

In Eq. (2.9) the initial value of the tagged-particle correlation function (denoted by a tilde) is

$$\tilde{C}_s^{\alpha\alpha}(12) = C_s^{\alpha\alpha}(12;t_1-t_2=0) = n_\alpha f_0^\alpha(p_1)\delta(12) = \omega_0^\alpha(1)\delta(12), \tag{2.10}$$

and the tagged-particle free-streaming Liouville operator (in field-point coordinates) is

$$L_0^\alpha(1) = -i\vec{p}_1/m_\alpha\cdot\vec{\nabla}_{r_1}. \tag{2.11}$$

The quantity $\phi_s^{\alpha\alpha}$ in Eq. (2.9) is referred to as the memory function of the kinetic equation. It describes the interaction of the tagged particle with the remaining $(N-1)$ particles in the fluid. As was the case for a simple fluid,[2] the static (i.e., mean-field) contribution to the memory function can be related to the average force on the particle which clearly vanishes for a system in equilibrium. Hence, there is only a dynamic (i.e., collisional) contribution to the memory function. It can be written

$$\phi_s^{\alpha\alpha}(12)\, n_\alpha f_0^\alpha(p_2) = -\sum_{\gamma,\epsilon}\int d\bar{1}\int d\bar{2}\, L_I^{\alpha\gamma}(1\bar{1})L_I^{\alpha\epsilon}(2\bar{2})G_s^{\alpha\gamma\alpha\epsilon}(1\bar{1};2\bar{2}). \tag{2.12}$$

In Eq. (2.12) the two-particle interaction Liouville operator is

$$L_I^{\alpha\gamma}(1\bar{1}) = i\vec{\nabla}_{r_1}V^{\alpha\gamma}(r_{1\bar{1}})\circ(\vec{\nabla}_{p_1} - \vec{\nabla}_{p_{\bar{1}}}), \tag{2.13}$$

and the four-point correlation function G_s is given by

$$G_s^{\alpha\gamma\alpha\epsilon}(1\bar{1};2\bar{2}) = C_s^{\alpha\gamma\alpha\epsilon}(1\bar{1};2\bar{2}) - \int d3\int d4\, C_s^{\alpha\gamma\alpha}(1\bar{1};3) \times C_s^{\alpha\alpha-1}(34)C_s^{\alpha\alpha\epsilon}(4;2\bar{2}), \tag{2.14}$$

where

$$C_s^{\alpha\gamma\alpha\epsilon}(1\bar{1};2\bar{2}) = -i\int_0^\infty e^{iz(t_1-t_2)}\langle f_s^\alpha(1,t_1)f^\gamma(\bar{1},t_1)f_s^\alpha(2,t_2) \times f^\epsilon(\bar{2},t_2)\rangle_0 d(t_1-t_2),$$

$$C_s^{\alpha\gamma\alpha}(1\bar{1};3) = -i\int_0^\infty e^{iz(t_1-t_3)}\langle f_s^\alpha(1,t_1)f^\gamma(\bar{1},t_1)f_s^\alpha(3,t_3)\rangle_0 \times d(t_1-t_3), \quad (2.15)$$

etc., and $C_s^{\alpha\alpha\,-1}(34)$ is the inverse of $C_s^{\alpha\alpha}(34)$. Equation (2.9) with Eq. (2.12) connects a two-point correlation function to a four-point correlation function. The next member of the hierarchy connects a four-point to a six-point, etc. For our purposes this second member of the hierarchy will be sufficient. Rather than dealing with G_s it proves convenient to work with $\bar{G}_s$ defined via

$$G_s^{\alpha\gamma\alpha\epsilon}(1\bar{1};2\bar{2}) = \sum_\nu \int d3\,d\bar{3} \sum_\mu \int d4\,d\bar{4}\,\tilde{G}_s^{\alpha\gamma\alpha\nu}(1\bar{1};3\bar{3})\,\bar{G}_s^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4})\tilde{G}_s^{\alpha\mu\alpha\epsilon}(4\bar{4};2\bar{2}), \quad (2.16)$$

where $\tilde{G}_s$ is the initial value of G_s.

Substituting Eq. (2.16) into Eq. (2.12), one finds that the memory function can be written in the symmetric form

$$\phi_s^{\alpha\alpha}(12)n_\alpha f_0^\alpha(p_2) = -\sum_\nu \int d3\,d\bar{3} \sum_\mu \int d4\,d\bar{4}\,v^{\alpha\alpha\nu}(1;3\bar{3})\bar{G}_s^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) \times v^{\alpha\alpha\mu}(2;4\bar{4}), \quad (2.17)$$

where the end-point vertex is defined as

$$v^{\alpha\alpha\nu}(1;3\bar{3}) \equiv \sum_\gamma \int d\bar{1}\, L_I^{\alpha\gamma}(1\bar{1})\tilde{G}_s^{\alpha\nu\alpha\mu}(1\bar{1};3\bar{3}) = -\omega_0^{\alpha\nu}(3\bar{3})\tilde{L}_I^{\alpha\nu}(3\bar{3})\delta(13). \quad (2.18)$$

In the second step of Eq. (2.18), use of the explicit form of $\tilde{G}_s$ [Eqs. (2.22a) and (2.22b)] is made. The operator $\tilde{L}_I$ represents the effective interaction of two particles in a dense system; that is, they interact by the potential of mean force $[-\beta^{-1}\ln g_2^{\alpha\nu}(r_{3\bar{3}})]$ rather than the bare intermolecular potential. Hence

$$\tilde{L}_I^{\alpha\nu}(3\bar{3}) = -i\beta^{-1}\vec{\nabla}_{r_3}\ln g_2^{\alpha\nu}(r_{3\bar{3}})\cdot(\vec{\nabla}_{p_3}-\vec{\nabla}_{p_{\bar{3}}}). \quad (2.19)$$

Following FRKT, we have derived a kinetic equation for the quantity $\bar{G}_s$ connecting it to a six-point correlation function. The formal solution can be written in the form

$$\bar{G}_s^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = \langle\alpha 3\nu\bar{3}\,|[z\tilde{G}_s - W_s - \Gamma_s(z)]^{-1}\,|\alpha 4\mu\bar{4}\rangle, \quad (2.20)$$

where

$$\langle\alpha 3\nu\bar{3}\,|\,\tilde{G}_s\,|\alpha 4\mu\bar{4}\rangle = \tilde{G}_s^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}), \quad (2.21)$$

etc. The quantities $\tilde{G}_s$, W_s, and $\Gamma_s(z)$ have been calculated and, for use in future approximations, are presented below.

Since we want to describe processes where particles can propagate independently of each other, it is vital that we write the various functions in terms of their "connected" and "disconnected" parts.[17] By a connected function we mean that if its field points are decomposed into arbitrary sets which are spatially independent then the function vanishes. Thus the "connected part" is the same as the cumulant of a given function. The disconnected part is that contribution which does not vanish under the above operation.

The initial value $\tilde{G}_s$ of the four-point correlation function is $\tilde{G}_s = \tilde{G}_D + \tilde{G}_c$ with

$$\tilde{G}_D^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = \tilde{C}_s^{\alpha\alpha}(34)\tilde{C}^{\nu\mu}(\bar{3}\bar{4}) \quad (2.22a)$$

and

$$\tilde{G}_c^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = \tilde{C}_s^{\alpha\alpha}(34)\{\delta_{\nu\mu}\delta(\bar{3}\bar{4})\omega_0^\nu(\bar{3})g_{2c}^{\alpha\nu}(\vec{r}_3,\vec{r}_{\bar{3}}) + \omega_0^\nu(\bar{3})\omega_0^\mu(\bar{4})[g_{3c}^{\alpha\nu\mu}(\vec{r}_3,\vec{r}_{\bar{3}},\vec{r}_{\bar{4}}) - g_{2c}^{\alpha\nu}(\vec{r}_3,\vec{r}_{\bar{3}})g_{2c}^{\alpha\mu}(\vec{r}_3,\vec{r}_{\bar{4}})]\} \equiv \delta(34)F^{\alpha\nu\mu}(3\bar{3}\bar{4}), \quad (2.22b)$$

where the initial value of the density correlation function, Eq. (2.8b), is

$$\tilde{C}^{\nu\mu}(34) = \delta_{\nu\mu}\delta(\bar{3}\bar{4})\omega_0^\nu(\bar{3}) + \omega_0^\nu(\bar{3})\omega_0^\mu(\bar{4})g_{2c}^{\nu\mu}(r_{\bar{3}\bar{4}}). \quad (2.23)$$

To lowest order in explicit density dependence one obtains the "diagonal" approximation for $\tilde{G}_s$, namely,

$$\tilde{G}_s^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = \delta_{\nu\mu}\delta(34)\delta(\bar{3}\bar{4})\omega_0^{\alpha\nu}(3\bar{3}). \quad (2.24)$$

We have presented this approximation here to facilitate comparison with the exact $\tilde{G}_s$. It corresponds to the inclusion of two-body effective interactions and the neglect of explicit three-body correlations in $\tilde{G}_s$.

The function W_s plays the role of a static (mean-field) memory function in Eq. (2.20). It too can be expressed in terms of the equilibrium structure of the fluid. Its disconnected part is

$$W_D^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = [L_0^\alpha(3) + L_0^\nu(\bar{3})]\tilde{G}_D^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) + \sum_\lambda \int d\bar{5}\, \phi_{mf}^{\nu\lambda}(\bar{3}\bar{5})\tilde{G}_D^{\alpha\lambda\alpha\mu}(3\bar{5};4\bar{4}),$$

where

$$\phi_{mf}^{\nu\lambda}(\bar{3}\bar{5}) = -n_\nu f_0^\nu(p_{\bar{3}})\, L_0^\nu(\bar{3}) C_{dc}^{\nu\lambda}(r_{\bar{3}\bar{5}}). \tag{2.25a}$$

$C_{dc}^{\nu\lambda}(r_{\bar{3}\bar{5}})$ is the species-dependent direct correlation function, and $\phi_{mf}^{\nu\lambda}$ is precisely the mean-field memory function of the kinetic equation for the density-fluctuation correlation function $C^{\nu\mu}(\bar{3}\bar{4})$.[18] The connected part of W_s is

$$W_c^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = [F^{\alpha\nu\mu}(3\bar{3}\bar{4})L_0^\alpha(3) - i\beta^{-1}\vec{\nabla}_{r_3} F^{\alpha\nu\mu}(3\bar{3}\bar{4})\cdot\vec{\nabla}_{p_3}]\delta(34) + \omega_0^\alpha(3)\omega_0^\nu(\bar{3})[g_{2c}^{\alpha\nu}(r_{3\bar{3}})L_0^\nu(\bar{3}) - i\beta^{-1}\vec{\nabla}_{r_{\bar{3}}} g_{2c}^{\alpha\nu}(r_{3\bar{3}})\cdot\vec{\nabla}_{p_{\bar{3}}}]\delta(34)\delta_{\nu\mu}\delta(\bar{3}\bar{4}). \tag{2.25b}$$

In subsequent sections we use the diagonal approximation to W_s. It is

$$W_s^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = \omega_0^{\alpha\nu}(3\bar{3})\tilde{L}^{\alpha\nu}(3\bar{3})\delta(34)\delta_{\nu\mu}\delta(\bar{3}\bar{4}) = \tilde{L}^{\alpha\nu}(3\bar{3})\tilde{G}_s(3\bar{3};4\bar{4}), \tag{2.26}$$

where the effective two-particle Liouville operator is

$$\tilde{L}^{\alpha\nu}(3\bar{3}) = L_0^\alpha(3) + L_0^\nu(\bar{3}) + \tilde{L}_I^{\alpha\nu}(3\bar{3}). \tag{2.27}$$

[When comparing $\tilde{G}_s$ and W_s to FRKT results, as well as $\Gamma_s(z)$ to come shortly, it should be noted that for tagged-particle motion one no longer has the invariance under the interchange $(3 \to \bar{3}$ and $4 \to \bar{4})$ that one has for density fluctuations.]

The function $\Gamma_s(z)$ plays the role of a dynamic (collisional) memory function in Eq. (2.20). Unlike $\tilde{G}_s$ and W_s, it is a very complex quantity depending on dynamical correlations in the fluid. Its disconnected part (with respect to the field points 3, $\bar{3}$, 4, and $\bar{4}$) has the form[19]

$$\Gamma_D^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = -F_z^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) + \sum_\theta \int d5\, d\bar{5} \sum_\phi \int d6\, d\bar{6}\, Q_z^{\alpha\nu\alpha\theta}(3\bar{3};5\bar{5}) G_s^{\alpha\theta\alpha\phi\,-1}(5\bar{5};6\bar{6})(Q^T)^{\alpha\phi\alpha\mu}(6\bar{6};4\bar{4}) - \sum_\theta \int d5\, d\bar{5} \sum_\phi \int d6\, d\bar{6}\, Q_{z_c}^{\alpha\nu\alpha\theta}(3\bar{3};5\bar{5}) G_c^{\alpha\theta\alpha\phi\,-1}(5\bar{5};6\bar{6})(Q^T)_{z_c}^{\alpha\phi\alpha\mu}(6\bar{6};4\bar{4}). \tag{2.28}$$

In Eq. (2.28) the quantity F is given as

$$F_z^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = -i\int_0^\infty d(t_3 - t_4)\, e^{iz(t_3-t_4)}\{\langle A_s^\alpha(3,t_3)A_s^\alpha(4,t_4)\rangle_c C^{\nu\mu}(\bar{3}\bar{4},t_3-t_4) + \langle A_s^\alpha(3,t_3)f_s^\alpha(4,t_4)\rangle_c \times \langle f^\nu(\bar{3},t_3)A^\mu(\bar{4},t_4)\rangle_c + \langle f_s^\alpha(3,t_3)A_s^\alpha(4,t_4)\rangle_c\langle A^\nu(\bar{3},t_3)f^\mu(\bar{4},t_4)\rangle_c + C_s^{\alpha\alpha}(34,t_3-t_4)\langle A^\nu(\bar{3},t_3)A^\mu(\bar{4},t_4)\rangle_c\}, \tag{2.29}$$

where

$$A_s^\alpha(3,t_3) \equiv \sum_\beta \int d\bar{3}'\, L_I^{\alpha\beta}(3\bar{3}')f_s^\alpha(3,t_3)f^\beta(\bar{3}',t_3), \tag{2.30a}$$

$$A^\nu(\bar{3},t_3) \equiv \sum_\beta \int d\bar{3}'\, L_I^{\nu\beta}(\bar{3}\bar{3}')f^\nu(\bar{3},t_3)f^\beta(\bar{3}',t_3), \tag{2.30b}$$

and where $\langle\cdots\rangle_c$ represents a cumulant (connected) thermal average. Also in Eq. (2.28) the quantity Q_{z_c} is given by

$$Q_{z_c}^{\alpha\nu\alpha\theta}(3\bar{3};5\bar{5}) = \langle A_s^\alpha(3)f^\nu(\bar{3});f_s^\alpha(5)f^\theta(\bar{5})\rangle_c^z + \langle f_s^\alpha(3)A^\nu(\bar{3});f_s^\alpha(5)f^\theta(\bar{5})\rangle_c^z - \int d7\, d8[\langle A_s^\alpha(3)f^\nu(\bar{3});f_s^\alpha(7)\rangle_c^z + \langle f_s^\alpha(3)A^\nu(\bar{3});f_s^\alpha(7)\rangle_c^z](C_s^{\alpha\alpha})^{-1}(78)\langle f_s^\alpha(8);f_s^\alpha(5)f^\theta(\bar{5})\rangle_c^z,$$

where we use the notation

$$\langle\cdots\rangle_c^z \equiv -i\int_0^\infty dt e^{izt}\langle\cdots\rangle_c. \tag{2.31}$$

Q_{z_c} is the connected part of the quantity

$$Q_z^{\alpha\nu\alpha\theta}(3\bar{3};5\bar{5}) = Q_{z_c}^{\alpha\nu\alpha\theta}(3\bar{3};5\bar{5}) + Q_{z_D}^{\alpha\nu\alpha\theta}(3\bar{3};5\bar{5}), \tag{2.32}$$

with

$$Q_{z_D}^{\alpha\nu\alpha\theta}(3\bar{3};5\bar{5}) = -i\int_0^\infty d(t_3-t_5)e^{iz(t_3-t_5)}\{\langle A_s^\alpha(3,t_3)f_s^\alpha(5,t_5)\rangle_c C^{\nu\theta}(\bar{3}\bar{5},t_3-t_5) + C_s^{\alpha\alpha}(35,t_3-t_5)\langle A^\nu(\bar{3},t_3)f^\theta(\bar{5},t_5)\rangle_c\}. \tag{2.33}$$

Finally in Eq. (2.28), G_c^{-1} is the inverse of the connected part of G_s, i.e.,

$$\sum_\phi \int d6\,d\bar{6}\,G_c^{\alpha\theta\alpha\phi^{-1}}(5\bar{5};6\bar{6})G_c^{\alpha\phi\alpha\xi}(6\bar{6};7\bar{7}) = \delta_{\theta\xi}(57)\delta(\bar{5}\bar{7}), \tag{2.34}$$

where G_c is given as

$$G_c^{\alpha\phi\alpha\xi}(6\bar{6};7\bar{7}) = G_s^{\alpha\phi\alpha\xi}(6\bar{6};7\bar{7}) - G_D^{\alpha\phi\alpha\xi}(6\bar{6};7\bar{7}), \tag{2.35a}$$

with

$$G_D^{\alpha\phi\alpha\xi}(6\bar{6};7\bar{7}) = -i\int_0^\infty d(t_6-t_7)\,e^{iz(t_6-t_7)}C_s^{\alpha\alpha}(67,t_6-t_7)C^{\phi\xi}(\bar{6}\bar{7},t_6-t_7). \tag{2.35b}$$

In terms of the above quantities, the connected part of the collisional memory function $\Gamma_s(z)$ is given by

$$\begin{aligned}\Gamma_c^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = &-(\langle A_s^\alpha(3)f^\nu(\bar{3});A_s^\alpha(4)f^\mu(\bar{4})\rangle_c^z + \langle A_s^\alpha(3)f^\nu(\bar{3});f_s^\alpha(4)A^\mu(\bar{4})\rangle_c^z\\ &+\langle f_s^\alpha(3)A^\nu(\bar{3});A_s^\alpha(4)f^\mu(\bar{4})\rangle_c^z + \langle f_s^\alpha(3)A^\nu(\bar{3});f_s^\alpha(4)A^\mu(\bar{4})\rangle_c^z\\ &-\int d5\,d6[(\langle A_s^\alpha(3)f^\mu(\bar{3});f_s^\alpha(5)\rangle_c^z + \langle f_s^\alpha(3)A^\nu(\bar{3});f_s^\alpha(5)\rangle_c^z)C^{\alpha\alpha^{-1}}(56)\\ &\times(\langle f_s^\alpha(6);A_s^\alpha(4)f^\mu(\bar{4})\rangle_c^z + \langle f_s^\alpha(6);f_s^\alpha(4)A^\mu(\bar{4})\rangle_c^z)]\\ &-\sum_\theta\int d5\,d\bar{5}\sum_\phi\int d6\,d\bar{6}\,Q_{z_c}^{\alpha\nu\alpha\theta}(3\bar{3};5\bar{5})G_c^{\alpha\theta\alpha\phi^{-1}}(5\bar{5};6\bar{6})(Q^T)_{z_c}^{\alpha\phi\alpha\mu}(6\bar{6};4\bar{4}).\end{aligned} \tag{2.36}$$

The expressions presented here for the memory function $\phi_s^{\alpha\alpha}$ are all formally exact, but they are difficult to interpret and work with. We invoke one more set of operator identities to cast our expression for $\phi_s^{\alpha\alpha}$ into a form more amenable to approximation. Schematically, we can write Eq. (2.17)

$$\phi_s = -\mathcal{V}_s\bar{G}_s\mathcal{V}_s, \tag{2.37}$$

with

$$\bar{G}_s = [z\tilde{G}_s - W_s - \Gamma_s(z)]^{-1}. \tag{2.38}$$

It is well known[2,4,5] that if one approximates $\bar{G}_s$ by its mean-field value

$$\bar{G}_M = [z\tilde{G}_s - W_s]^{-1}, \tag{2.39}$$

and makes simple approximations for $\tilde{G}_s$ and W_s, the Enskog theory is retrieved. This motivates rewriting Eq. (2.37) in the formally exact form

$$\phi_s = -\mathcal{V}_s\bar{G}_M\mathcal{V}_s - \mathcal{V}_s\bar{G}_M\{\bar{G}_M^{-1}[\bar{G}_s - \bar{G}_M]\bar{G}_M^{-1}\}\bar{G}_M\mathcal{V}_s, \tag{2.40}$$

where the first term contains the Enskog approximation to ϕ_s and the second term contains higher-order contributions. As we will see in Secs. II C–II E, in the form of Eq. (2.40), ϕ_s is readily amenable to physical approximation.

C. Enskog approximation

The derivation from FRKT of the Enskog approximation to the memory function is well established.[2,4,5] One neglects the second term of Eq. (2.40) and makes two approximations to the first term. The first approximation is to keep only the diagonal contributions to $\tilde{G}_s$ and W_s; that is, one uses Eq. (2.24) for $\tilde{G}_s$ and Eq. (2.26) for W_s. The resultant approximate memory function is

$$\begin{aligned}\phi_s^{\alpha\alpha}(12)n_\alpha f_0^\alpha(p_2) &= \sum_\nu\int d3\int d\bar{3}\,\delta(13)\tilde{L}_I^{\alpha\nu}(3\bar{3})[z-\tilde{L}^{\alpha\nu}(3\bar{3})]^{-1}\\ &\quad\times\omega_0^{\alpha\nu}(3\bar{3})\tilde{L}_I^{\alpha\nu}(3\bar{3})\delta(23).\end{aligned} \tag{2.41}$$

Now note that $\tilde{L}_I^{\alpha\nu}$ is sharply peaked near the point where the collision occurs; that is, at an interparticle separation equal to an effective hard-core separation of $\sigma_{\alpha\nu}$. Hence the integrand is restricted to the separation where $|\vec{r}_3 - \vec{r}_{\bar{3}}| \approx \sigma_{\alpha\nu}$. In view of this one makes the additional approximation in Eq. (2.41) that

$$\tilde{L}_I^{\alpha\nu}(3\bar{3}) \approx L_I^{\alpha\nu}(3\bar{3}) \tag{2.42a}$$

and

$$\omega_0^{\alpha\nu}(3\bar{3})\tilde{L}_I^{\alpha\nu}(3\bar{3}) \approx \omega_0^\alpha(3)\omega_0^\nu(\bar{3})\tilde{g}^{\alpha\nu}(\sigma_{\alpha\nu})e^{-\beta V^{\alpha\nu}(r_{3\bar{3}})}L_I^{\alpha\nu}(3\bar{3}), \tag{2.42b}$$

where we have written $g^{\alpha\nu}$ in terms of its low-density limit $e^{-\beta V^{\alpha\nu}}$ as

$$g^{\alpha\nu}(r_{3\bar{3}}) = \tilde{g}^{\alpha\nu}(r_{3\bar{3}}) e^{-\beta V^{\alpha\nu}(r_{3\bar{3}})} . \tag{2.43}$$

One then substitutes Eq. (2.42) into Eq. (2.41) and after some straightforward manipulations finds that the Enskog memory function $\phi^{\alpha\alpha}_{s_E}$ is

$$\phi^{\alpha\alpha}_{s_E}(12) f^{\alpha}_0(p_2) = \sum_{\nu} n_\nu \int d3\, d\bar{3} f^{\alpha}_0(p_3) f^{\nu}_0(p_{\bar{3}}) \delta(13) \times T^{\alpha\nu}_E(3\bar{3}; z)\delta(23), \tag{2.44}$$

where the Enskog binary collision operator[20] is

$$T^{\alpha\nu}_E(3\bar{3}; z) = \tilde{g}^{\alpha\nu}(\sigma_{\alpha\nu})[z - L^{\alpha\nu}_0(3\bar{3})] e^{-\beta V^{\alpha\nu}(r_{3\bar{3}})} \times \{[z - L^{\alpha\nu}(3\bar{3})]^{-1} - [z - L^{\alpha\nu}_0(3\bar{3})]^{-1}\} \times [z - L^{\alpha\nu}_0(3\bar{3})] . \tag{2.45}$$

The Enskog approximation, in which the tagged particle undergoes only uncorrelated collisions with the bath particles, is good only for moderately dense systems. As the density increases, one must include other dynamical events. We use Eq. (2.44) as our approximation to the first term in Eq. (2.40) for all densities.

D. Ring approximation

The derivation from FRKT of the ring approximation in simple fluids is also well established.[3-5] For the mixture one proceeds in an analogous fashion.

First we rewrite the second term of Eq. (2.40) in the formally exact form

$$\delta\phi_s = -\tau \tilde{G}_D \bar{G}_{M_D} \tilde{G}_D \tilde{G}_s^{-1} \{\bar{G}_M^{-1}[\bar{G}_s \bar{G}_M]\bar{G}_M^{-1}\} \times \tilde{G}_s^{-1} \tilde{G}_D \bar{G}_{M_D} \tilde{G}_D \tau^T , \tag{2.46}$$

where the operators τ and τ^T are given by

$$\tau = v_s \bar{G}_M \tilde{G}_s (\tilde{G}_D)^{-1} (\bar{G}_{M_D})^{-1} (\tilde{G}_D)^{-1} ,$$

and (2.47)

$$\tau^T = (\tilde{G}_D)^{-1} (\bar{G}_{M_D})^{-1} (\tilde{G}_D)^{-1} \tilde{G}_s \bar{G}_M v_s .$$

The advantage of introducing the operator τ and its transpose τ^T is that if we replace the various quantities appearing in their definitions by their diagonal approximations and then again assume $\tilde{L}^{\alpha\nu}_I(3\bar{3})$ is sharply peaked at $|\vec{r}_3 - \vec{r}_{\bar{3}}| \approx \sigma_{\alpha\nu}$, (i.e., make the same two approximations as were made in the Enskog term) one finds that

$$(\tau^T)^{\alpha\mu\alpha}(4\bar{4}; 2) = -T^{\alpha\mu}_E(4\bar{4}; z)\delta(24)$$

and (2.48)

$$\tau^{\alpha\alpha\nu}(1; 3\bar{3}) = \int d\bar{5} (T^T)^{\alpha\nu}_E(1\bar{5}; z)\delta(13)\delta(\bar{5}\bar{3}) ,$$

where T^T_E is the transpose of T_E. Under these simple approximations τ and τ^T represent Enskog binary encounters between the tagged particle and bath particles. In fact, Eq. (2.46) is now simply interpreted as a collision between the tagged particle and a bath particle (the operator τ^T), then some complicated intermediate propagation, and a terminating collision (τ) between the tagged particle and the same bath particle or another one which has interacted dynamically with it since the collision (τ^T). The collisions τ^T and τ are hence referred to as correlated collisions.

The simplest approximation one can make for the complicated intermediate propagation is to assume the tagged and bath particles propagate independently of one another between the collisions τ^T and τ. This is the essence of the ring approximation. In mathematical terms it means approximate the intermediate propagation by its "fully" disconnected form.[19] Hence Eq. (2.46) reduces to the form

$$\delta\phi_s = -\tau[G_D - G_{M_D}]\tau^T , \tag{2.49}$$

where

$$G_D = \tilde{G}_D[z\tilde{G}_D - W_D - \Gamma_D(z)]^{-1}\tilde{G}_D$$

and (2.50)

$$G_{M_D} = \tilde{G}_D[z\tilde{G}_D - W_D]^{-1}\tilde{G}_D .$$

Solving Eq. (2.50) with use of Eqs. (2.22a) and (2.25a) yields

$$G^{\alpha\nu\alpha\mu}_{M_D}(3\bar{3}; 4\bar{4}) = -i\int_0^\infty d(t_3 - t_4)\, e^{iz(t_3 - t_4)} \times C^{\alpha\alpha}_{s_0}(34, t_3 - t_4) C^{\nu\mu}_{mf}(\bar{3}\bar{4}, t_3 - t_4) , \tag{2.51}$$

where $C^{\alpha\alpha}_{s_0}$ is the free-particle form of the tagged-particle correlation function $C^{\alpha\alpha}_s$, and $C^{\nu\mu}_{mf}$ is the density fluctuation correlation function $C^{\nu\mu}$ calculated in the mean-field approximation.

To calculate G_D we must know what $\Gamma_D(z)$ is. To obtain the ring kinetic theory we only include the fully disconnected part of $\Gamma_D(z)$. That is, we approximate Eq. (2.28) as

$$\Gamma^{\alpha\nu\alpha\mu}_D(3\bar{3}; 4\bar{4}) = -F^{\alpha\nu\alpha\mu}_z(3\bar{3}; 4\bar{4}) + \sum_\theta \int d5\, d\bar{5} \sum_\phi \int d6\, d\bar{6}\, Q^{\alpha\nu\alpha\theta}_{z_D}(3\bar{3}; 5\bar{5}) G^{\alpha\theta\alpha\phi^{-1}}_D(5\bar{5}; 6\bar{6}) (Q^T)^{\alpha\phi\alpha\mu}_{z_D}(6\bar{6}; 4\bar{4}) . \tag{2.52}$$

We now can follow FRKT III using operator identities to express Γ_D in terms of the collisional memory functions $\phi_s^{\alpha\alpha}$ and $\phi^{(c)\nu\mu}$ for the kinetic equations for $C_s^{\alpha\alpha}$ and $C^{\nu\mu}$, respectively. Replacing $\phi_s^{\alpha\alpha}$ and $\phi^{(c)\nu\mu}$ by their Enskog values $\phi_{s_E}^{\alpha\alpha}$ and $\phi_E^{(c)\nu\mu}$[18], we obtained the following simple approximation[21] for Γ_D

$$\Gamma_D^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = \int d5\,\phi_{s_E}^{\alpha\alpha}(35)\tilde{G}_D^{\alpha\nu\alpha\mu}(5\bar{3};4\bar{4}) + \sum_\lambda \int d\bar{5}\,\phi_E^{(c)\nu\lambda}(3\bar{5})\tilde{G}_D^{\alpha\lambda\alpha\mu}(3\bar{5};4\bar{4}). \tag{2.53}$$

Substituting Eqs. (2.25) and (2.53) into Eq. (2.52) for G_D and following the same procedure as used for evaluating G_{M_D}, we find that

$$G_D^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = -i\int_0^\infty d(t_3-t_4)e^{i\varepsilon(t_3-t_4)}C_{s_E}^{\alpha\alpha}(34,t_3-t_4) \times C_E^{\nu\mu}(\bar{3}\bar{4};t_3-t_4), \tag{2.54}$$

where $C_{s_E}^{\alpha\alpha}$ and $C_E^{\nu\mu}$ are the correlation functions $C_s^{\alpha\alpha}$ and $C^{\nu\mu}$ calculated in the Enskog approximation.

Substituting Eqs. (2.51) and (2.54) into Eq. (2.49), the ring memory function takes the form

$$\delta\phi_R^{\alpha\alpha}(12)n_\alpha f_0^\alpha(p_2) = -\sum_\nu \int d3\,d\bar{3}\sum_\mu \int d4\,d\bar{4}\,\tau^{\alpha\alpha\nu}(1;3\bar{3}) \times(-i)\int_0^\infty d(t_3-t_4)e^{i\varepsilon(t_3-t_4)}\left[C_{s_E}^{\alpha\alpha}(34,t_3-t_4)C_E^{\nu\mu}(\bar{3}\bar{4},t_3-t_4)-C_{s_0}^{\alpha\alpha}(34,t_3-t_4)\right. \times\left.C_{mf}^{\nu\mu}(\bar{3}\bar{4},t_3-t_4)\right](\tau^T)^{\alpha\mu\alpha}(4\bar{4};2). \tag{2.55}$$

It represents the process in which the tagged particle and a bath particle first collide (τ^T) and then propagate independently of one another but interacting with the rest of the bath. Then the tagged particle and the same bath particle, or another one which has dynamically interacted with it since the τ^T collision, undergo another collision (τ) which terminates the disturbance.

The ring kinetic theory extends the description of the dynamical properties of fluids to higher densities than the Enskog theory. It predicts the long-time tail of the velocity $(t^{-3/2})$ (Refs. 3, 5, 8) and angular velocity $(t^{-5/2})$ (Ref. 12) autocorrelation functions. It also provides a qualitative description of the "cage" effect,[10] important at high densities.[6]

As we have indicated in the introduction, though, when the tagged-particle effective diameter is less than the bath-particle mean-free path, one must consider contributions to the memory function in which the tagged particle undergoes many correlated collisions with a single bath particle, as the larger particle moves from the field-point 2 to the field-point 1. In the next section we incorporate such contributions into the kinetic theory.

E. Repeated-ring approximation

Let us return to Eqs. (2.46)–(2.48). We have interpreted this term as describing processes in which the tagged particle and a bath particle collide (τ^T) and then undergo some complicated intermediate propagation before the terminating collision (τ). In the ring approximation, this intermediate propagation is assumed to be such that the tagged particle and its initial-collision partner interact with the remaining bath particles, but independently of one another. In the repeated-ring approximation we also allow, during this intermediate propagation, the tagged particle to interact with its initial-collision partner or another particle dynamically correlated with its initial-collision partner. Such contributions are to be found in the connected parts of W_S and $\Gamma_s(z)$.[22]

To obtain these contributions we return to Eq. (2.26), which expresses W_s in the diagonal approximation. Clearly, the contribution to W_s in which the particles at 4 and $\bar{4}$ (after the collision τ^T) are able to interact during the propagation to 3 and $\bar{3}$ (where they undergo the collision τ) is

$$W_{s_I}^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = \omega_0^{\alpha\nu}(3\bar{3})\tilde{L}_I^{\alpha\nu}(3\bar{3})\delta(34)\delta_{\nu\mu}\delta(\bar{3}\bar{4}). \tag{2.56a}$$

In the diagonal approximation for $\tilde{G}_D$, and assuming $\tilde{L}_I$ is sharply peaked at $|\vec{r}_5-\vec{r}_{\bar{5}}|\sim\sigma_{\alpha\lambda}$ [see Eq. (2.42)],

$$W_{s_I}^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = \sum_\lambda \int d5\,d\bar{5}\,\tilde{G}_D^{\alpha\nu\alpha\lambda}(3\bar{3};5\bar{5}) \times\tilde{g}^{\alpha\lambda}(\sigma_{\alpha\lambda})e^{-\beta V^{\alpha\lambda}(r_{5\bar{5}})}L_I^{\alpha\lambda}(5\bar{5}) \times\delta(54)\delta_{\nu\mu}\delta(\bar{5}\bar{4}). \tag{2.56b}$$

We use W_{s_I} as our approximation to W_c. The quan-

tity W_D is still given exactly by Eq. (2.25).

In Appendix A we demonstrate that the appropriate approximation to the connected part of $\Gamma_s(z)$ is

$$\Gamma_c^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = \sum_\lambda \int d5\, d\bar{5}\, \tilde{G}_D^{\alpha\nu\alpha\lambda}(3\bar{3};5\bar{5}) L_I^{\alpha\lambda}(5\bar{5}) \times \bar{g}^{\alpha\lambda}(\sigma_{\alpha\lambda}) e^{-\beta V^{\alpha\lambda}(r_{5\bar{5}})} \times [z - L^{\alpha\lambda}(5\bar{5})]^{-1} L_I^{\alpha\lambda}(5\bar{5}) \times \delta(54)\delta_{\lambda\mu}\delta(\bar{5}\bar{4}) \quad (2.57)$$

in the diagonal approximation for $\tilde{G}_D$. We still use the approximation for $\Gamma_D(z)$ given by Eq. (2.53).

Summing Eqs. (2.56b) and (2.57) one has, with Eq. (2.45),

$$W_c^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) + \Gamma_c^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = \sum_\lambda \int d5\, d\bar{5}\, \tilde{G}_D^{\alpha\nu\alpha\lambda}(3\bar{3};5\bar{5}) T_E^{\alpha\lambda}(5\bar{5};z) \times \delta(54)\delta_{\lambda\mu}\delta(\bar{5}\bar{4}) \equiv \overline{T}^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}). \quad (2.58)$$

The operator $\overline{T}$ represents a collision between the tagged particle and its initial-collision partner or another particle dynamically correlated with its initial-collision partner. Incorporating this connected term in the memory function, Eq. (2.38) becomes

$$\overline{G}_s = [z\tilde{G}_s - W_D - \Gamma_D(z) - \overline{T}]^{-1} = \overline{G}_s' + \overline{G}_s'\overline{T}\overline{G}_s' + \overline{G}_s'\overline{T}\overline{G}_s'\overline{T}\overline{G}_s' + \cdots, \quad (2.59)$$

where

$$\overline{G}_s' = [z\tilde{G}_s - W_D - \Gamma_D(z)]^{-1}. \quad (2.60)$$

We substitute Eq. (2.59) into Eq. (2.46) and note that the operators τ, τ^T, and $\overline{T}$ all represent collisions between the tagged particle and its original-collision partner or another bath particle dynamically correlated with it. Between these operators we make the "fully" disconnected approximation[19] and find that

$$\delta\phi = -\tau\{[G_D + G_D T G_D + G_D T G_D T G_D + \cdots] - G_{M_D}\}\tau^T, \quad (2.61)$$

where

$$T = \tilde{G}_D^{-1}\overline{T}\tilde{G}_D^{-1}, \quad (2.62)$$

and G_{M_D} and G_D are given by Eqs. (2.51) and (2.54), respectively.

The interpretation of Eq. (2.61) is straightforward. The term $-\tau[G_D - G_{M_D}]\tau^T$ is the ring approximation. Remember that τ, τ^T, and T are all expressed in terms of the Enskog collision operator T_E. Consider the term in Eq. (2.61) with n T_E operators. It describes processes in which first the tagged particle and another particle i undergo a collision. They then travel independently of one another interacting with the rest of the bath via Enskog collisions. After some time, the tagged particle again collides with i or with some other particle j which has collided with particle i since the tagged particle and the particle i first collided. This process continues until there have been n such correlated binary collisions.

It is also fruitful to note that since Eq. (2.61) represents a geometric series that we can resum it to write

$$\delta\phi = -\tau\{G_D' - G_{M_D}\}\tau^T, \quad (2.63)$$

where

$$G_D'^{\alpha\nu\alpha\mu}(3\bar{3},4\bar{4}) = \sum_\lambda \int d5\, d\bar{5}\{[z - L_0^{\alpha\nu}(3\bar{3}) - T_E^{\alpha\nu}(3\bar{3})]\delta(35)\delta_{\nu\lambda}\delta(\bar{3}\bar{5}) - \phi_{s_E}^{\alpha\alpha}(35)\delta_{\nu\lambda}\delta(\bar{3}\bar{5}) - \phi_E^{\nu\lambda}(\bar{3}\bar{5})\delta(35)\}^{-1}\tilde{C}_s^{\alpha\alpha}(54)\tilde{C}^{\lambda\mu}(\bar{5}\bar{4}). \quad (2.64)$$

G_D' describes the propagation between the initial collision, where the tagged particle and its collision partner are at 4 and $\bar{4}$, respectively, and the final collision at 3 and $\bar{3}$. This propagation is comprised of contributions in which the two particles free stream (L_0) and interact ($T_E^{\alpha\lambda}$) with one another, and of contributions in which the tagged particle interacts with the rest of the medium ($\phi_{s_E}^{\alpha\alpha}$), but independently of its initial-collision partner's interaction with the rest of the medium ($\phi_E^{\nu\lambda}$).

The memory function given in Eqs. (2.44), (2.63), and (2.64) with Eq. (2.9) for the two-point self-correlation function $C_s^{\alpha\alpha}(12)$ specifies the repeated-ring kinetic equation. It has a rather complicated structure, but, as we shall see, its solution can be expressed in terms of the solution of the ring kinetic equation. In Sec. III we solve both the ring and, using these results, the repeated-ring kinetic theory for velocity autocorrelation in a dilute solution of large tagged particles in a dense solvent of small particles.

III. SOLUTION OF THE KINETIC EQUATION

A. Assumptions

We consider here a dilute solution of hard-sphere tagged particles with diameter σ_B and mass

m_B in a solvent of hard-sphere bath particles with diameter σ_b and mass m_b. By dilute we mean that the number densities of tagged and bath particles, n_B and n_b, respectively, are such that $n_B\sigma_B^3 \ll n_b\sigma_b^3$; hence, we can neglect the interactions among the tagged particles.

We also restrict this analysis to bath-particle diameters σ_b and mean-free paths $l_b = [4\sqrt{\pi}\, n_b\sigma_b^2\tilde{g}^{bb}(\sigma_b)]^{-1}$ much smaller than the tagged-particle diameter σ_B: $\sigma_B \gg \sigma_b \gtrsim l_b$. As pointed out in the Introduction, when $l_b \ll \sigma_B$, it is evident that the bath particles may undergo many correlated collisions with the tagged particle, so that in this regime the effect of repeated-ring events will be significant. For a rather dense solvent, $\frac{1}{10}\sqrt{2} \leq n_b\sigma_b^3 \leq \frac{2}{3}\sqrt{2}$, the bath mean-free path satisfies the inequality $0.825\,\sigma_b \geq l_b \geq 0.026\sigma_b$. Thus, the tagged particle does not have to be too much larger than the bath particle to have the condition $l_b \ll \sigma_B$ satisfied. However, when $\sigma_B \approx \sigma_b \gg l_b$, the coupling of the tagged-particle motion to the longitudinal and transverse collective modes in the bath must be incorporated into the intermediate propagation between correlated collisions. Here we treat only the limit $\sigma_B \gg \sigma_b \gtrsim l_b$ where, as we demonstrate below, further simplification arises since the coupling of the tagged-particle motion to the longitudinal collective modes in the bath is negligible.

Henceforth we shall refer to the tagged particle as the B particle. By B we mean a big particle, but not necessarily a Brownian particle, since this usage is reserved for particles whose mass is such that $m_b/m_B \to 0$.

Since the tagged and fluid particles are assumed to be hard spheres, the Enskog binary-collision operator T_E^{Bb} describing a collision between a tagged and a bath particle in the fluid is frequency independent. It is[23]

$$T_E^{Bb}(3\bar{3}) = i\tilde{g}^{Bb}(\sigma_{Bb})(\vec{p}_{\bar{3}3}\cdot\hat{r}_{\bar{3}3}/m_{Bb})\theta(\vec{p}_{\bar{3}3}\cdot\hat{r}_{\bar{3}3}) \times \delta(|\vec{r}_{\bar{3}3}| - \sigma_{Bb})[b_{3\bar{3}} - 1]. \tag{3.1}$$

In Eq. (3.1) the separation of the two spheres at collision is $\sigma_{Bb} = \frac{1}{2}(\sigma_B + \sigma_b)$, the reduced mass is $m_{Bb} = m_B m_b/(m_B + m_b)$, the unit vector joining the centers of the spheres at contact is $\hat{r}_{\bar{3}3} = \vec{r}_{\bar{3}3}/\sigma_{Bb}$, the relative momentum before the collision is $\vec{p}_{\bar{3}3} = (m_B\vec{p}_{\bar{3}} - m_b\vec{p}_3)/(m_B + m_b)$ and the Heaviside step function is $\Theta(x) = 1$ for $x \geq 0$ and $\Theta(x) = 0$ for $x < 0$. The operator $b_{3\bar{3}}$ changes the precollision momenta of the two particles to their postcollision values; i.e., $b_{3\bar{3}}f(\vec{p}_3, \vec{p}_{\bar{3}}) = f(\vec{p}_3^{\,*}, \vec{p}_{\bar{3}}^{\,*})$, where

$$\vec{p}_3^{\,*} = \vec{p}_3 + 2\hat{r}_{\bar{3}3}(\hat{r}_{\bar{3}3}\cdot\vec{p}_{\bar{3}3})$$

and

$$\vec{p}_{\bar{3}}^{\,*} = \vec{p}_{\bar{3}} - 2\hat{r}_{\bar{3}3}(\hat{r}_{\bar{3}3}\cdot\vec{p}_{\bar{3}3}). \tag{3.2}$$

We concentrate on the tagged-particle velocity autocorrelation function, $\psi_v^B(z)$, which can be written as the following momentum moment of the tagged-particle phase-space correlation function C_s^{BB}:

$$\psi_v^B(z) = \frac{1}{m_B^2}\,\frac{1}{n_B}\,\frac{1}{\Omega}\int d1\int d2\, p_{1_z} C_s^{BB}(12) p_{2_z}. \tag{3.3}$$

The tagged-particle diffusion coefficient D^B, which is also of interest here, is given in terms of ψ_v^B as

$$D^B = \lim_{z\to i0^+} i\psi_v^B(z). \tag{3.4}$$

The velocity autocorrelation function is to be obtained from the formal solution

$$C_s^{BB}(12) = \int d3[\, z\delta(13) - \phi_{s_E}^{BB}(13) - \delta\phi_s^{BB}(13)]^{-1}\tilde{C}_s^{BB}(32) \tag{3.5}$$

of our repeated-ring kinetic theory; where $\phi_{s_E}^{BB}$ is given in Eq. (2.44) and $\delta\phi_s^{BB}$ is given in Eq. (2.63). We assume that $\phi_{s_E}^{BB}$ and $\delta\phi_s^{BB}$ are "diagonal"[24] on p_{1z} so that the velocity autocorrelation function is given by

$$\psi_v^B(z) = (k_BT/m_B)[z - \Lambda(z) - R(z)]^{-1}, \tag{3.6a}$$

with

$$\Lambda(z) = (m_B/k_BT)\Omega^{-1}\int d1\, d3\, p_{1z}\,\phi_{s_E}^{BB}(13) f_0^B(p_3) p_{3z} \tag{3.6b}$$

and

$$R(z) = (m_B/k_BT)\Omega^{-1}\int d1\, d3\, p_{1z}\delta\phi_s^{BB}(13) f_0^B(p_3) p_{3z}. \tag{3.6c}$$

B. Enskog solution

The simple form of the hard-sphere collision operator T_E^{Bb} of Eq. (3.1) allows one to calculate readily the matrix element $\Lambda(z)$ of the Enskog memory function. It is found to be frequency independent and of the form

$$\Lambda(z) = -i\lambda_E. \tag{3.7}$$

The Enskog velocity relaxation frequency is

$$\lambda_E = \{4m_b/[3(m_B + m_b)]\}\tau_E^{Bb^{-1}}, \tag{3.8}$$

and the B-particle–bath-particle collision frequency is[7]

$$\tau_E^{Bb^{-1}} = 2n_b\sigma_{Bb}^2\tilde{g}^{Bb}(\sigma_{Bb})[2\pi(m_B + m_b)/\beta m_B m_b]^{1/2}. \tag{3.9}$$

In the Enskog approximation $R(z) = 0$ the velocity

autocorrelation function decays exponentially in time;

$$\psi^B_{v_E}(t) = (k_B T/m_B) e^{-\lambda_E t} . \tag{3.10}$$

From Eq. (3.8) it is clear that as the mass of the B particle increases $\lambda_E \ll \tau_E^{Bb^{-1}}$. Hence it takes many collisions for the lighter bath particles to slow down a heavy B particle. It should also be noted, though, that the initial value of $\psi^B_{v_E}$, the mean-squared B-particle velocity, decreases as m_B increases. The net effect is that the area under the curve of $\psi^B_{v_E}(t)$ vs t (i.e., the diffusion coefficient) is rather insensitive to the mass ratio m_B/m_b. The Enskog diffusion coefficient has the form

$$D^B_E = (k_B T/m_B)\lambda_E^{-1} . \tag{3.11}$$

Its weak dependence on the mass ratio m_B/m_b is best exhibited by noting that

$$\lim_{m_B/m_b \gg 1} D^B_E = \tfrac{1}{2}\sqrt{2} \lim_{m_B/m_b \to 1} D^B_E . \tag{3.12a}$$

By contrast, the diffusion coefficient is a sensitive function of the B-particle size. In particular

$$\lim_{\sigma_B/\sigma_b \gg 1} D^B_E = \left(\frac{\sigma_b}{\frac{1}{2}\sigma_B}\right)^2 \lim_{\sigma_B/\sigma_b \to 1} D^B_E . \tag{3.12b}$$

Thus, almost independently of its mass, as the cross section of the B particle increases its Enskog diffusion coefficient decreases rapidly.

The Enskog theory is appropriate for a tagged particle's motion when $\sigma_B \ll l_b$. However, for dense fluids, where $l_b \ll \sigma_B$, the Enskog theory does not predict the inverse diameter dependence for the B-particle diffusion coefficient.

C. Ring solution

The velocity autocorrelation function of the B particle is obtained, in the ring approximation, by substituting Eq. (2.55) for $\delta\phi_s$ into Eqs. (3.6). One finds

$$\psi^B_v(z) = k_B T/m_B [z + i\lambda_E - R_1(z)]^{-1} , \tag{3.13}$$

where the ring memory function is

$$R_1(z) = -n_B^{-1}\Omega^{-1}\int d1\,d2\int d3\,d\bar{3}\int d4\,d\bar{4}\,(m_B k_B T)^{-1/2} p_{1z}\tau^{BBb}(1;3\bar{3})$$
$$\times(-i)\int_0^\infty d(t_3 - t_4)\, e^{iz(t_3-t_4)}[C^{BB}_{s_E}(34, t_3-t_4)\, C^{b,b}_E(\bar{3}\bar{4}, t_3-t_4) - C^{BB}_{s_0}(34, t_3-t_4)\, C^{bb}_{mf}(\bar{3}\bar{4}, t_3-t_4)]$$
$$\times(\tau^T)^{BbB}(4\bar{4};2)(m_B k_B T)^{-1/2} p_{2z} . \tag{3.14}$$

We introduce the spatial Fourier representation of the correlation function C^{BB}_s as

$$C^{BB}_s(34, t_3 - t_4) = \Omega^{-1}\sum_{\vec{q}} e^{-i\vec{q}\cdot\vec{r}_{34}} C^{BB}_s(\vec{q}, \vec{p}_3, \vec{p}_4; t_3 - t_4) , \tag{3.15a}$$

where

$$C^{BB}_s(\vec{q}, \vec{p}_3, \vec{p}_4, t_3 - t_4) = \Omega^{-1}\int d\vec{r}_3\, d\vec{r}_4\, e^{i\vec{q}\cdot\vec{r}_{34}} C^{BB}_s(34, t_3 - t_4) . \tag{3.15b}$$

Substituting Eq. (3.15a) and the analogous Fourier representation for $C^{bb}(\bar{3}\bar{4}, t_3 - t_4)$ into Eq. (3.14) we find (in the limit $\Omega \to \infty$)

$$R_1(z) = -\frac{1}{n_B}\left(\frac{1}{2\pi}\right)^3 \int d\vec{q}\int d\vec{p}_1 d\vec{p}_2 \int d\vec{p}_3 d\vec{p}_{\bar{3}} \int d\vec{p}_4 d\vec{p}_{\bar{4}} (m_B k_B T)^{-1/2} p_{1z}\tau^{BBb}(\vec{q}; \vec{p}_1; \vec{p}_3, \vec{p}_{\bar{3}})(-i)$$
$$\times\int_0^\infty d(t_3 - t_4)\, e^{iz(t_3-t_4)}[C^{BB}_{s_E}(\vec{q}; \vec{p}_3, \vec{p}_4; t_3 - t_4) C^{bb}_E(-\vec{q}; \vec{p}_{\bar{3}}, \vec{p}_{\bar{4}}; t_3 - t_4)$$
$$- C^{BB}_{s_0}(\vec{q}; \vec{p}_3, \vec{p}_4; t_3 - t_4) C^{bb}_{mf}(-\vec{q}; \vec{p}_{\bar{3}}, \vec{p}_{\bar{4}}; t_3 - t_4)]$$
$$\times(\tau^T)^{BbB}(\vec{q}; \vec{p}_5, \vec{p}_{\bar{5}}; \vec{p}_2)(m_B k_B T)^{-1/2} p_{2z} . \tag{3.16a}$$

The Fourier-transformed collision operator τ^T has the form

$$(\tau^T)^{BbB}(\vec{q}; \vec{p}_4, \vec{p}_{\bar{4}}, \vec{p}_2) = -\int d\vec{r}_{\bar{4}4}\, e^{i\vec{q}\cdot\vec{r}_{\bar{4}4}} T^{Bb}_E(4\bar{4})\delta(\vec{p}_2 - \vec{p}_4) , \tag{3.16b}$$

and, similarly

$$\tau^{BBb}(\vec{q}; \vec{p}_1 \vec{p}_3, \vec{p}_{\bar{3}}) = \int dr_{\bar{4}1}\int dp_{\bar{4}}(T^T)^{Bb}_E(1\bar{4})[e^{+i\vec{q}\cdot\vec{r}_{\bar{4}1}}\delta(\vec{p}_1 - \vec{p}_3)\delta(\vec{p}_{\bar{4}} - \vec{p}_{\bar{3}})] . \tag{3.16c}$$

The full momentum dependence in the correlation functions C^{BB}_s and C^{bb}, as well as in the collision

terms τ and τ^T, leads to considerable difficulty in the evaluation of (3.16a). We follow Furtado *et al.*[11] to evaluate these correlation functions. First, we expand C_s^{BB} in the formally-exact form

$$C_s^{BB}(\vec{q};\vec{p}_3,\vec{p}_4;t_3-t_4)=\sum_{I,J=1}^{\infty} f_0^B(p_3)H_I^B(p_3)n_B C_{s_{IJ}}^{BB}(q,t_3-t_4)f_0^B(p_4)H_J^B(p_4)\,. \tag{3.17}$$

The momentum-contracted correlation functions are

$$C_{s_{IJ}}^{BB}(\vec{q},t_3-t_4)=n_B^{-1}\int d\vec{p}_3\int d\vec{p}_4 H_I^B(\vec{p}_3)\,C_s^{BB}(\vec{q};\vec{p}_3,\vec{p}_4;t_3-t_4)H_J^B(\vec{p}_4)\,; \tag{3.18}$$

and the momentum functions $H_I^B(\vec{p}_3)$ form a complete orthonormal set. C^{bb} is expanded in the same basis set. The first five momentum functions are listed below in terms of the dimensionless momentum $\vec{\xi}^B = (m_B k_B T)^{-1/2}\vec{p}_B$:

$$H_1^B(\vec{p})=1,\quad H_2^B(\vec{p})=\xi_{x_q}^B,\quad H_3^B(\vec{p})=\xi_{y_q}^B,\quad H_4^B(\vec{p})=\xi_{z_q}^B,\quad H_5^B(\vec{p})=\tfrac{1}{6}(\xi^2-3)\,. \tag{3.19}$$

We have defined the z direction in the $\vec{q}$ reference frame to lie along $\vec{q}$; $z_q=\vec{q}/|\vec{q}|$. In this basis the (momentum-contracted) correlation function $C_{s_{11}}^{BB}(\vec{q},t_3-t_4)$ is the self-part of the van Hove correlation function while $C_{s_{44}}^{BB}(\vec{q}=0,t_3-t_4)$ is the velocity autocorrelation function.

We now employ the quasihydrodynamic approximation[11] for the correlation functions appearing in Eq. (3.16a). The product $C_{s_E}^{BB}C_E^{bb}$ is written

$$\begin{aligned}C_{s_E}^{BB}(\vec{q};\vec{p}_3,\vec{p}_4;t_3-t_4)\,C_E^{bb}(-\vec{q};\vec{p}_{\bar{3}},\vec{p}_{\bar{4}},t_3-t_4)&\\ \approx n_B n_b f_0^B(p_3)f_0^B(p_4)f_0^b(p_{\bar{3}})f_0^b(p_{\bar{4}})&\\ \times\sum_{\bar{I},\bar{J}=1}^{5} H_{\bar{I}}^b(\vec{p}_{\bar{3}})[C_{s_{E_{11}}}^{BB}(q,t)C_{E_{\bar{I}\bar{J}}}^{bb}(-q,t)-e^{-(\lambda_B+\lambda_b)t}C_{s_{0_{11}}}^{BB}(q,t)\,C_{0_{\bar{I}\bar{J}}}^{bb}(-q,t)]H_{\bar{J}}^b(\vec{p}_{\bar{4}})\,.&\end{aligned} \tag{3.20}$$

In Eq. (3.20) the quantities λ_B and λ_b are nonhydrodynamic relaxation frequencies and will be discussed shortly. The subscript 0 again implies free-particle quantities. The nature of the quasihydrodynamic approximation is evident in Eq. (3.20). The first term $C_{s_{E_{11}}}^{BB}(q,t)\,C_{E_{\bar{I}\bar{J}}}^{bb}(-q,t)$ represents the contributions from the correlation functions of the conserved variables (those which persist for times much longer than the B-particle mean free time for C_s^{BB} and much longer than the bath-particle mean free time for C^{bb}). In the tagged-particle motion there is only one such correlation function, $C_{s_{E_{11}}}^{BB}(q,t)$. However for the bath fluctuations the correlation functions of the conserved variables are $C_{E_{\bar{I}\bar{J}}}^{bb}(-q,t)$ with $\bar{I}\le 5,\bar{J}\le 5$. [Note that $C_{E_{11}}^{bb}(-q,t)$ is the van Hove correlation function, $C_{E_{22}}^{bb}(-q,t)=C_{E_{33}}^{bb}(-q,t)$ are the transverse-current correlation functions, $C_{E_{44}}^{bb}(-q,t)$ is the longitudinal-current correlation function and $C_{E_{55}}^{bb}(-q,t)$ is the energy correlation function.] The second term, $e^{-(\lambda_B+\lambda_b)t}C_{s_{0_{11}}}^{BB}C_{0_{\bar{I}\bar{J}}}^{bb}$, represents the approximate contributions from the correlation functions of the nonconserved variables. We set the nonhydrodynamic relaxation frequencies λ_B and λ_b equal to the smallest nonhydrodynamic matrix element of the collisional memory functions $\phi_{s_E}^{BB}$ and $\phi_E^{(c)bb}$, respectively. Hence $\lambda_B=\lambda_E$ defined in Eq. (3.8) and $\lambda_b=\frac{4}{5}\tau_E^{bb-1}$,[25] where the bath-particle collision frequency is $\tau_E^{bb-1}=[4n_b\sigma_b^2\tilde{g}^{bb}(\sigma_b)(\pi/\beta m_b)^{1/2}]$. One makes the same type of approximation to the product of mean-field correlation functions $C_{s_0}^{BB}C_{mf}^{bb}$ of Eq. (3.16a). Thus we approximate the term in square brackets $[\cdots]$ in Eq. (3.16a) as

$$\begin{aligned}[C_{s_E}^{BB}(\vec{q};\vec{p}_3,\vec{p}_4;t_3-t_4)\,C_E^{bb}(-\vec{q},\vec{p}_{\bar{3}},\vec{p}_{\bar{4}},t_3-t_4)-C_{s_0}^{BB}(\vec{q},\vec{p}_3,\vec{p}_4;t_3-t_4)\,C_{mf}^{bb}(-\vec{q};\vec{p}_{\bar{3}};\vec{p}_{\bar{4}};t_3-t_4)]&\\ \approx n_B n_b f_0^B(p_3)f_0^B(p_4)f_0^b(p_{\bar{3}})f_0^b(p_{\bar{4}})\sum_{\bar{I},\bar{J}=1}^{5}H_{\bar{I}}^b(\vec{p}_{\bar{3}})\Delta_{11\bar{I}\bar{J}}(q,t)H_{\bar{J}}^b(\vec{p}_{\bar{4}})\,,&\end{aligned} \tag{3.21a}$$

where

$$\begin{aligned}\Delta_{11\bar{I}\bar{J}}(q,t)=&\,C_{s_{E_{11}}}^{BB}(q,t)\,C_{E_{\bar{I}\bar{J}}}^{bb}(-q,t)-e^{-(\lambda_B+\lambda_b)t}C_{s_{0_{11}}}^{BB}(q,t)\,C_{0_{\bar{I}\bar{J}}}^{bb}(-q,t)\\ &-C_{s_{0_{11}}}^{BB}(q,t)\,C_{mf_{\bar{I}\bar{J}}}^{bb}(-q,t)+C_{s_{0_{11}}}^{BB}(q,t)\,C_{0_{\bar{I}\bar{J}}}^{bb}(-q,t)\,.\end{aligned} \tag{3.21b}$$

In Eq. (3.16a) the z component of $\vec{p}_1$ (and $\vec{p}_2$) is in the laboratory reference frame, not the $\vec{q}$ reference frame. We designate the Euler angles[26] of the reference frame $\vec{q}$ relative to the laboratory reference frame as θ_q, ϕ_q, and ψ_q. Thus, we can write p_{1z} in the $\vec{q}$ reference frame as

$$(m_B k_B T)^{-1/2}p_{1z}=\sum_{k=2}^{4}H_k^B(\vec{p}_1)\epsilon_k\,, \tag{3.22}$$

where $\epsilon_2 = \sin\theta_q \cos\phi_q$, $\epsilon_3 = \sin\phi_q \sin\phi_q$, and $\epsilon_4 = \cos\theta_q$.

Substituting Eq. (3.21) for the correlation functions and Eq. (3.22) into Eq. (3.16a), we find that the ring memory function takes the form

$$R_1(z) = -n_b \sum_{\bar{I},\bar{J}=1}^{5} \sum_{K,M=2}^{4} \left(\frac{1}{2\pi}\right)^3 \int d\vec{q}\, \epsilon_K \epsilon_M B^{Bb}_{K\bar{I}}(q)(B^T)^{Bb}_{M\bar{J}}(q)(-i) \int_0^\infty dt\, e^{izt} \Delta_{11\bar{I}\bar{J}}(q,t). \tag{3.23}$$

In Eq. (3.23) $(B^T)^{Bb}_{M\bar{J}}(q)$, which is a momentum matrix element of the Enskog collision operator, is

$$(B^T)^{Bb}_{M\bar{J}}(q) = \int d\vec{p}_2\, d\vec{p}_4\, d\vec{p}_{\bar{4}}\, f_0^B(p_4) f_0^b(p_{\bar{4}}) H^b_{\bar{J}}(\vec{p}_{\bar{4}}) (\tau^T)^{BbB}(\vec{q};\vec{p}_4,\vec{p}_{\bar{4}};\vec{p}_2) H^B_M(\vec{p}_2)$$

$$= -\int d\vec{r}_{\bar{4}\bar{4}} \int d\vec{p}_4\, d\vec{p}_{\bar{4}}\, e^{-i\vec{q}\cdot\vec{r}_{\bar{4}\bar{4}}} f_0^B(p_4) f_0^b(p_{\bar{4}}) H^b_{\bar{J}}(\vec{p}_{\bar{4}}) T^{Bb}_E(4\bar{4}) H^B_M(\vec{p}_4). \tag{3.24}$$

$B^{Bb}_{K\bar{I}}(q)$ is related to $(B^T)^{Bb}_{K\bar{I}}(q)$ as

$$B^{Bb}_{K\bar{I}}(q) = -(B^T)^{Bb}_{K\bar{I}}(q). \tag{3.25}$$

Because of the simple structure of the hard-sphere Enskog collision operator T^{Bb}_E, these matrix elements can be evaluated. The techniques one employs to evaluate these terms have been presented elsewhere.[27] The nonzero matrix elements required in this work are listed in Table I. One should note that, unlike the matrix element Λ_E of the Enskog tagged-particle memory function, the $B^{Bb}_{K\bar{I}}$ factors are nonlocal ($\vec{q}$ dependent). This arises because they couple the tagged-particle momentum change in a collison to the bath-particle momentum [see Eq. (3.24)] which is a nonlocal process. Due to spatial isotropy, though, the $B^{Bb}_{K\bar{I}}$ factors depend only on the magnitude $q \equiv |\vec{q}|$ of the wave vector $\vec{q}$. This wave-vector magnitude dependence is of the form $q\sigma_{Bb}$ since, at collision, the particles are separated by the distance σ_{Bb}.

We utilize formulas for the bath correlation functions $C^{bb}_{E\bar{I}\bar{J}}$ which were proposed by Resibois[10] and by Furtado *et al.*[11] These formulas incorporate the short-time ($t \ll \tau^{bb}_E$) and long-time ($t \gg \tau^{bb}_E$) behaviors of these correlation functions and interpolate between them for intermediate times. The interpolation formulas include collisional transfer effects. For short times and large wave vectors, $q \gg l_b^{-1}$, free-particle behavior is obtained. In the long-time (generalized hydrodynamic) form, the transport coefficients and sound speed are wave-vector dependent. For the tagged-particle correlation function $C^{BB}_{s_{E_{11}}}(q,t)$ we again utilize these interpolation formulas suitably modified for an arbitrary tagged particle, which for short times ($t \ll \tau^{Bb}_E$) reduces to $\exp(-q^2t^2/2m_B\beta)$ and for long times ($t \gg \tau^{Bb}_E$) to $\exp(-q^2 D^B_E t)$. At present, these interpolation formulas are the best analytic approximation, for all q and t, for these Enskog correlation functions. These expressions for the Enskog correlation functions were substituted into Eq. (3.23) and the q integration was performed numerically. We find that, when the tagged particle is about the same size as the bath particles $\sigma_B \approx \sigma_b$, the contributions from all the correlation functions $C^{bb}_{\bar{I}\bar{J}}$ must be retained. However, in the limit where $\sigma_{Bb} \gg \sigma_b \gtrsim l_b$, the dominant contributions come from the transverse-current correlations functions, $C^{bb}_{E_{22}}(-q,t)$ and $C^{bb}_{E_{33}}(-q,t)$, independently of the mass ratio m_B/m_b.[28] In this limit then the approximation to the ring memory function reduces to

$$R_1(z) = -n_b \left(\frac{1}{2\pi}\right)^3 \int d\vec{q}\, (\epsilon_2)^2 B^{Bb}_{22}(q)(B^T)^{Bb}_{22}(q)(-i) \int_0^\infty dt\, e^{izt} \{2 C^{BB}_{s_{E_{11}}}(q,t)\, C^{bb}_{E_{22}}(-q,t)\}. \tag{3.26}$$

The contributions from the two transverse correlation functions are identical, and hence the factor of 2 in the curly brackets above. In Eq. (3.26), the angular $\vec{q}$ integration is readily performed leading to a factor of $\frac{4}{3}\pi$. We are then left with the radial integration of the form

$$\int_0^\infty dq\, j_1^2(q\sigma_{Bb}) C^{BB}_{s_{E_{11}}}(q,t) C^{bb}_{E_{22}}(-q,t),$$

where the explicit form of expression for B^{bb}_{22} has been used. The "cut-off" factor $j_1^2(q\sigma_{Bb})$ restricts the q integration to the range $0 \leq q\sigma_{Bb} \leq 4$, or in the limit $\sigma_{Bb} \gg l_b$, to the range $0 \leq q l_b \ll 1$. For such small values of q, our generalized interpolation formulas are well approximated by their hydrodynamic forms

$$C^{BB}_{s_E}(q,t) = e^{-D^B_E q^2 t} \tag{3.27a}$$

and

$$C^{bb}_{E_{22}}(q,t) = e^{-\nu_E q^2 t}. \tag{3.27b}$$

Here D^B_E is the Enskog tagged-particle diffusion coefficient and ν_E is the Enskog kinematic shear viscosity,[29]

TABLE I. Factors $B_{KI}^{Bb}(q)$.

$K\bar{I}$	$B_{KI}^{Bb}(q)$ [a]
22 = 33	$4i\frac{j_1(q\sigma_{Bb})}{q\sigma_{Bb}}$
44	$4i\left(j_0(q\sigma_{Bb})-\frac{2j_1(q\sigma_{Bb})}{q\sigma_{Bb}}\right)$
41	$(2\pi)^{1/2}\left(\frac{m_B+m_b}{m_B}\right)^{1/2} j_1(q\sigma_{Bb})$
45	$\left(\frac{\pi}{3}\right)^{1/2}\left(\frac{m_B}{m_B+m_b}\right)^{1/2} j_1(q\sigma_{Bb})$

[a] The factors $B_{KI}^{Bb}(q)$ are listed here in units of $[(m_Bm_b)^{1/2}/(m_B+m_b)](n_b\tau_E^{Bb})^{-1}$. The function j_n is the nth spherical Bessel function.

$$\nu_E=(l_b^2/\tau_E^{bb})\{\tfrac{5}{4}\,[1+\tfrac{1}{15}\sqrt{\pi}(\sigma_b/l_b)]^2+\tfrac{1}{15}(\sigma_b/l_b)^2\}. \tag{3.28}$$

Once again our numerical integration of (3.26) indicates that the approximations (3.27) are very good. Substituting Eq. (3.27) into Eq. (3.26) and performing the angular integration and the Laplace transformation yields

$$R_1(z)=-\frac{n_b}{3\pi^2}\left(4(n_b\sigma_{Bb}\tau_E^{Bb})^{-1}\frac{(m_Bm_b)^{1/2}}{m_B+m_b}\right)^2 \times\int_0^\infty dq\, j_1^2(q\sigma_{Bb})[z+iq^2\nu_E]^{-1}. \tag{3.29}$$

In writing Eq. (3.29) we have noted that in the limit $\sigma_B\gg\sigma_b$, $\nu_E\gg D_E^B$ independently of the mass ratio m_B/m_b. The q integration in Eq. (3.29) is done in Appendix B. The result is

$$R_1(z)=-\frac{n_b}{12\pi}\left(4(n_b\sigma_{Bb}\tau_E^{Bb})^{-1}\frac{(m_Bm_b)^{1/2}}{m_B+m_b}\right)^2 \times\frac{1}{(-iz)\sigma_{Bb}}\left\{f\left[i\left(\frac{-iz\sigma_{Bb}^2}{\nu_E}\right)^{1/2}\right]-f(0)\right\},$$

where

$$f(x)=(1/x^3)[e^{2ix}(1-ix)^2-(1+x^2)]. \tag{3.30}$$

We obtain the long-time behavior of the B-particle velocity autocorrelation function and the B-particle diffusion coefficient by first developing $R_1(z)$ in the series about $z=0$ and then inserting the result in Eq. (3.13) for $\psi_v^B(z)$. To order $z^{1/2}$, we have

$$R_1(z)=\frac{in_b\sigma_{Bb}}{6\pi\nu_E}\left(4(n_b\sigma_{Bb}\tau_E^{Bb})^{-1}\frac{(m_Bm_b)^{1/2}}{m_B+m_b}\right)^2 \times\left[\frac{2}{15}-\frac{1}{9}\left(-\frac{iz\sigma_{Bb}^2}{\nu_E}\right)^{1/2}\right] \tag{3.31a}$$

$$\equiv i[r_1-(-iz)^{1/2}\delta r_1]. \tag{3.31b}$$

Inserting this result in Eq. (3.13) gives

$$\psi_v^B(z)=\frac{k_BT}{m_B}[z+i(\lambda_E-r_1)+i(-iz)^{1/2}\delta r_1]^{-1}. \tag{3.32}$$

From Eq. (3.32), one obtains the long-time behavior of $\psi_v^B(t)$,[30]

$$\psi_v^B(t)\sim(1-r_1/\lambda_E)^2\tfrac{2}{3}(k_BT/m_bn_b)(4\pi\nu_Et)^{-3/2}, \tag{3.33}$$

and the diffusion coefficient (relative to its Enskog value)

$$D_{R_1}^B/D_E^B=(1-r_1/\lambda_E)^{-1}. \tag{3.34}$$

Note that our derivation, from Eq. (3.32), of the long-time tail differs from that presented in recent ring theories.[3,5] There it is implicitly assumed that, for a tagged particle mechanically equivalent to the bath particles, r_1/λ_E is small so that Eq. (3.32) can be expanded about $(z+i\lambda_E)^{-1}$ and r_1 ignored to solve for the long-time behavior of $\psi_v^B(t)$. One obtains a result like Eq. (3.33), but with $r_1/\lambda_E=0$. When $\sigma_B\gg\sigma_b\gtrsim l_b$, r_1/λ_E is not a small quantity and the above procedure must not be employed.

Evidently in the ring kinetic theory the ratio r_1/λ_E plays an important role in the asymptotic form of the velocity autocorrelation function and in the diffusion coefficient. From Eq. (3.31) for $R_1(z)$, Eq. (3.28) for ν_E and Eqs. (3.8) for λ_E, we find that

$$\frac{r_1}{\lambda_E}\propto n_b\sigma_b^3\frac{\sigma_{Bb}}{\sigma_b}\left(\frac{m_B}{m_B+m_b}\right)^{1/2}.$$

For a fixed density n_b, as we increase the size of the B particle r_1/λ_E increases, but almost independently of the mass ratio m_B/m_b. As r_1/λ_E increases the ratio $D_{R_1}^B/D_E^B$ increases until we reach a critical value of σ_B/σ_b for which $r_1/\lambda_E>1$ and the diffusion coefficient becomes negative.[31] This is clearly unphysical. The coefficient of the $t^{-3/2}$ decay also exhibits unusual behavior when the B particle is large. The ring theory predicts that this coefficient varies as $(\sigma_B/\sigma_b)^2$ in contradiction with the results of fluctuating hydrodynamics where, for $\sigma_B/\sigma_b\gg1$ (and thus $\nu_E\gg D_E^B$) it is independent of σ_B. In summary, the ring kinetic theory breaks down as the B particle increases in size to the point where $\sigma_B\ll l_b$.

D. Repeated-ring solution

In our repeated-ring kinetic theory, the B-particle velocity autocorrelation function is obtained from

$$\psi_v^B(z)=k_BT/m_B[z+i\lambda_E-R(z)]^{-1}. \tag{3.35}$$

When the repeated-ring memory function of Eq. (2.61) is substituted in Eq. (3.6c), it yields

$$R(z)=R_1(z)-n_B^{-1}\Omega^{-1}\int d1\,d2\int d3\,d\bar{3}\int d4\,d\bar{4}\,(m_Bk_BT)^{-1/2}p_{1z}T^{BBb}(1;3\bar{3})$$
$$\times\{G_D^{BbBb}(3\bar{3};5\bar{5})T^{BbBb}(5\bar{5};6\bar{6})G_D^{BbBb}(6\bar{6};4\bar{4})$$
$$+G_D^{BbBb}(3\bar{3};5\bar{5})T^{BbBb}(5\bar{5};6\bar{6})G_D^{BbBb}(6\bar{6};7\bar{7})$$
$$\times T^{BbBb}(7\bar{7};8\bar{8})G_D^{BbBb}(8\bar{8};4\bar{4})+\cdots\}(\tau^T)^{BbB}(4\bar{4};2)(m_Bk_BT)^{-1/2}p_{2z}. \tag{3.36}$$

In Eq. (3.36) G_D^{BbBb} is given by Eq. (2.35) with both C_s^{BB} and C^{bb} evaluated in the Enskog approximation, and T^{BbBb} is defined by Eq. (2.62). Within the curly brackets of Eq. (3.36), integration over repeated field-point variables is implied.

As in the evaluation of the ring memory function, $R_1(z)$, we introduce the Fourier representations of the correlation functions $G_D^{BbBb}(3\bar{3};5\bar{5})$ [see Eq. (3.15a)] and approximate the momentum-dependent correlation-function product

$$C_{s_E}^{BB}(\vec{q};\vec{p}_3,\vec{p}_5;t_3-t_5)C_E^{bb}(-\vec{q};\vec{p}_{\bar{3}}\vec{p}_{\bar{5}};t_3-t_5),$$

via the quasihydrodynamic approximation [see Eq. (3.20)]. After much algebra we find that

$$R(z)=R_1(z)-n_b\sum_{K=2}^{4}\sum_{I,J=1}^{5}\left(\frac{1}{2\pi}\right)^3\int d\vec{q}\,n_b\sum_{K'=2}^{4}\sum_{I',J'=1}^{5}\left(\frac{1}{2\pi}\right)^3\int d\vec{q}'\,\epsilon_K B_{KI}^{Bb}(q)\Delta'_{11IJ}(q,z)$$
$$\times\left(n_BT_{JI'}^{Bb}(\vec{q}+\vec{q}')+n_b\sum_{I'',J''=1}\left(\frac{1}{2\pi}\right)^3\int d\vec{q}''\,n_BT_{JI''}^{Bb}(\vec{q}+\vec{q}'')\Delta'_{11I''J''}(q,z)n_BT_{J''I''}^{Bb}(\vec{q}''-\vec{q}')+\cdots\right)$$
$$\times\Delta'_{11I'J'}(q,z)(B^T)_{K'J'}^{Bb}(q)\epsilon_{K'}. \tag{3.37}$$

In Eq. (3.37), the quantity $\Delta'_{IIJJ}(q,z)$ is

$$\Delta'_{11IJ}(q,z)=(-i)\int_0^\infty dt\,e^{izt}[C_{s_{E_{11}}}^{BB}(q,t)C_{E_{IJ}}^{bb}(-q,t)-e^{-(\lambda_B+\lambda_b)t}C_{s_{0_{11}}}^{BB}(q,t)C_{0_{IJ}}^{bb}(-q,t)], \tag{3.38a}$$

and the matrix elements of T are

$$T_{JI}^{Bb}(\vec{q}+\vec{q}')=\Omega^{-1}\int d4\,d\bar{4}\int d5\,d\bar{5}\,f_0^B(p_4)f_0^b(p_{\bar{4}})f_0^B(p_5)f_0^b(p_{\bar{5}})e^{-i\vec{q}\cdot\vec{r}_{\bar{4}4}}H_J^b(p_{\bar{4}})T^{BbBb}(4\bar{4};5\bar{5})$$
$$\times e^{-i\vec{q}'\cdot\vec{r}_{\bar{5}5}}H_I^b(p_{\bar{5}}). \tag{3.38b}$$

The T-matrix elements correlate the change in bath-particle momentum with its precollisional value as a consequence of the collision with the B particle [cf. also Eq. (C1)]. That is, the T-matrix elements carry the information about how the bath collides with the B particle.

The wave-vector integrations $\int d\vec{q}\int d\vec{q}'\cdots$ that appear in Eq. (3.37) are, at first sight, difficult to handle because of the coupling introduced by the matrix elements $T_{IJ}(\vec{q}\pm\vec{q}')$. As just discussed, it is precisely these T factors that carry the information on the bath-particle trajectories to and from the B particle. Thus, it is crucial that we properly handle the wave-vector integrals. By following the procedures used to obtain the explicit form of the $B_{KI}^{Bb}(q)$'s for hard spheres, we find that the $T(\vec{q}\pm\vec{q}')$ factors can also be expressed in terms of spherical Bessel functions but with argument $|\vec{q}\pm\vec{q}'|\sigma_{Bb}$. One then utilizes "addition theorems" for spherical Bessel functions[32] to uncouple the wave-vector integrations. For example,

$$\frac{j_0(|\vec{y}+\vec{y}'|)}{yy'}=4\pi\sum_{s=0}^{\infty}(-1)^s\frac{j_s(y)}{y}\frac{j_s(y')}{y'}$$
$$\times\sum_{m_s=-s}^{s}Y_s^{m_s*}(\theta_q,\psi_q)Y_s^{m_s}(\theta_{q'},\psi_{q'}), \tag{3.39}$$

where $Y_s^{m_s}$ is a spherical harmonic and $\vec{y}=\vec{q}\sigma_{Bb}$. Note that the summation over s decouples the wave-vector-magnitude integrations and the summation over m_s decouples the angular wave-vector integrations. Of course, this procedure will only be useful if a small number of terms contribute to the sum in Eq. (3.39). The above procedure must be performed for all T factors that appear in the repeated-ring expression, Eq. (3.37), and for all the momentum matrix elements of T.

However, as was the case for the ring memory function, when $\sigma_B\gg\sigma_b\gtrsim l_b$, the dominant contributions to the tagged-particle motion arise from the coupling, during the intermediate propagation, to the bath transverse-current modes, $C_{E_{22}}^{bb}(-q,t)$ and

$C^{bb}_{E_{33}}(-q,t)$. Thus, these are the only modes needed for our evaluation of Eq. (3.37). In Appendix C, we present the form of the transverse matrix element $T^{Bb}_{22}(\vec{q}+\vec{q}')$. It is also shown in Appendix C how the wave-vector decoupling scheme [Eq. (3.39)] is implemented in the general term in Eq. (3.37) (i.e., a term containing an arbitrary number of correlated collisions). Due to the orthonormality of the spherical harmonics, the wave-vector integrations pick out only one term in an expansion such as Eq. (3.39). Substituting Eqs. (C11) and (C12) into Eq. (3.37) in this large B-particle regime yields

$$R(z)=R_1(z)+n_b\frac{1}{6\pi^2}\int_0^\infty dq\,q^2B^{Bb}_{22}(q)2\Delta'_{1122}(q,z)(B^T)^{Bb}_{22}(q)$$
$$\times\left((-i\lambda_E)^{-1}-(-i\lambda_E)^{-1}\frac{n_b}{6\pi^2}\int_0^\infty dq''\,q''^2B^{Bb}_{22}(q'')\,2\Delta'_{1122}(q'',z)(B^T)^{Bb}_{22}(q'')(-i\lambda_E)^{-1}+\cdots\right)$$
$$\times\frac{n_b}{6\pi^2}\int_0^\infty dq'\,q'^2B^{Bb}_{22}(q')2\Delta'_{1122}(q',z)(B^T)^{Bb}_{22}(q')\,. \tag{3.40}$$

We emphasize that the wave-vector decoupling scheme is exact; it does not depend on the relative sizes or masses of the bath and B particles. The above simple result does depend on the condition $\sigma_B\gg\sigma_b\gtrsim l_b$ since it is only here that one may neglect all but the transverse-current couplings. Equation (3.40) simplifies further when we note that $\Delta'_{1122}(q,z)=\Delta_{1122}(q,z)$ [cf. Eqs. (3.38a) and (3.21b)] since, for the transverse modes, $C^{bb}_{mf_{22}}(-q,t)=C^{bb}_{0_{22}}(-q,t)$. (Note that $\Delta'_{11IJ}\neq\Delta_{11IJ}$ if I and J represent longitudinal basis functions, i.e., $I,J=1,4,5$.) Consequently, in the limit $\sigma_B\gg\sigma_b\gtrsim l_b$, $R(z)$ can be simply expressed in terms of $R_1(z)$ [Eq. (3.26)] and the Enskog memory function [Eq. (2.44)] as

$$R(z)=R_1(z)+R_1(z)\{(-i\lambda_E)^{-1}+(-i\lambda_E)^{-1}R_1(z)$$
$$\times(-i\lambda_E)^{-1}+\cdots\}R_1(z)\,. \tag{3.41}$$

The B-particle velocity autocorrelation function is then given by substituting Eq. (3.41) into (3.35):

$$\psi^B_v(z)=(k_BT/m_B)\,[z+i\lambda_E-R_1(z)-R_1(z)\,(-i\lambda_E)^{-1}R_1(z)$$
$$-R_1(z)(-i\lambda_E)^{-1}R_1(z)$$
$$\times(-i\lambda_E)^{-1}R_1(z)\ldots]^{-1}$$
$$=(k_BT/m_B)[z+i\lambda_E(1+R_1(z)/i\lambda_E)^{-1}]^{-1}\,. \tag{3.42}$$

Note that in the second step of Eq. (3.42) we have resummed the geometric series appearing in the square brackets. Equation (3.42) represents our repeated-ring approximation to the B-particle velocity autocorrelation function. We could numerically invert the Laplace transform Eq. (3.42) to find the complete time dependence of $\psi_v(t)$. However, in this paper, our principal interests are to extract the long-time behavior of the B-particle velocity autocorrelation function, and the B-particle diffusion coefficient. We expand $\psi^B_v(z)$ as given in Eq. (3.42) to order $z^{1/2}$ with the use of Eq. (3.31) for $R_1(z)$ to obtain

$$\psi^B_v(z)=(k_BT/m_B)(i\lambda_E)^{-1}\{1+[\gamma_1-(iz)^{1/2}\delta\gamma_1]/\lambda_E\}\,. \tag{3.43}$$

From Eq. (3.43), one finds[30] that the long-time behavior of $\psi^B_v(t)$ is

$$\psi^B_v(t)\sim\tfrac{2}{3}(k_BT/m_bn_b)[4\pi\nu_Et]^{-3/2}\,, \tag{3.44}$$

and that the diffusion coefficient is

$$D^B_R=D^B_E+k_BT/5\pi\eta_ER_B\,. \tag{3.45}$$

In Eq. (3.45), $R_B=\sigma_{Bb}\approx\frac{1}{2}\sigma_B$ is the radius of the B particle, and $\eta_E=\nu_Em_bn_b$ is the Enskog value of the fluid's shear viscosity.

In the limit $\sigma_B\gg\sigma_b\gtrsim l_b$, our repeated-ring kinetic theory provides a very good description of B-particle motion in the fluid. In contrast to the predictions of the ring kinetic theory the coefficient of the $t^{-3/2}$ long-time tail of the velocity autocorrelation function is found to be independent of σ_{Bb} and to have the same form as that derived using fluctuating hydrodynamics.[16] The B-particle diffusion coefficient is given in Eq. (3.45) as the sum of two terms. The first term is just the Enskog diffusion coefficient, while the second term represents the contributions from successive correlated collisions.[33] When $\sigma_B\gg\sigma_b$, the diffusion coefficient is found not to turn negative as it did in the ring theory; instead, the second term dominates over the first and the diffusion coefficient takes on the functional form of the Stokes-Einstein law, $D^B_R\propto k_BT/\eta_ER_B$. It should be noted that in the long-time tail of $\psi^B_v(t)$, Eq. (3.43), and in the diffusion coefficient, Eq. (3.44), it is the Enskog value of the shear viscosity which appears in our theory, rather than the phenomenological shear viscosity which is predicted by hydrodynamic theories.

IV. DISCUSSION

We have presented a method for approximating the exact equations of motion for the tagged-par-

ticle phase-space density correlation function $C_s^{\alpha\alpha}$(12). Our techniques are in the spirit of the FRKT presented by Mazenko[2-5] in that we use a hierarchy expressed directly in terms of correlation functions, and approximations are made to cast the dynamics of the system in terms of effective binary collisions. Explicit three-body and higher equilibrium and dynamical correlations are ignored. Because the particles are not assumed to be points, the collision frequency is given by its Enskog value, in which the excluded volume and shielding effects are fully incorporated via the radial distribution function. Our theory differs from FRKT in that we have included a much larger set of dynamical events (repeated rings) in addition to those of FRKT (rings). The calculations presented in this work indicate that the inclusion of repeated rings is most important in describing the motion of a large tagged particle in a fluid. Further, since in a dense fluid $\sigma_B > l_b$ even for mechanically equivalent particles, we suggest that self-motion will be better described by the repeated-ring kinetic theory presented here than by the ring theory.

In this work, we have explored the validity of the repeated-ring kinetic equation by obtaining approximate solutions to it for a large tagged particle; $\sigma_B \gg \sigma_b \gtrsim l_b$. In this limit, we have demonstrated that the difficult problem of the fluid propagation between the correlated collisions is vastly simplified. The fluid propagation reduces to the hydrodynamic form for the transverse bath current. This enables us to obtain an explicit solution in z space. From this solution we obtain the long-time behavior of the B-particle velocity autocorrelation function, Eq. (3.44) and its diffusion coefficient, Eq. (3.45). The long-time behavior agrees with the predictions of fluctuating hydrodynamics, although our expression is given in terms of the Enskog kinematic shear viscosity rather than its phenomenological value. For the diffusion coefficient we obtain a Stokes-Einstein-like proportionality, but with a factor of $\frac{1}{5}$. Once again, our expression involves the Enskog shear viscosity η_E rather than its phenomenological value. In contrast to these predictions of repeated-ring theory, we have shown that if one stops at just the ring order and calculates the long-time behavior of $\psi_v^B(t)$, Eq. (3.33) and the diffusion coefficient, Eq. (3.34) then, as the tagged particle increases in size, nonsensical results are obtained. We can interpret this failure of the ring kinetic theory as an indication that the fluid momentum flow about a large tagged particle is not being correctly described. It is reasonable that, for a large particle, the bath particles will repeatedly return to the tagged particle and that each intermediate excursion into the fluid and subsequent return to the tagged particle will be dynamically correlated with the previous one. The repeated ring kinetic theory incorporates sequences of 2, 3, 4, ... correlated collisions between the fluid and the tagged particle and, as a consequence, should more correctly describe the dynamics of the tagged particle than the ring theory (only two correlated collisions).

The intermediate propagation of the tagged particle and bath particles between correlated collisions is, in our derivation, given by Enskog propagation. This leads to the appearance of the Enskog value of the shear viscosity in our results. One is tempted to further "renormalize" the repeated-ring theory by replacing the Enskog propagators by the full many-body intermediate propagators. This would lead to the appearance of the phenomenological shear viscosity in our results. However, modifying the kinetic equation in this fashion would not be a consistent procedure since the correlated-collision operator should also change. Thus, such a procedure would be appropriate to a mode-coupling phenomenological theory, but not to a kinetic-theory derivation. Of course, the repeated-ring concept is perfectly acceptable as a mode-coupling description of tagged-particle motion and it should be investigated further.

In addition to obtaining the Enskog shear viscosity, not the phenomenological viscosity, the diffusion coefficient involves a factor of $\frac{1}{5}$ in the repeated-ring calculation. A hydrodynamic calculation[34] using the Navier-Stokes equation with "stick" boundary conditions for the fluid velocity at the surface of the large fixed particle predicts $D = k_B T/6\pi\eta R_B$, while for "slip" boundary conditions $D = k_B T/4\pi\eta R_B$. In this regard, the repeated-ring derivation presented here differs significantly from the work presented by Dorfman, van Beijeren, and McClure.[14] They calculated the viscous drag on a *fixed* large particle immersed in a gas moving with mean velocity $\vec{V}$. The gas particles undergo repeated correlated collisions with the large particle. The intermediate propagation of the gas particles between correlated collisions is given in terms of the steady-state form of the fluid flow in the presence of a macroscopic object as in conventional hydrodynamics. When the gas and large particles are assumed to be hard spheres, their kinetic theory predicts that the viscous force is given by the Stokes form $\vec{F} = -4\pi\eta R_B \vec{V}$. As they demonstrate, hard-sphere gas dynamics with a stationary sphere combine to be equivalent to a macroscopic "slip" boundary condition. Thus, the Stokes friction formula should be recovered. In our calculations the tag-

ged particle is described by dynamical variables and is thus allowed to move about the fluid according to the dynamics of the kinetic equation. Examination of the "fully" disconnected approximation made in Eqs. (2.51) and (2.54) shows that it splits the intermediate propagation into a product of propagators for the tagged particle and bath motion. The bath and tagged-particle motion are of course coupled via the τ and T Enskog collision operators [cf. Eq. (2.61)], but, between these correlated collisions, the propagation of the bath is independent of the presence of the tagged particle. Thus, our intermediate propagators are not the same as those of hydrodynamics in the presence of a macroscopic fixed object. To obtain the proper Stokes-Einstein coefficient ($\frac{1}{4}$ instead of $\frac{1}{5}$) in a purely kinetic-theory derivation one would have to incorporate more information about the massive particle's effect on the bath propagation than is done here. We speculate that the derivation of a kinetic theory which incorporates this effect will be a formidable task.

We have stressed that the repeated-ring theory must be used when the tagged particle is large with respect to the fluid mean free path. It is important to determine when the repeated-ring events become important, since, if the tagged particle were required to be of macroscopic size, there would be little relevance here to molecular processes. For sufficiently high bath densities we have remarked previously (cf. Sec. III A) that $\sigma_b > l_b$. Hence, even if the tagged particle is only slightly larger than a bath particle, $\sigma_B \gtrsim \sigma_b > l_b$. Thus, the repeated-ring kinetic theory will, in dense fluids, be important in the description of the dynamics of a tagged particle of molecular size (and mass).

To explore the repeated-ring kinetic theory for a tagged particle of size comparable with the bath particles and the transition to the regime studied here, we have to perform the wave-vector integrations for all the modes for all multiples of T matrix elements. Fortunately, the wave-vector decoupling technique used in Appendix C for the transverse modes also works for all the other modes. Thus, in principal, we can sum the contributions from all repeated-ring terms for all the mode couplings. Once this is done we can use the quasihydrodynamic approximation to evaluate the intermediate propagation. Note, however, that interpolation formulas must now be used. There are difficult problems involved in the quantitative description of the bath propagation for all times and wave vectors. Thus, the solution of the one-component fluid kinetic theory is much more complicated than is the large tagged-particle limit treated here. In this context, it is interesting to recall that for self-diffusion the molecular dynamics simulations of Alder *et al.*[6a] as well as experiments[35] show that $D = k_B T/c\eta R_B$ (c a constant); there is no Enskog contribution. We speculate that for dense fluids

$$D = D_E + k_B T/c\eta R_B + D_L \ ,$$

where D_L incorporates the effects of the longitudinal mode contributions on the diffusion coefficient. These longitudinal modes, which are responsible for the cage effect at high densities, give a negative contribution and may well cancel the (positive) Enskog term D_E, leaving the experimentally observed self-diffusion result.

Having placed the kinetic equation that we previously assumed[1] on a firm footing here, and having solved the kinetic equation in the simplest circumstance, we defer the solution of our repeated-ring kinetic theory for an arbitrary tagged particle to a future publication.

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APPENDIX A

In this appendix we justify the approximation of Eq. (2.57) for $\Gamma_c(z)$.

Consider the first term in Eq. (2.36) for $\Gamma_c(z)$. In time, this cumulant average can be written in terms of the (nonvanishing) equilibrium averages as[17]

$$\begin{aligned}\langle A_s^\alpha(3t_3) f^\nu(\bar{3}t_3) A_s^\alpha(4t_4) f^\mu(\bar{4}t_4)\rangle_c = {} & \langle A_s^\alpha(3t_3) f^\nu(\bar{3}t_3) A_s^\alpha(4t_4) f^\mu(\bar{4}t_4)\rangle_0 - \langle f^\nu(\bar{3})\rangle_0 \langle A_s^\alpha(3t_3) A_s^\alpha(4t_4) f^\mu(\bar{4}t_4)\rangle_0 \\ & - \langle f^\mu(\bar{4})\rangle_0 \langle A_s^\alpha(3t_3) f^\nu(\bar{3}t_3) A_s^\alpha(4t_4)\rangle_0 - \langle A_s^\alpha(3t_3) A_s^\alpha(4t_4)\rangle_0 \langle f^\nu(\bar{3}t_3) f^\mu(\bar{4}t_4)\rangle_0 \\ & + 2\langle A_s^\alpha(3t_3) A_s^\alpha(4t_4)\rangle_0 \langle f^\nu(\bar{3})\rangle_0 \langle f^\mu(\bar{4})\rangle_0 \ . \end{aligned} \tag{A1}$$

In view of the definition [Eq. (2.30)] of A_s^α, it is readily verified that to lowest order in density, the first term in Eq. (A1) dominates. Hence, as a first approximation we write

$$\langle A_s^\alpha(3t_3)f^\nu(\bar{3}t_3)A_s^\alpha(4t_4)f^\mu(\bar{4}t_4)\rangle_c \approx \langle A_s^\alpha(3t_3)f^\nu(\bar{3}t_3)A_s^\alpha(4t_4)f^\mu(\bar{4}t_4)\rangle_0$$
$$= \sum_\lambda \int d\bar{3}' \sum_\xi \int d\bar{4}'\, L_I^{\alpha\lambda}(3\bar{3}')L_I^{\alpha\xi}(4\bar{4}')\langle f_s^\alpha(3t_3)f^\lambda(\bar{3}'t_3)f^\nu(3t_3)$$
$$\times f_s^\alpha(4t_4)f^\xi(\bar{4}'t_4)f^\mu(\bar{4}t_4)\rangle_0$$
$$\equiv \sum_\lambda \int d\bar{3}' \sum_\xi \int d\bar{4}'\, L_I^{\alpha\lambda}(3\bar{3}')L_I^{\alpha\xi}(4\bar{4}')C_s^{\alpha\lambda\nu\,\alpha\xi\mu}(3\bar{3}'\bar{3};\,4\bar{4}'\bar{4},\,t_3-t_4)\,, \quad \text{(A2)}$$

where we have used Eq. (2.30) for A_s. The initial (i.e., $t_3 = t_4$) value of this correlation function can be written, neglecting three-particle and higher-order equilibrium correlations, as

$$\langle A_s^\alpha(3)f^\nu(\bar{3})A_s^\alpha(4)f^\mu(\bar{4})\rangle_0$$
$$\approx \sum_\lambda \int d\bar{3}' \sum_\xi \int d\bar{4}'\, L_I^{\alpha\lambda}(3\bar{3}')L_I^{\alpha\xi}(4\bar{4}')\{\delta(34)\delta_{\alpha\nu}\delta(3\bar{3})\delta_{\alpha\mu}\delta(3\bar{4})\delta_{\lambda\xi}\delta(\bar{3}'\bar{4}')\omega_0^{\alpha\lambda}(3\bar{3}')$$
$$+\delta(34)\delta_{\lambda\nu}\delta(\bar{3}'\bar{3})\delta_{\nu\xi}\delta(\bar{3}\bar{4}')\delta_{\nu\mu}\delta(\bar{3}\bar{4})\omega_0^{\alpha\nu}(3\bar{3})$$
$$+\delta(34)\delta_{\alpha\nu}\delta(3\bar{3})\delta_{\lambda\xi}\delta(\bar{3}'\bar{4}')\delta_{\lambda\mu}\delta(\bar{3}'\bar{4})\omega_0^{\alpha\lambda}(3\bar{3}')$$
$$+\delta(34)\delta_{\alpha\mu}\delta(3\bar{4})\delta_{\lambda\xi}\delta(\bar{3}'\bar{4}')\delta_{\lambda\nu}\delta(\bar{3}'\bar{3})\omega_0^{\alpha\lambda}(3\bar{3}')+O(n^3)\}$$
$$\equiv \sum_\lambda \int d\bar{3}' \sum_\xi \int d\bar{4}'\, L_I^{\alpha\lambda}(3\bar{3}')L_I^{\alpha\xi}(4\bar{4}')\tilde{\tilde{C}}_s^{\alpha\lambda\nu\alpha\xi\mu}(3\bar{3}'\bar{3};\,4\bar{4}'\bar{4})\,. \quad \text{(A3)}$$

In the disconnected part of $\Gamma_s(z)$, we have the contributions in which, during the intermediate propagation, (i) the tagged particle at 3 ($t_3 \geq t_4$) interacts with the rest of the bath $\bar{3}'$ independently of the particles at $\bar{3}$ and (ii) the particles at $\bar{3}$ interact with the rest of the bath $\bar{3}'$ independently of the tagged particle at 3. In $\Gamma_c(z)$ let us look for the analogous contribution in which (iii) the particle at 3 interacts with the particles at $\bar{3}$ independently of the dynamics of the rest of the bath $\bar{3}'$. Hence we approximate the kinetic equation for the six-point C_s in Eq. (A2) as

$$[z - L^{\alpha\nu}(3\bar{3})]C_s^{\alpha\lambda\nu\alpha\xi\mu}(3\bar{3}'\bar{3};\,4\bar{4}'\bar{4}) = \tilde{\tilde{C}}_s^{\alpha\lambda\nu\alpha\xi\mu}(3\bar{3}'\bar{3};\,4\bar{4}'\bar{4})\,. \quad \text{(A4)}$$

There is no memory function in this simple approximation.[36] In Eq. (A4), to be consistent with the condition (iii) above, the dynamics of the kinetic equation must be governed by only the two-particle Liouville operator $L^{\alpha\nu}(3\bar{3})$. Also note that the propagator $\bar{G}_s = [z\tilde{G}_s - W_s - \Gamma_s(z)]^{-1}$ is "sandwiched" between τ and τ^T [cf. Eq. (2.46)], so that not all of Eq. (A3) contributes to $\Gamma_c(z)$ in this expression. Thus, for example, $(\tau^T)^{\alpha\mu\alpha}(4\bar{4};2)$ precludes $4 = \bar{4}$ and $\tau^{\alpha\alpha\nu}(1;3\bar{3})$ precludes $3 = \bar{3}$. Furthermore, in the intermediate propagation, initially $3 = 4$, so that we must solve the kinetic equation with the initial conditions $3 = \bar{4}$ and $4 = \bar{3}$ *forbidden*. Therefore, the initial condition simplifies to

$$\tilde{\tilde{C}}_s^{\alpha\lambda\nu\alpha\xi\mu}(3\bar{3}'\bar{3};\,4\bar{4}'\bar{4}) = \delta(34)\delta_{\lambda\nu}\delta(\bar{3}'\bar{3})\delta_{\nu\xi}\delta(\bar{3}\bar{4}')$$
$$\times \delta_{\nu\mu}\delta(\bar{3}\bar{4})\omega_0^{\alpha\nu}(3\bar{3})\,. \quad \text{(A5)}$$

Substituting Eq. (A5) into Eq. (A4), and the result into the Laplace transform of Eq. (A2), we have

$$\langle A_s^\alpha(3)f^\nu(\bar{3});A_s^\alpha(4)f^\mu(\bar{4})\rangle_c^z \approx \sum_\lambda \int d\bar{3}' \sum_\xi \int d\bar{4}'\, L_I^{\alpha\lambda}(3\bar{3}')L_I^{\alpha\xi}(4\bar{4}')[z - L^{\alpha\nu}(3\bar{3})]^{-1}$$
$$\times\{\delta(34)\delta_{\lambda\nu}\delta(\bar{3}'\bar{3})\delta_{\nu\xi}\delta(\bar{3}\bar{4}')\,\delta_{\nu\mu}\delta(\bar{3}\bar{4})\omega_0^{\alpha\nu}(3\bar{3})\}\,. \quad \text{(A6)}$$

Upon integrating and summing we obtain,

$$\langle A_s^\alpha(3)f^\nu(\bar{3});A_s^\alpha(4)f^\nu(\bar{4})\rangle_c^z$$
$$= -[-i\vec{\nabla}_{r_3}V^{\alpha\nu}(r_{3\bar{3}})\cdot\vec{\nabla}_{p_3}][z - L^{\alpha\nu}(3\bar{3})]^{-1}\omega_0^{\alpha\nu}(3\bar{3})$$
$$\times[-i\vec{\nabla}_{r_3}V^{\alpha\nu}(r_{3\bar{3}})\cdot\vec{\nabla}_{p_3}]\,\delta(34)\delta_{\nu\mu}\delta(\bar{3}\bar{4}). \quad \text{(A7)}$$

In an analogous fashion, we approximate the other similar terms in Eq. (2.36) as

$$\langle A_s^\alpha(3)f^\nu(\bar{3});f_s^\alpha(4)A^\mu(\bar{4})\rangle_c^z$$
$$\approx[-i\vec{\nabla}_{r_3}V^{\alpha\nu}(r_{3\bar{3}})\cdot\vec{\nabla}_{p_3}][z - L^{\alpha\nu}(3\bar{3})]^{-1}\omega_0^{\alpha\nu}(3\bar{3})$$
$$\times[-i\vec{\nabla}_{r_3}V^{\alpha\nu}(r_{3\bar{3}})\cdot\vec{\nabla}_{p_{\bar{3}}}]\,\delta(34)\delta_{\nu\mu}\delta(\bar{3}\bar{4}),$$

$$\langle f_s^\alpha(3)A^\nu(\bar{3});A_s^\alpha(4)f^\mu(\bar{4})\rangle_c^z$$
$$\approx[-i\vec{\nabla}_{r_3}V^{\alpha\nu}(r_{3\bar{3}})\cdot\vec{\nabla}_{p_{\bar{3}}}][z - L^{\alpha\nu}(3\bar{3})]^{-1}\omega_0^{\alpha\nu}(3\bar{3})$$
$$\times[-i\vec{\nabla}_{r_3}V^{\alpha\nu}(r_{3\bar{3}})\cdot\vec{\nabla}_{p_3}]\,\delta(34)\delta_{\nu\mu}\delta(\bar{3}\bar{4})\,,$$

and

$$\langle f_s^{\alpha}(3)A^{\nu}(\bar{3});f_s^{\alpha}(4)A^{\mu}(\bar{4})\rangle_c^s \approx -[-i\vec{\nabla}_{r_3}V^{\alpha\nu}(r_{3\bar{3}})\cdot\vec{\nabla}_{p_{\bar{3}}}][z-L^{\alpha\nu}(3\bar{3})]^{-1}\omega_0^{\alpha\nu}(3\bar{3})[-i\vec{\nabla}_{r_3}V^{\alpha\nu}(r_{3\bar{3}})\cdot\vec{\nabla}_{p_{\bar{3}}}]\,\delta(34)\delta_{\nu\mu}\delta(\bar{3}\bar{4})\,. \tag{A8}$$

Since all the other terms in Eq. (2.36) are of higher order in the density, we neglect them and substitute Eqs. (A7) and (A8) into (2.36) to obtain the simple approximation

$$\Gamma_c^{\alpha\nu\alpha\mu}(3\bar{3};4\bar{4}) = L_I^{\alpha\nu}(3\bar{3})[z-L^{\alpha\nu}(3\bar{3})]^{-1}\omega_0^{\alpha\nu}(3\bar{3})\,L_I^{\alpha\nu}(3\bar{3})\,\delta(34)\,\delta_{\nu\mu}\,\delta(\bar{3}\bar{4})$$
$$=\sum_{\lambda}\int d5\,d\bar{5}\,\tilde{G}_D^{\alpha\nu\alpha\lambda}(3\bar{3};5\bar{5})L_I^{\alpha\lambda}(5\bar{5})\tilde{g}^{\alpha\lambda}(\sigma_{\alpha\lambda})e^{-\beta V^{\alpha\lambda}(r_{5\bar{5}})}[z-L^{\alpha\lambda}(5\bar{5})]^{-1}L_I^{\alpha\lambda}(5\bar{5})\delta(54)\delta_{\lambda\mu}\delta(\bar{5}\bar{4})\,, \tag{A9}$$

in the diagonal approximation for $\tilde{G}_D$. In writing the second step of Eq. (A9) we have once again used the property that $L_I^{\alpha\lambda}$ is steeply peaked at $|r_5 - r_{\bar{5}}| = \sigma_{\alpha\lambda}$ to put $g^{\alpha\lambda}(r_{5\bar{5}}) = \tilde{g}^{\alpha\lambda}(\sigma_{\alpha\lambda})e^{-\beta V^{\alpha\lambda}(r_{5\bar{5}})}$ and the property that

$$[z-L^{\alpha\lambda}(5\bar{5})]^{-1}e^{-\beta V^{\alpha\lambda}(r_{5\bar{5}})}\omega_0^{\alpha}(5)\omega_0^{\lambda}(\bar{5})$$
$$= e^{-\beta V^{\alpha\lambda}(r_{5\bar{5}})}\omega_0^{\alpha}(5)\omega(\bar{5})[z-L^{\alpha\lambda}(5\bar{5})]^{-1}\,. \tag{A10}$$

APPENDIX B

Here we evaluate the integral

$$I(z)\equiv\int_0^{\infty} dq\, j_1^2(q\sigma)[z+iq^2\nu]^{-1}\,, \tag{B1}$$

by contour integration. Let $z =$ is so that $\mathrm{Re}\,s > 0$. Noting that the integrand is an even function of q we can write

$$I(is)=\frac{\sigma}{2i\nu}\int_{-\infty}^{\infty} dx\, j_1^2(x)[x^2+a]^{-1}\,, \tag{B2}$$

where $x = q\sigma$ and $a = s\sigma^2/\nu$. We write $j_1^2(x)$ in its exponential form,

$$j_1^2(x)=(-1/4x^4)\{e^{2ix}[1-ix]^2-2[1+x^2]$$
$$+e^{-2ix}[1+ix]^2\}\,. \tag{B3}$$

Substituting Eq. (B3) into Eq. (B2) and replacing x by $-x$ in the last term we find

$$I(is)=-\frac{\sigma}{4i\nu}\int_{-\infty}^{\infty} dx[x^2+a]^{-1}/x^4$$
$$\times\{e^{2ix}[1-ix]^2-[1+x^2]\}\,. \tag{B4}$$

Written in this form, the integrand is well behaved in the upper half of the complex $Z = x + iy$ plane. The function $f(Z)$

$$f(Z)=(1/Z^3)\{e^{2iZ}[1-iZ]^2-[1+Z^2]\}\,, \tag{B5}$$

which appears in the integrand of (B4), has no poles. The integrand only has simple poles at $Z = 0$ and $Z = \pm i\sqrt{a}$. We manifest this behavior by writing

$$I(is)=-\frac{\sigma}{4i\nu}\int_{-\infty}^{\infty} dx f(x)x^{-1}[x-i\sqrt{a}\,]^{-1}[x+i\sqrt{a}\,]^{-1}$$
$$\equiv\int_{-\infty}^{\infty} dx F(x)\,. \tag{B6}$$

We evaluate $I(is)$ by calculating the integral of $F(Z)$ around the contour in Fig. 1. This contour is to be used in the limits as $R\to\infty$ and $\rho\to 0$. The only pole enclosed within the contour is the one at $Z = i\sqrt{a}$; hence we have

$$\lim_{\substack{\rho\to 0\\ R\to\infty}}\left(\int_{-R}^{-\rho} dx\,F(x)+\int_{c_\rho} dZ\,F(Z)+\int_{\rho}^{R} dx\,F(x)\right.$$
$$\left.+\int_{c_R} dZ\,F(Z)\right)=2\pi i\,\mathrm{Res}(i\sqrt{a}\,)\,, \tag{B7}$$

where $\mathrm{Res}(i\sqrt{a}\,)$ is the residue of the function $F(Z)$ evaluated at $Z = i\sqrt{a}$. The integral on C_R vanishes and the one on C_ρ gives the contribution $-\pi i\,\mathrm{Res}(0)$. Hence the principal value of our integral can be written

$$P\int_{-\infty}^{\infty} dx\,F(x)=\lim_{\rho\to 0}\left(\int_{-\infty}^{-\rho} dx\,F(x)+\int_{\rho}^{R} dx\,F(x)\right)$$
$$=2\pi i\,\mathrm{Res}(i\sqrt{a}\,)+\pi i\,\mathrm{Res}(0)\,. \tag{B8}$$

Evaluating the residues and substituting the results into Eq. (B8), we find

$$I(is)=\pi\sigma/4a\nu[f(i\sqrt{a}\,)-f(0)]\,, \tag{B9}$$

with f defined in Eq. (B5). It is straightforward to demonstrate that for small s

$$I(is)=-i\pi\sigma/2\nu[\tfrac{2}{15}-\tfrac{1}{9}\sigma(s/\nu)^{1/2}]+O(s)\,. \tag{B10}$$

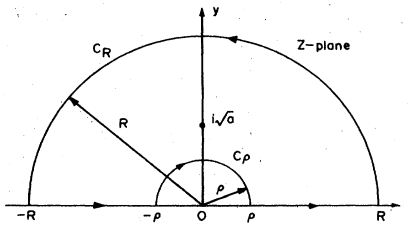

FIG. 1. Contour used in evaluating $I(is)$.

APPENDIX C

In this appendix we investigate the angular integrations over the matrix elements $T^{Bb}_{JI'}(\vec{q}+\vec{q}')$ which appear in Eq. (3.37).

Substituting Eq. (2.62) for T into Eq. (3.38b) and using the diagonal approximation for $\tilde{G}_D$,

$$\tilde{G}_D^{BbBb}(5\bar{5};\,6\bar{6}) = \delta(\bar{5}\bar{6})\delta(56)\omega_0^B(5)\omega_0^b(\bar{5}),$$

one finds

$$T^{Bb}_{JI'}(\vec{q}+\vec{q}') = (n_b n_B \Omega)^{-1}\int d4\, d\bar{4} f_0^B(p_4) f_0^b(p_{\bar{4}}) e^{-i(\vec{q}+\vec{q}')\cdot\vec{r}_{44}} \times H^b_J(p_4) T^{Bb}_E(4\bar{4}) H^b_{I'}(p_{\bar{4}}). \quad \text{(C1)}$$

The matrix elements $T^{Bb}_{JI'}$ couple the change in the bath-particle momentum to its precollision value. Note that the basis functions H^b_J and $H^b_{I'}$ are defined in the $\vec{q}$ and $\vec{q}'$ reference frames, respectively.

Following techniques analogous to those employed to calculate the matrix element $(B^T)^{Bb}_{MJ}$ (Ref. 27) one finds that, for example,

$$T^{Bb}_{22}(\vec{q}+\vec{q}') = -i\,\frac{1}{n_B n_b}\,(n_b \tau^{Bb}_E)^{-1}\,\frac{1}{\pi}\,\frac{m_B}{m_B+m_b} \times K_{22}(\vec{q}+\vec{q}'), \quad \text{(C2)}$$

where

$$K_{22}(\vec{q}+\vec{q}') = \int d\hat{\rho}\,\hat{\rho}_{x_q}\hat{\rho}_{x_{q'}} e^{-i\sigma_{Bb}(\vec{q}+\vec{q}')\cdot\hat{\rho}}, \quad \text{(C3)}$$

where $\hat{\rho}$ is the unit vector from the center of the B particle to the center of the b particle at collision and $\hat{\rho}_{x_q}$ is its x component in the $\vec{q}$ reference frame. From Eq. (3.37), it is clear that in the first repeated-ring contribution we must evaluate angular integrals of the form

$$\mathcal{K}_{22}(\vec{q}+\vec{q}') \equiv \int d\hat{\Omega}_q \int d\hat{\Omega}_{q'}\,\epsilon_2\epsilon_{2'} \int d\hat{\rho}\,\hat{\rho}_{x_q}\hat{\rho}_{x_{q'}} e^{-i\sigma_{Bb}(\vec{q}+\vec{q}')\cdot\hat{\rho}}, \quad \text{(C4)}$$

where

$$\int d\Omega_q = \frac{1}{2\pi}\int_0^{2\pi} d\psi_q \int_0^{2\pi} d\phi_q \int_0^{\pi} d\theta_q \sin\theta_q \quad \text{(C5)}$$

is an integration over the Euler angles. Now $\hat{\rho}_{x_q}$ and $\hat{\rho}_{x_{q'}}$, as well as $(\vec{q}+\vec{q}')\cdot\hat{\rho} = q\hat{\rho}_{z_q} + q'\hat{\rho}_{z_{q'}}$ can be expressed in terms of the laboratory frame components $\hat{\rho}_x, \hat{\rho}_y, \hat{\rho}_z$ via transformation matrices involving the appropriate Euler angles. Invoking such transformations and performing the ϕ_q and $\phi_{q'}$ integrations one finds

$$\mathcal{K}_{22}(\vec{q}+\vec{q}') = -\frac{1}{4yy'}\int_0^{2\pi} d\psi_q \int_0^{\pi} d\theta_q \sin^2\theta_q \int_0^{2\pi} d\psi_{q'} \times\int_0^{\pi} d\theta_{q'} \sin^2\theta_{q'}\left[\left(\frac{\partial}{\partial\theta_q}\right)\left(\frac{\partial}{\partial\theta_{q'}}\right) + \frac{1}{\sin\theta_q}\left(\frac{\partial}{\partial\psi_q}\right)\frac{1}{\sin\theta_{q'}}\left(\frac{\partial}{\partial\psi_{q'}}\right)\right] \times \int d\hat{\rho}\, e^{-i(\vec{y}+\vec{y}')\cdot\hat{\rho}}, \quad \text{(C6)}$$

where $\vec{y} = \vec{q}\sigma_{Bb}$. Peforming the $\hat{\rho}$ integration to obtain the spherical Bessel function $j_0(|\vec{y}+\vec{y}'|)$, integrating by parts over θ_q and $\theta_{q'}$ and noting that the ψ_q and $\psi_{q'}$ integrations vanish in the second term one obtains

$$\mathcal{K}_{22}(\vec{q}+\vec{q}') = -4\pi\int_0^{2\pi} d\psi_q \int_0^{\pi} d\theta_q \sin\theta_q\cos\theta_q \int_0^{2\pi} d\psi_{q'} \int_0^{\pi} d\theta_{q'} \sin\theta_{q'}\cos\theta_{q'} \frac{j_0(|\vec{y}+\vec{y}'|)}{yy'}. \quad \text{(C7)}$$

Remember that the term $\mathcal{K}_{22}(\vec{q}+\vec{q}')$ is also integrated over the q and q' wave-vector magnitudes in Eq. (3.37). These wave-vector magnitude integrations can be uncoupled by utilizing the "addition theorem" for spherical Bessel functions[32] which states that

$$\frac{j_0(|\vec{y}+\vec{y}|)}{yy'} = \sum_{s=0}(2s+1)\frac{j_s(y)}{y}\frac{j_s(y')}{y'}P_s(-\cos\beta_{yy'}), \quad \text{(C8)}$$

where P_s is the sth Legendre polynomial and $\beta_{yy'}$ is the angle between the vectors $\vec{y}$ and $\vec{y}'$. Further, we uncouple the angular (Ω_q and $\Omega_{q'}$) integrations by using the addition theorem[37] for spherical harmonics $Y_s^{m_s}(\theta,\psi)$,

$$P_s(-\cos\beta_{yy'}) = (-1)^s\sqrt{\tfrac{4}{3}\pi}\; Y_s^0(\beta_{yy'},0) = (-1)^s\frac{4\pi}{2s+1}\sum_{m_s=-s}^{s} Y_s^{m_s*}(\theta_q,\psi_q)Y_s^{m_s}(\theta_{q'},\psi_{q'}). \quad \text{(C9)}$$

Substituting Eqs. (C8) and (C9) into (C7) and performing the angular integrals we have

$$\mathcal{K}_{22}(\vec{q}+\vec{q}') = -4\pi \sum_{s=0}^{\infty} (-1)^s (2s+1) \frac{j_s(y)}{y} \frac{j_s(y')}{y'} \frac{4\pi}{(2s+1)} \frac{4\pi}{3}$$
$$\times \sum_{m_s=-s}^{s} \int_0^{2\pi} d\psi_q \int_0^{\pi} d\theta_q \sin\theta_q \, Y_1^0(\theta_q,\psi_q) Y_s^{m_s*}(\theta_q,\psi_q)$$
$$\times \int_0^{2\pi} d\psi_{q'} \int_0^{\pi} d\theta_{q'} \sin\theta_{q'} \, Y_s^{m_s}(\theta_{q'},\psi_{q'}) Y_1^{0*}(\theta_{q'},\psi_{q'})$$
$$= -4\pi \sum_{s=0}^{\infty} (-1)^s (2s+1) \frac{j_s(y)}{y} \frac{j_s(y')}{y'} \frac{4\pi}{2s+1} \frac{4\pi}{3} \sum_{m_s=-s}^{s} \delta_{m_s,0}\delta_{s,1}$$
$$= 12\pi \tfrac{4}{3}\pi \frac{j_1(y)}{y} \frac{4\pi}{3} \frac{j_1(y')}{y'} \quad . \tag{C10}$$

In the second step of Eq. (C10) we have used the orthonormality relationship for spherical harmonics. Note that the sum over spherical Bessel functions of increasing order has, when integrated over the wave vectors, collapsed to one term ($s=1$). This result is exact and is, in part, responsible for the relatively simple results of the repeated-ring calculations. From Eqs. (C2), (C4) and (C10), it is clear that

$$\int d\hat{\Omega}_q \int d\hat{\Omega}_{q'} \epsilon_2 \epsilon_{2'} T_{22}^{Bb}(\vec{q}+\vec{q}) = -i \frac{1}{n_B n_b} (n_b \tau_E^{Bb})^{-1} \frac{1}{\pi} \frac{m_B}{m_B+m_b} 12\pi \tfrac{4}{3}\pi \frac{j_1(y)}{y} \frac{4\pi}{3} \frac{j_1(y')}{y'}$$
$$= \frac{1}{n_B} \left(\frac{4\pi}{3}\right)^2 (B^T)_{22}^{Bb}(q)(i\lambda_E)^{-1} B_{22}^{Bb}(q') , \tag{C11}$$

using the definition of $B_{22}(q)$ given in Table I and the definition of λ_E given in Eq. (3.8).

Following the procedures outlined above, one can show that performing the angular integrations in a term containing $(n-1)$ T-matrix elements leads to the result

$$\int d\hat{\Omega}_{q_1} \int d\hat{\Omega}_{q_2} \cdots \int d\hat{\Omega}_{q_n} \epsilon_{2_1} \epsilon_{2_n} T_{22}^{Bb}(\vec{q}_1+\vec{q}_2) T_{22}^{Bb}(\vec{q}_2+\vec{q}_3) \cdots T_{22}^{Bb}(\vec{q}_{n-1}-\vec{q}_n)$$
$$= (1/n_B)^{n-1} (\tfrac{4}{3}\pi)^n (B^T)_{22}^{Bb}(q_1)(i\lambda_E)^{-1} B_{22}^{Bb}(q_2)(B^T)_{22}^{Bb}(q_2)(i\lambda_E)^{-1} B_{22}^{Bb}(q_3) \cdots (B^T)_{22}^{Bb}(q_{n-1})(i\lambda_E)^{-1} B_{22}^{Bb}(q_n) . \tag{C12}$$

Equations (C11) and (C12) are substituted into Eq. (3.37) in the large-particle limit to yield Eq. (3.40).

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[1] A preliminary account of this investigation was presented by J. R. Mehaffey and R. I. Cukier [Phys. Rev. Lett. 38, 1039 (1977)].

[2] G. F. Mazenko, Phys. Rev. A 7, 209 (1973).

[3] G. F. Mazenko, Phys. Rev. A 7, 222 (1973).

[4] G. F. Mazenko, Phys. Rev. A 9, 360 (1974).

[5] G. F. Mazenko and S. Yip, in Modern Theoretical Chemistry, edited by B. J. Berne (Plenum, New York, to be published).

[6] (a) B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970); (b) W. W. Wood, in *Fundamental Problems in Statistical Mechanics III*, edited by E. G. D. Cohen (North-Holland, Amsterdam, 1975), p. 331.

[7] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases*, 3rd ed. (Cambridge University, Cambridge, 1970), Chap. 16.

[8] K. Kawasaki and I. Oppenheim, Phys. Rev. 136, A1519 (1964); J. R. Dorfman and E. G. D. Cohen, Phys. Rev. Lett. 25, 1257 (1970); Phys. Rev. A 6, 776 (1972); 12, 292 (1975); P. Résibois and J. L. Lebowitz, J. Stat. Phys. 12, 483 (1975); I. deSchepper, Ph.D. thesis (Catholic University of Nijmegen, 1974) (unpublished); J. Dufty, Phys. Rev. A 5, 2247 (1972).

[9] B. J. Alder and T. E. Wainwright, Phys. Rev. Lett. 18, 988 (1967); Phys. Rev. A 1, 18 (1970).

[10] P. Résibois, J. Stat. Phys. 13, 393 (1975).

[11] P. M. Furtado, G. F. Mazenko, and S. Yip, Phys. Rev. A 14, 869 (1976).

[12] J. R. Mehaffey, R. C. Desai, and R. Kapral, J. Chem. Phys. 66, 1665 (1977); Chem. Phys. Lett. 45, 322 (1977).

[13] M. H. Ernst and J. R. Dorfman, Physica (Utr.) 61, 157 (1972).

[14] J. R. Dorfman, H. van Beijeren, and C. F. McClure, Arch. Mech. Stosow. 28, 333 (1976).

[15] A. Einstein, *Investigations on the Theory of the Brownian Movement* (Dover, New York, 1956), Chap. 5.

[16] E. H. Hauge and A. Martin-Lof, J. Stat. Phys. 7, 259 (1973).

[17] R. Kubo, J. Phys. Soc. Jpn. 17, 1100 (1962).

[18] The density fluctutations at the generalized Boltzmann level in fluid mixtures have been investigated by J. I. Castresana, G. F. Mazenko, and S. Yip [Phys. Rev. A 14, 1814 (1976); and Ann. Phys. (N.Y.) 103, 1 (1977)].

[19] It should be noted that our split up of $\Gamma_s(z)$ into connected and disconnected parts differs from the one presented in FRKT (Ref. 4). Consider a four-point

function A defined such that

$$A(1\bar{1};2\bar{2}) \equiv \int d3\, d\bar{3} A^1(1\bar{1};3\bar{3}) A^2(3\bar{3};2\bar{2}).$$

The disconnected part of A can be written in terms of the connected and disconnected parts of A^1 and A^2 as

$$\begin{aligned} A_D(1\bar{1};2\bar{2}) = &\int d3\, d\bar{3} A^1_D(1\bar{1};3\bar{3}) A^2_D(3\bar{3};2\bar{2}) \\ &+ \int d3\, d\bar{3} A^1_D(1\bar{1};3\bar{3}) A^2_c(3\bar{3},2\bar{2}) \\ &+ \int d3\, d\bar{3} A^1_c(1\bar{1};3\bar{3}) A^2_D(3\bar{3};2\bar{2}). \end{aligned}$$

We refer to the approximation

$$A_D(1\bar{1};2\bar{2}) \approx \int d3\, d\bar{3} A^1_D(1\bar{1};3\bar{3}) A^2_D(3\bar{3};2\bar{2})$$

as the "fully" disconnected approximation for A.

[20]This is a generalization of Zwanzig's binary collision operator [R. Zwanzig, Phys. Rev. 129, 486 (1963)] incorporating the equilibrium structure.

[21]This approximation is strictly valid only for hard-core interactions.

[22]In FRKT (Ref. 4) Mazenko noted that the connected part of $\Gamma_s(z)$ could contribute at high densities, but this point was not pursued further there.

[23]The technique one uses to reduce the Enskog collision operator T^{Bb}_E of Eq. (2.45) to its hard-sphere form is given in the appendix of G. F. Mazenko, T. Y. C. Wei, and S. Yip, Phys. Rev. A 6, 1981 (1972). See also H. H. U. Konijnendijk and J. M. J. van Leeuwen, Physica (Utr.) 64, 342 (1975).

[24]This type of diagonal approximation is often made in kinetic theory, though it only has been justified for the Boltzmann-level kinetic theory (cf. Ref. 7, Chap. 10). A rationale for its validity has been presented by [R. I. Cukier and J. T. Hynes, J. Chem. Phys. 64, 2674 (1976)].

[25]P. M. Furtado, G. F. Mazenko, and S. Yip, Phys. Rev. A 13, 1641 (1976).

[26]H. Goldstein, *Classical Mechanics* (Addison-Wesley, Cambridge, Mass., 1950), p. 107.

[27]J. R. Mehaffey and R. C. Desai, J. Chem. Phys. 66, 4721 (1977).

[28]We have also compared the contributions from the transverse and longitudinal current correlation functions found by substituting the hydrodynamic forms of $C^{bb}_{E22}(-q,t)$, $C^{bb}_{E44}(-q,t)$, and $C^{BB}_{sE11}(q,t)$ into Eq. (3.23) and performing the q integration analytically. Again the contribution from the transverse mode is found to dominate when $\sigma_B \gg \sigma_b \gtrsim l_b$. The numerical integration mentioned above, where we used the interpolation formulas for $C^{bb}_{E\bar{I}\bar{J}}$ and C^{BB}_{sE11}, in which the full q and t dependence are better approximated, is a superior test of the dominance of the transverse mode.

[29]This value is the $q \to 0$ limit of the wave-vector-dependent kinematic viscosity in Ref. 10 and 11. A more accurate expression is given in Ref. 7 and in P. M. Furtado, G. F. Mazenko, and S. Yip, Phys. Rev. A 13, 1641 (1976).

[30]G. Doetsch, *Guide to the Application of the Laplace and Z Transforms*, 2nd ed. (Van Nostrand Reinhold, London, 1971), p. 150.

[31]This has also been noted by T. Keyes [Chem. Phys. Lett. 51, 370 (1977)].

[32]C. J. Tranter, *Bessel Functions with Some Physical Applications* (Hart, New York, 1968), pp. 37–38.

[33]In a recent stochastic theory [K. Lindenberg and R. I. Cukier, J. Chem. Phys. 67, 568 (1977)] the diffusion coefficient was also found to split into an Enskog contribution and a correlated collision contribution. A similar split was found via mode-coupling theory [T. Keyes and I. Oppenheim, Phys. Rev. A 8, 937 (1973); R. Kapral and M. Weinberg, *ibid.* 8, 1008 (1973)], but here the first term is a "bare" (not an Enskog) diffusion coefficient and the second contribution is from bilinear modes. It is also interesting that, for *rotational* diffusion [J. T. Hynes, R. Kapral, and M. Weinberg, Chem. Phys. Lett. 46, 463 (1977); 46, 575 (1977)] a microscopic boundary layer calculation leads to a split of the rotational diffusion constant into Enskog and collective terms.

[34]L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley, Reading, Mass., 1959), Chap. 2.

[35]E. McLaughlin, Trans. Faraday Soc. 55, 28 (1959); M. A. McCool and L. A. Woolf, Chem. Soc. Faraday Trans. I 68, 1971 (1972); J. J. Van Loef, Physica (Utr.) 75, 115 (1974); H. J. Parkhurst and J. Jonas, J. Chem. Phys. 63, 2698, 2706 (1975).

[36]One can also derive the Enskog approximation to $\phi^{\alpha\alpha}_s$ by making a similar approximation for the four-point quantity G_s in Eq. (2.12).

[37]J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1967), p. 68.