Journal of Statistical Physics, Vol. 33, No. 1, 1983

An Enskog Repeated-Ring Kinetic Equation; Long-Time Tails and the Brownian Limit[1]

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Received February 11, 1983

A kinetic equation for the motion of a particle of arbitrary size and mass through a moderately dense gas is derived and discussed. The "long-time tail" of the velocity correlation function is calculated and found to agree with existing results. For a Brownian particle, the theory gives the Stokes–Einstein law for the self-diffusion coefficient, with the shear viscosity given by its Enskog value.

KEY WORDS: Kinetic theory; Stokes–Einstein law; long-time tails.

1. INTRODUCTION

The diffusion constant (D) and the velocity correlation function (VCF) of a tagged, hard-sphere particle moving in a surrounding fluid may be accurately calculated from the Lorentz–Boltzmann equation,[1,2] provided that the fluid is sufficiently dilute and that the collision radius of the tagged particle (a_1) is much less than the mean free path of the surrounding gas (l). If we now increase the size of the tagged particle, so that either $a_1/l \gg 1$ or $a_1/l \sim 1$, but still retaining the low-density fluid, the Lorentz–Boltzmann equation no longer works and a new kinetic theory is needed. Recent work has shown that a very good candidate equation for this role is the repeated-ring approximation (RRA), first derived by Ernst and Dorfman[3] and discussed in great detail by Dorfman in Ref. 4. When the

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[1] Supported by NSF Grant No. CHE81-11422 and by the Petroleum Research Fund.

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tagged particle is small, the RRA correctly reduces to the Lorentz–Boltzmann equation. Furthermore, in the Brownian particle limit, when the tagged particle is both large and massive, the RRA yields the expected Stokes–Einstein behavior,[5,6] where the fluid transport coefficients involved in these relationships are given by their low-density, Boltzmann values. Finally there are very persuasive arguments[7,8] indicating that the RRA becomes the exact kinetic equation for the motion of a tagged particle of any size in a dilute gas, provided that the particle be sufficiently massive. Unfortunately, the RRA leads to equations that are very difficult to solve for a particle of arbitrary mass and size, but recently we believe we have made some progress in this regard by[9] employing the variational methods first introduced into kinetic theory by Cercignani and coworkers.[10] Although more work should be done to check more carefully the approximate numerical methods that were used, we believe that the values for (the diffusion constant), D, reported in Ref. 9 are fairly accurate estimates of the solution of the RRA equations. Thus, for a dilute fluid, there exists both a very plausible kinetic theory of tagged-particle motion and also what we believe to be a reasonably accurate way of solving the equations numerically.

A problem of even greater interest is that of describing tagged-particle motion in a denser fluid. The RRA equation describes a tagged-particle interacting with a fluid which, far away from the particle, obeys the linearized Boltzmann equation. As the fluid becomes denser, the Boltzmann equation ceases to give a good description of its behavior, and so we cannot expect the RRA to be an adequate kinetic theory in such a situation. We require a more general, higher-density kinetic theory. If the surrounding fluid is very dense, say, a liquid, then at present there exists no completely adequate kinetic description, though the mode-coupling approach of Leutheusser[11] seems to have made progress in this respect. In this paper we shall restrict ourselves to considering the simpler problem of attempting to find a good, approximate kinetic theory for the tagged-particle motion in a moderately dense gas. This problem has already received a lot of attention. Provided that the tagged particle is small, an excellent description is given by Enskog kinetic theory.[1,2] This theory, just like the Lorentz–Boltzmann theory, only takes into account uncorrelated binary collisions between the tagged particle and gas particles, but the collision frequency is modified by a factor of the radial distribution function at contact. Thus the theory includes corrections to the Lorentz–Boltzmann theory arising from the static, equilibrium properties of the system to all orders in the gas density, but ignores any effects arising from dynamical correlations coming from more complicated collision sequences. So, although the theory is not a consistent theory in the density of the gas, in practice it turns out to be remarkably successful over a wide range of gas density.[12] When the tagged particle becomes bigger, however, the Enskog theory fails. In order to describe the motion of a larger tagged particle in a moderately dense gas, one might imagine that an Enskog version of the RRA (ERRA) would be needed. This theory would be expected to reduce to the Enskog theory for small particles, and, in the Brownian limit, would be expected to yield the Stokes–Einstein relation with the Enskog shear viscosity.

Much progress has already been made toward obtaining such a theory. Dorfman and Cohen[13] (DC), in a very careful analysis, derived a ring kinetic theory, which consistently took into account those effects of equilibrium static structure and collisional transfer of momentum which affected the long-time behavior of the VCF. One result of including these effects was to introduce Enskog transport coefficients into the coefficient of the long-time tail. Mazenko[14] also has developed a ring theory which yields a long-time behavior of the VCF different from that found by DC; in its later form the difference is a multiplicative factor of $(D/D_E)^2$, where D and D_E are the true and Enskog values of the diffusion constant respectively. A more consistent theory would set $D = D_E$ here, whereupon the result of DC is recovered. Although the ring theories are good for studying the long-time tails of correlation functions, it is well known from low-density studies that repeated-ring collision sequences, at least, must be included in any theory that hopes to yield Stokes–Einstein behavior. Mehaffey and Cukier[15] (MC) have proposed such a repeated-ring theory which contains, in addition to the ring events discussed by DC and Mazenko, many other repeated-ring events. It is our belief, though, that a still more complex description is required in order to obtain the Stokes–Einstein result. In the remainder of this paper, we derive an ERRA theory, which we show both predicts an asymptotic long-time tail coefficient for the VCF in agreement with that obtained by DC, and also yields the Stokes–Einstein relation for Brownian motion with transport coefficients given by their Enskog values. We analyze the nature of the approximations basic to the theory. In the final section we give a brief discussion of our results and consider possible ways in which the theory might be extended to tagged-particle motion in a fluid of arbitrary density.

2. THE REPEATED-RING EQUATIONS

We wish to obtain a set of approximate equations so that we may calculate the VCF of a hard-sphere tagged particle, denoted by particle 1 moving in a fluid of hard spheres. To do this we use the hard-sphere version of Mori's generalized Langevin equation.[16] This technique has previously been used by Leutheusser,[11] and also by Cukier *et al.*,[6] and a very closely related approached was employed by Konijnendijk and Van Leeuwen.[17] We take as variables the quantities

$$A(\bar{1}) \equiv A(\bar{\mathbf{v}}_1) = \delta(\bar{\mathbf{v}}_1 - \mathbf{v}_1) \tag{1a}$$

and

$$\begin{aligned} B(\bar{1},\bar{2}) &\equiv B(\bar{\mathbf{v}}_1, \bar{\mathbf{v}}_2, \bar{\mathbf{r}}_{12}) \\ &= \delta(\bar{\mathbf{v}}_1 - \mathbf{v}_1)\left\{ \sum_{j>1} \delta(\bar{\mathbf{v}}_2 - \mathbf{v}_j)\delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1_j}) - \rho\phi_0(\bar{2})G(\bar{r}_{12}) \right\}, \\ &\qquad |\bar{\mathbf{r}}_{12}| > a_1 \end{aligned} \tag{1b}$$

In these equations the barred variables are field variables, whereas the unbarred quantities are dynamical variables. The position and velocity of particle i are denoted by $\mathbf{r}_i$ and $\mathbf{v}_i$ respectively, and $\mathbf{r}_{1_i} = \mathbf{r}_1 - \mathbf{r}_i$. The Maxwellian velocity distribution function is denoted by $\phi_0(\bar{1})$, for a particle of mass m_1, and $\phi_0(\bar{i})$ $(i > 1)$ a particle of mass m. $G(\bar{r})$ represents the radial distribution function for fluid around the tagged particle, and ρ is the number density of the fluid. The reason for the restriction upon the values of $|\bar{\mathbf{r}}_{12}|$ in Eq. (1b) is that for $|\bar{\mathbf{r}}_{12}| < a_1$, the value of $B(\bar{1},\bar{2})$ would be identically zero. If these values were to be included there would not exist the inverse to the correlation function $\langle BB \rangle$, which is required in the Mori formalism. Finally we note that we should work in a grand canonical ensemble, again so that the inverse of $\langle BB \rangle$ might exist. This last point is discussed in detail by Ronis, Bedeaux, and Oppenheim.[18]

We now wish to calculate the correlation function $\langle A(\bar{1};z)A(\bar{1}')\rangle$, given by

$$\langle A(\bar{1};z)A(\bar{1}')\rangle = \int_0^\infty dt\, e^{-zt}\langle A(\bar{1};t)A(\bar{1}')\rangle \tag{2a}$$

The Laplace transform of the VCF, which we call $C(z)$, is given by

$$C(z) = \int\int d\bar{\mathbf{v}}_1\, d\bar{\mathbf{v}}_1'\, (\bar{\mathbf{v}}_1 \cdot \bar{\mathbf{v}}_1')\langle A(\bar{1};z)A(\bar{1}')\rangle \tag{2b}$$

Mori theory allows us to rewrite Eq. (2b) in the form

$$C(z) = \int\int d\bar{\mathbf{v}}_1\, d\bar{\mathbf{v}}_1'\, (\bar{\mathbf{v}}_1 \cdot \bar{\mathbf{v}}_1')\phi_0(\bar{1})\phi_0(\bar{1}')R_{AA}(\bar{1};\bar{1}') \tag{3a}$$

where $R_{AA}(\bar{1};\bar{1}')$ is obtained from the coupled equations

$$R_{AA}(\bar{1};\bar{1}') * R_{AA}^{-1}(\bar{1}';\bar{1}'') + R_{AB}(\bar{1};\bar{1}'\bar{2}) * R_{BA}^{-1}(\bar{1}'\bar{2};\bar{1}'') = \delta(\bar{\mathbf{v}}_1 - \bar{\mathbf{v}}_1'') \tag{3b}$$

and

$$R_{AA}(\bar{1};\bar{1}')*R_{AB}(\bar{1}';\bar{1}''\bar{3})+R_{AB}(\bar{1};\bar{1}'\bar{2})*R_{BB}^{-1}(\bar{1}'\bar{2};\bar{1}''\bar{3})=0 \quad (3c)$$

where the star means integrate over repeated variables, the range of the spatial integral being the whole of space exterior to the collision sphere. The functions R_{AA}^{-1}, R_{AB}^{-1}, etc. are given by

$$R_{AA}^{-1}(\bar{1};\bar{1}')=z\langle A(\bar{1})A(\bar{1}')\rangle-\langle\left[i\mathscr{L}_{+}A(\bar{1})\right]A(\bar{1}')\rangle \quad (4a)$$

$$R_{AB}^{-1}(\bar{1};\bar{1}'\bar{2})=-\langle\left[i\mathscr{L}_{+}A(\bar{1})\right]B(\bar{1}'\bar{2})\rangle \quad (4b)$$

$$R_{BA}^{-1}(\bar{1}\bar{2};\bar{1}')=-\langle\left[i\mathscr{L}_{+}B(\bar{1}\bar{2})\right]A(\bar{1}')\rangle \quad (4c)$$

and

$$R_{BB}^{-1}(\bar{1}\bar{2};\bar{1}'\bar{3})=z\langle B(\bar{1}\bar{2})B(1'3)\rangle-\langle\left[i\mathscr{L}_{+}B(\bar{1}\bar{2})\right]B(1'3)\rangle$$
$$-\langle\left[i\mathscr{L}_{+}\left[z-Qi\mathscr{L}_{+}\right]^{-1}Qi\mathscr{L}_{+}B(\bar{1}\bar{2})\right]B(\bar{1}'\bar{3})\rangle \quad (4d)$$

$i\mathscr{L}_{+}$ is the hard-sphere, pseudo-Liouville operator which propagates a variable forward in time. For backward propagation the required operator is denoted $i\mathscr{L}_{-}$. The explicit forms of $i\mathscr{L}_{\pm}$ [19] are given by

$$i\mathscr{L}_{\pm}=\sum_{i}\mathbf{v}_{i}\cdot\nabla_{i}\pm\frac{1}{2}\sum_{i\neq j}T_{\pm}(ij) \quad (5a)$$

where the binary collision operators $T_{\pm}(ij)$ are given by

$$T_{\pm}(ij)=\sigma_{ij}^{2}\int d\hat{\sigma}\,|\mathbf{v}_{ij}\cdot\hat{\sigma}|\Theta(\mp\mathbf{v}_{ij}\cdot\hat{\sigma})\delta(\mathbf{r}_{ij}-\sigma_{ij}\hat{\sigma})\times\left\{\hat{b}(i,j)-1\right\} \quad (5b)$$

In this equation, σ_{ij} is the collision radius of particles i and j, which is equal to a_1 if one of the particles is the tagged particle and is equal to a otherwise. $\hat{\sigma}$ is the unit vector along the line joining the center of particle i to particle j, $\Theta(x)=1$, $x>0$, and equals zero otherwise, and the operator $\hat{b}(ij)$ converts the precollision velocities $\mathbf{v}_i,\mathbf{v}_j$ into the postcollision velocities $\mathbf{v}_i'$ and $\mathbf{v}_j'$, where

$$\mathbf{v}_i'=\mathbf{v}_i-\frac{2\mu_{ij}}{m_i}\hat{\sigma}(\hat{\sigma}\cdot\mathbf{v}_{ij}) \quad (6a)$$

and

$$\mathbf{v}_j'=\mathbf{v}_j+\frac{2\mu_{ij}}{m_j}\hat{\sigma}(\hat{\sigma}\cdot\mathbf{v}_{ij}) \quad (6b)$$

where $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, m_i is the mass of particle i, denoted by m_1 if $i = 1$ and m otherwise, and μ_{ij} is the reduced mass of the particles i and j. Finally, the operator Q in Eq. (4d), is the Mori projection operator which projects a dynamical variable onto the space orthogonal to the variables A and B. Clearly any such projection will leave behind only irreducible three-particle terms, and later on we argue that this memory term in Eq. (4d) contains only dynamical events over and above repeated-ring events, and so for a moderately dense gas may be ignored.

We now introduce the functions $\mathbf{\Phi}(\bar{1})$ and $\boldsymbol{\theta}(\bar{1}\bar{2})$ defined by

$$\mathbf{\Phi}(\bar{1}) = \int d\bar{1}\, \phi(\bar{1}')\bar{\mathbf{v}}' R_{AA}(\bar{1}'; \bar{1}) \tag{7a}$$

and

$$\boldsymbol{\theta}(\bar{1}\bar{2}) = \int d\bar{1}\, \phi_0(\bar{1}')\bar{\mathbf{v}}' R_{AB}(\bar{1}'; \bar{1}, \bar{2}) \tag{7b}$$

In these integrals $d\bar{1} \equiv d\mathbf{v}_1$ and later on we use the notation $d\bar{1}\, d\bar{2} \equiv d\bar{\mathbf{v}}_1\, d\bar{\mathbf{v}}_2\, d\bar{\mathbf{r}}_2$. We may now multiply Eqs. (3b) and (3c) by $\bar{\mathbf{v}}_1\phi_0(\bar{1})$ and integrate over $\bar{\mathbf{v}}_1$, which yields the exact kinetic equations

$$\mathbf{\Phi}(\bar{1}') * R_{AA}^{-1}(\bar{1}', \bar{1}) + \boldsymbol{\theta}(\bar{1}'\bar{2}) * R_{BA}^{-1}(\bar{1}'\bar{2}; \bar{1}) = \bar{\mathbf{v}}_1\phi_0(\bar{1}) \tag{8a}$$

and

$$\mathbf{\Phi}(\bar{1}') * R_{AB}^{-1}(\bar{1}'; \bar{1}\bar{2}) + \boldsymbol{\theta}(\bar{1}'\bar{3}) * R_{BB}^{-1}(\bar{1}'\bar{3}; \bar{1}\bar{2}) = 0 \tag{8b}$$

The VCF is given in terms of $\mathbf{\Phi}(\bar{1})$ by

$$C(z) = \int d\bar{1}\, \phi_0(\bar{1})\bar{\mathbf{v}}_1 \cdot \mathbf{\Phi}(\bar{1}) \tag{8c}$$

We now write out Eqs. (8a) and (8b) explicitly, dropping the third term on the right-hand side of Eq. (4d), the memory term. We obtain

$$\begin{aligned} &z\mathbf{\Phi}(1) - \rho G(a_1)\int d2\, \phi_0(2) T_+(12)\mathbf{\Phi}(1) \\ &\quad - \rho\int d2\, \phi_0(2) G(12)\left[\mathbf{v}_1 \cdot \nabla_1 + \mathbf{v}_2 \cdot \nabla_2 + T_+(12)\right]\boldsymbol{\theta}(12) \\ &\quad - \rho^2\int d2\, d3\, \phi_0(2)\phi_0(3)\left[G(123) - G(12)G(13)\right]T_+(13)\boldsymbol{\theta}(12) \\ &\quad - \rho^2\int d2\, d3\, \phi_0(2)\phi_0(3) G(123) T_+(23)\boldsymbol{\theta}(12) = \mathbf{v}_1 \end{aligned} \tag{9a}$$

and, for $|\mathbf{r}_{12}| > a_1$,

$$
\begin{aligned}
zG(12)\boldsymbol{\theta}(12) &+ z\rho\int d3\,\phi_0(3)\big[G(123) - G(12)G(13)\big]\boldsymbol{\theta}(13)\\
&- G(12)\big[\mathbf{v}_1\cdot\boldsymbol{\nabla}_1 + \mathbf{v}_2\cdot\boldsymbol{\nabla}_2 + T_+(12)\big]\boldsymbol{\theta}(12)\\
&- \rho\int d3\,\phi_0(3)\big[G(123) - G(12)G(13)\big]T_+(12)\boldsymbol{\theta}(13)\\
&- \rho\int d3\,\phi_0(3)G(123)\big[T_+(13) + T_+(23)(1+P_{23})\big]\boldsymbol{\theta}(12)\\
&- \rho\int d3\,\phi_0(3)\big[G(123) - G(12)G(13)\big]\\
&\times(\mathbf{v}_1\cdot\boldsymbol{\nabla}_1 + \mathbf{v}_3\cdot\boldsymbol{\nabla}_3 + T_+(13))\boldsymbol{\theta}(13)\\
&- \rho^2\int d3\,d4\,\phi_0(3)\phi_0(4)\big[G(1234) - G(12)G(134)\big]T_+(34)\boldsymbol{\theta}(13)\\
&- \rho^2\int d3\,d4\,\phi_0(3)\phi_0(4)\big[G(1234) - G(12)G(134) - G(13)G(124)\\
&\qquad\qquad + G(12)G(13)G(14)\big]T_+(14)\boldsymbol{\theta}(13)\\
= {}& G(12)T_+(12)\boldsymbol{\Phi}(1)\\
&+ \rho\int d3\,\phi_0(3)\big[G(123) - G(12)G(13)\big]T_+(13)\boldsymbol{\Phi}(1)
\end{aligned}
\tag{9b}
$$

and we have made the approximation that

$$\boldsymbol{\theta}(1'3) * M(1'3;12) \simeq 0 \tag{9c}$$

where

$$M(1'3;12) = \big\langle\big[i\mathscr{L}_+(z - Qi\mathscr{L}_+)^{-1}Qi\mathscr{L}_+\,B(1'3)\big]B(12)\big\rangle \tag{9d}$$

the memory term. In these equations we have dropped the overbars on the variables, as from now on all the variables will be field variables unless specifically stated otherwise. We have also used the abbreviation $G(12\ldots n)$ to represent the n-particle static distribution function for fluid particles surrounding the tagged particle. The operator P_{23} permutes the indices 2 and 3. The restriction to values of $|\mathbf{r}_{12}| \geqslant a_1$, in Eq. (9b) arises from the restricted range of values of $|\mathbf{r}_{12}|$ allowed in the variable $B(12)$.

We now wish to justify in more detail the approximation made in Eq. (9c). We want to show firstly that the term $\boldsymbol{\theta} * M$ contains no term of the form $T_+(12)\boldsymbol{\theta}(1i)$, and secondly that the dynamical collision sequences contained within it are more complex than are required by a repeated ring theory.

To do this, we write out this term more fully, this time using barred variables for field variables, unbarred for dynamic variables. We have

$$\boldsymbol{\theta}(\bar{1}'\bar{3}) * M(\bar{1}'\bar{3};\bar{1}\bar{2}) = \left\langle \left[i\mathscr{L}_{+}(z - Qi\mathscr{L}_{+})^{-1} Qi\mathscr{L}_{+} \sum_{j>1} \boldsymbol{\theta}(1j) \right] B(\bar{1}\bar{2}) \right\rangle \tag{10}$$

The definition of the projection operator Q shows that

$$Qi\mathscr{L}_{+}\, \boldsymbol{\theta}(1j) = Q\left\{ \left[\sum_{\substack{k\neq j\\ k>1}} T_{+}(1k) + \frac{1}{2} \sum_{\substack{k\neq j\\ kj>1}} T_{+}(jk) \right] \boldsymbol{\theta}(1j) \right\} \tag{11}$$

Thus, $i\mathscr{L}_{+}[z - Qi\mathscr{L}_{+}]^{-1} Qi\mathscr{L}_{+}\, \boldsymbol{\theta}(1j)$ describes a binary collision of either particle 1 or j with a third particle, followed by some form of propagation, ending up with a binary collision, described by the $i\mathscr{L}_{+}$. This would appear to constitute a more complex sequence of events than is required in a repeated-ring theory, for a repeated-ring theory only has terms of the form static distribution function times a binary collision operator or free streaming operator acting upon $\boldsymbol{\Phi}(1)$ or $\boldsymbol{\theta}(12)$ in Eq. (9b). To make this clearer, by definition of Q the term $[z - Qi\mathscr{L}_{+}]^{-1} Qi\mathscr{L}_{+}\, \boldsymbol{\theta}(1j)$ is orthogonal to the variables $A(\bar{1})$ and $B(\bar{1}\bar{2})$. Thus this term contains no part that is of the form static distribution function times $\boldsymbol{\theta}(1k)$, for some fluid particle k, for this would then be a linear combination of the variables A and B. Hence the memory term, Eq. (9c), makes no contribution to ring or repeated-ring events. Furthermore, we can show that it contains no term involving the operator $T_{+}(\bar{1}\bar{2})$ acting upon something. If there were such a contribution, it would be contained in the term

$$\left\langle \sum_{j>1} \left[i\mathscr{L}_{+}(1j)[z - Qi\mathscr{L}_{+}]^{-1} Qi\mathscr{L}_{+} \sum_{k>1} \boldsymbol{\theta}(1k) \right] \times \delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1j})\delta(\bar{\mathbf{v}}_{1} - \mathbf{v}_{1})\delta(\bar{\mathbf{v}}_{2} - \mathbf{v}_{j}) \right\rangle$$

where $i\mathscr{L}_{\pm}(1j) = \mathbf{v}_1 \cdot \boldsymbol{\nabla}_1 + \mathbf{v}_j \cdot \boldsymbol{\nabla}_j \pm T_{\pm}(1j)$. However, using the stationary relationship for hard spheres, we may reexpress this correlation function as

$$-\left\langle \left[(z - Qi\mathscr{L}_{+})^{-1} Qi\mathscr{L}_{+} \sum_{k>1} \boldsymbol{\theta}(1k) \right] Qi\mathscr{L}_{-}(1j) \times \left[\delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1j})\delta(\bar{\mathbf{v}}_{1} - \mathbf{v}_{1})\delta(\bar{\mathbf{v}}_{2} - \mathbf{v}_{j}) \right] \right\rangle$$

which is zero, because Q acting upon a two-body term is zero. Hence the memory function contains no contribution involving $T_{+}(12)$ or $(\mathbf{v}_1 \cdot \boldsymbol{\nabla}_1 + \mathbf{v}_2 \cdot \boldsymbol{\nabla}_2)$ acting upon a function of $\boldsymbol{\theta}(12)$. This point is important, because the coefficient of the $T_{+}(12)\boldsymbol{\Phi}(1)$ and $T_{+}(12)\boldsymbol{\theta}(12)$ terms in a repeated-ring equation have, in the past, been a matter of controversy; these terms determine the boundary conditions obeyed by $\boldsymbol{\theta}$ at $r_{12} = a_1$. As will soon be shown, our theory gives the exact boundary conditions, which further supports the arguments given above.

As they stand, the proposed ERRA equations, Eqs. (9a) and (9b), look rather complicated. It is possible, though, to simplify them somewhat. Firstly, we note that the value of an operator, $\hat{O}(12)$ acting upon $\boldsymbol{\theta}(12)$ at $|\mathbf{r}_{12}| = a_1$, in either of the equations, is obtained as the limit of $\hat{O}(12)\boldsymbol{\theta}(12)$ for $|\mathbf{r}_{12}| > a_1$, as $|\mathbf{r}_{12}| \to a_1$. Thus $\boldsymbol{\theta}(12)$ should be regarded as a continuous function at $|\mathbf{r}_{12}| = a_1$, and hence the only terms in Eq. (9b) involving δ functions at $|\mathbf{r}_{12}| = a_1$ come from the terms involving $T_+(12)$. We can therefore split these terms off to give boundary conditions at $|\mathbf{r}_{12}| = a_1$, a procedure discussed by Van Beijeren and Dorfman.[5] Secondly we can make use of the hard sphere version of the YBG hierarchy, which gives[17]

$$\nabla_1 G(12) - G(a_1)\nabla_1 W(12) = \rho a_1^2 \int d\mathbf{r}_3\, d\hat{\sigma}\, G(123)\delta(\mathbf{r}_{13} - a_1\hat{\sigma})\hat{\sigma} \tag{12a}$$

$$\nabla_1 G(12) - G(a_1)\nabla_1 W(12) = -\rho a^2 \int d\mathbf{r}_3\, d\hat{\sigma}\, G(123)\delta(\mathbf{r}_{23} - a\hat{\sigma})\hat{\sigma} \tag{12b}$$

and

$$\nabla_3 G(123) - G(123)\nabla_3 W(123) = \rho a^2 \int d\mathbf{r}_4\, d\hat{\sigma}\, G(1234)\delta(\mathbf{r}_{34} - a\hat{\sigma})\hat{\sigma} \tag{12c}$$

$$\text{where } W(12\ldots n) = 0, \text{ if any particles overlap, and } = 1, \text{ otherwise.} \tag{12d}$$

We finally obtain

$$\begin{aligned} &z\boldsymbol{\Phi}(1) - \rho G(a_1)\int d2\,\phi_0(2)T_+(12)\boldsymbol{\Phi}(1) \\ &\quad -\rho^2\int d2\,d3\,\phi_0(2)\phi_0(3)\big[G(123) - G(12)G(13)\big]\overline{T}_+(13)\boldsymbol{\theta}(12) \\ &\quad -\rho G(a_1)\int d2\,\phi_0(2)\overline{T}_+(12)\boldsymbol{\theta}(12) = \mathbf{v}_1 \end{aligned} \tag{13a}$$

$$\begin{aligned} &zG(12)\boldsymbol{\theta}(12) + z\rho\int d3\,\phi_0(3)\big[G(123) - G(12)G(13)\big]\boldsymbol{\theta}(13) \\ &\quad - G(12)\big[\mathbf{v}_1\cdot\nabla_1 + \mathbf{v}_2\cdot\nabla_2\big]\boldsymbol{\theta}(12) \\ &\quad -\rho\int d3\,\phi_0(3)G(123)\big[T_+(13) + T_+(23)(1+P_{23})\big]\boldsymbol{\theta}(12) \\ &\quad -\rho\int d3\,\phi_0(3)\boldsymbol{\theta}(13)\big[G(12)G(13)\nabla_3 W(13) - G(123)\nabla_3 W(123)\big]\mathbf{v}_3 \\ &\quad -\rho\int d3\,\phi_0(3)\big[G(123) - G(12)G(13)\big]\mathbf{v}_1\cdot\nabla_1\boldsymbol{\theta}(13) \\ &\quad -\rho\int d3\,d4\,\phi_0(3)\phi_0(4)\big[G(1234) - G(124)G(134)/G(14)\big] \\ &\quad \times T_+(14)\boldsymbol{\theta}(13) = 0 \end{aligned} \tag{13b}$$

for $|\mathbf{r}_{12}| > a_1$, and finally the boundary conditions

$$G(a_1)\left[T_+(12)\boldsymbol{\Phi}(1) + T_+(12)\boldsymbol{\theta}(12)\right] + \rho\int d3\,\phi_0(3)\left[G(123) - G(12)G(13)\right]T_+(12)\boldsymbol{\theta}(13) = 0 \quad (13c)$$

We have introduced the modified binary collision opearator $\bar{T}_+(12)$ into Eq. (13a). It is given by[19]

$$\bar{T}_+(12) = T_+(12) - \mathbf{v}_{12}\cdot\boldsymbol{\nabla}_1 W(12) \quad (14)$$

We now would like to compare these equations with previous ring and repeated-ring equations. The ring equation of Dorfman and Cohen may be written in the form of two coupled equations, the first one given by Eq. (13a) without the ρ^2 term on the right-hand side, and the second by

$$\left[z - \mathbf{v}_1\cdot\boldsymbol{\nabla}_1 - \mathbf{v}_2\cdot\boldsymbol{\nabla}_2 - \rho\Lambda(12\,|\,3) - \rho\hat{A}(12)\right]\boldsymbol{\theta}(12) = G(a_1)T_+(12)\boldsymbol{\Phi}(1) \quad (15)$$

where

$$\Lambda(12\,|\,3) = \int d3\,\phi_0(3)\left[G(a_1)T_+(13) + g(a)T_+(23)(1 + P_{23})\right] \quad (16a)$$

and $\hat{A}(12)$ is the mean field term, given by

$$\hat{A}(12)\boldsymbol{\theta}(12) = \int d3\,\phi_0(3)\left[\boldsymbol{\nabla}_3 c(23) - g(a)\boldsymbol{\nabla}_3 W(23)\right]\mathbf{v}_3\boldsymbol{\theta}(13) \quad (16b)$$

$g(r_{23})$ and $c(23) \equiv c(r_{23})$ being the radial distribution and direct correlation functions of the pure fluid, respectively. Actually we have modified DC's equation slightly in two ways. Firstly we have allowed the tagged particle to be of a different size than the fluid particles, and secondly we have changed their equation so that the particle propagates forward rather than backward in time, so that we changed the operator $i\mathscr{L}_-$ used by DC to $i\mathscr{L}_+$.

For large values of $|\mathbf{r}_{12}|$, Eqs. (13b) and (15) are equivalent. To show this, we first find the large $-r_{12}$ form of Eq. (13b), which simplifies the G's. Next, we note that we have used an unusual (if straightforward) version of the Mori formalism, which avoids taking some inverses; this is why, e.g., the term linear in z on the left-hand side of Eq. (13b) appears more complicated than the usual $z\boldsymbol{\theta}$ (corresponding to $\partial\boldsymbol{\theta}/\partial t$) appearing in Eq. (15). Thus, to make the comparison, we must reintroduce the inverse, which in fact requires multiplication of the entire equation by $\delta(\mathbf{v}_2 - \mathbf{v}_3) - \rho c(23)\phi_0(v_2)$. The result is the left-hand side of Eq. (15). Of course, we do not obtain anything like the right-hand side, as we have already removed the singular parts of Eq. (13b) to obtain the boundary conditions. For smaller values of $|\mathbf{r}_{12}|$ the equations are different, largely because Eq. (13b) takes into account more details of the fluid structure as perturbed by the presence of the tagged particle. The boundary conditions at $|\mathbf{r}_{12}| = a_1$ are very different. In the ring theory Eq. (15) is true for all $|\mathbf{r}_{12}|$, and the boundary conditions are obtained by equating the $G(a_1)T_+(12)\mathbf{\Phi}(1)$ term to the effects of the gradient operator acting on a discontinuous function. In Eqs. (13), the function $\boldsymbol{\theta}(12)$ is continuous at $|\mathbf{r}_{12}| = a_1$, the coefficients given by Eq. (13c).

The first RRA equation of Mehaffey and Cukier[15] is identical to that of DC, and the second may be obtained from Eq. (15) by adding $G(a_1)T_+(12)\boldsymbol{\theta}(12)$ to the right-hand side. We again have modified their equations somewhat for the sake of comparison, firstly by doing the same things we did to the ring theory of DC, and secondly by adding on to their equations the mean field term obtained by DC. Again, for large $|\mathbf{r}_{12}|$, their equation is equivalent to Eq. (13b), and contains less information about the fluid structure around the tagged particle compared to Eq. (13b) at smaller values of $|\mathbf{r}_{12}|$. Finally, the boundary condition obtained by MC at $|\mathbf{r}_{12}| = a_1$ are given by

$$G(a_1)T_+(12)\left[\boldsymbol{\theta}(12) + \mathbf{\Phi}(1)\right] = 0 \tag{17}$$

a form slightly different from Eq. (13c).

In sum, our proposed ERRA equations become identical to those obtained by previous authors in the limit of large $|\mathbf{r}_{12}|$, but for smaller values of $|\mathbf{r}_{12}|$, Eq. (13b) contains more complicated terms than have previously been considered. The boundary conditions are also different in the various theories. As mentioned earlier, however, our boundary conditions are exact. To show this, first note that, according to definitions in Eqs. (1), (3)–(5), and (7),

$$\begin{aligned} BC(12) &\equiv \int d1'\,d2'\,\boldsymbol{\theta}(1'2',z)\langle B(1'2')B(12)\rangle \\ &\quad + \int d1'\,\phi(1',z)\langle A(1')A(1)\rangle\rho\phi_0(2)G(12) \\ &= \int d1'\,d1''\,\phi_0(1')v_1'(\langle AA\rangle^{-1})1',1''\langle A(1'',z)B^{(2)}(12)\rangle \end{aligned} \tag{18}$$

where $B^{(2)}$ is the true two-body part of B, that is, $B^{(2)}$ is given by Eq. (1b) without the second term in the parenthesis.

Now, it is necessary that $T(12)\langle A(1'',z)B^{(2)}(12)\rangle = 0$. Without going into detail, this is because the T simultaneously converts $B^{(2)}(12)$ into $(B^{(2)}(\mathbf{v}_1, \mathbf{v}_2, \mathbf{r}_{12}) - B^{(2)}(\mathbf{v}_1', \mathbf{v}_2', \mathbf{r}_{12}))$ and requires that $\mathbf{r}_{12}$ be on the collision sphere of a tagged-particle–bath-particle pair. On that sphere, since the v dependence of $B^{(2)}$ is just the density or expectation of getting that v, $B^{(2)}(\mathbf{v})$ and $B^{(2)}(\mathbf{v}')$ must give the same result when averaged with $A(z)$.

This follows from nothing more than the specularly reflecting boundary condition at the surface of two smooth spheres—every $\mathbf{v}$ immediately becomes a $\mathbf{v}'$, so the expectation of $\mathbf{v}$ and $\mathbf{v}'$ are equal. Thus

$$T(12)BC(12) = 0 \tag{19}$$

Combination of Eqs. (18) and (19), along with the use of explicit expressions for $\langle BB\rangle$ and $\langle AA\rangle$ in Eq. (18), leads directly to our boundary condition, Eq. (13c). So, for a moderately dense gas, any errors in our theory must reside in the "boundary layer" ($r_{12} \gtrsim a_1$) behavior of Eq. (13b). This equation is, to be sure, the first attempt to treat the boundary layer at all, but the treatment is approximate.

Finally we briefly discuss some of the collision sequences contained in these RRA equations. To do this, we first subtract Eq. (13c) from Eq. (13b), and write the resulting equation in the form

$$\mathscr{R}\mathscr{R}^{-1}(12)\boldsymbol{\theta}(12) = G(a_1)T_+(12)\boldsymbol{\Phi}(1) \tag{20}$$

valid for $|\mathbf{r}_{12}| \geqslant a_1$, the limit as $|\mathbf{r}_{12}| \to a_1$ to be taken as described previously. This may be formally inverted and the resulting solution for $\boldsymbol{\theta}(12)$ substituted into Eq. (13a). Thus we obtain

$$\begin{aligned}
&z\boldsymbol{\Phi}(1) - \rho G(a_1)\int d2\,\phi_0(2)T_+(12)\boldsymbol{\Phi}(1) \\
&\quad -\rho^2 G(a_1)\int d2\,d3\,\phi_0(2)\phi_0(3)\left[G(123) - G(12)G(13)\right]\overline{T}_+(13) \\
&\quad \times RR(12)T_+(12)\boldsymbol{\Phi}(1) \\
&\quad -\rho G^2(a_1)\int d2\,\phi_0(2)\overline{T}_+(12)\mathscr{R}\mathscr{R}(12)T_+(12)\boldsymbol{\Phi}(1) = \mathbf{v}_1
\end{aligned} \tag{21}$$

where again the operator $\mathscr{R}\mathscr{R}(12)$ requires that $|\mathbf{r}_{12}| \geqslant a_1$. If the third and fourth terms on the left-hand side of Eq. (21) were to be dropped, the remaining equation would be that given by Enskog kinetic theory for the diffusion of a small particle in a moderately dense gas. We may now make an expansion of the operator $\mathscr{R}\mathscr{R}(12)$ by expanding around the free streaming term, and also by making a density expansion of the distribution functions. Thus, we may formally write Eq. (21) in the form

$$\left[z - \sum_{n=1}^{\infty} \rho^n \hat{R}_n(1)\right]\Phi(1) = \mathbf{v}_1 \tag{22a}$$

to be compared with the exact kinetic equation, written in the form

$$\left[z - \sum_{n=1}^{\infty} \rho^n \hat{B}_n(1)\right]\boldsymbol{\Phi}(1) \equiv \mathbf{v}_1 \tag{22b}$$

where the methods for obtaining the operators $B_n(1)$ are given by DC.[14] For $n = 1$, we have the result

$$\hat{B}_1(1) = \hat{R}_1(1) = \int d2\, \phi_2(2) T_+(12) \tag{23}$$

That is, to lowest order in the density, the exact kinetic operator is the Lorentz–Boltzmann operator. For $n = 2$, the number of terms contributing to $\hat{B}_2(1)$ increases. A full discussion of this term is given by Sengers *et al.*[20] Out of all of these terms, we have simply retained the term present in Enskog kinetic theory, a term given by

$$\int d2\, d3\, \phi_0(2)\phi_0(3) W(12) W(13)[W(23) - 1] \bar{T}_+(13) G_0 T_+(12) \Phi(1)$$

and the three-particle ring term, given by

$$\int \int d2\, d3\, \phi_0(2) \bar{T}_+(12) G_0 W(123)[T_+(13) + T_+(23)(1 + P_{23})] G_0 T(12)$$

where G_0 is the free streaming operator. DC did not include the second term, and they did not retain the $W(123)$ factor in the ring term, which forbids, for example, particle 3 to be within the space occupied by particle 1.

For $n \geqslant 3$, the number of terms present both in $\hat{B}_n$ and $\hat{R}_n$ increase enormously. We shall therefore simply content ourselves to state that the operators $\hat{R}_n(1)$ contain all the terms considered by DC, except that the $\hat{R}_n(1)$ operators also retain extra terms describing the structure of the fluid close to the tagged particle, and also contain repeated-ring collision sequences.[4] As DC concluded, these extra terms do not affect the long-time behavior of the VCF, but we show in Section 4 that these terms are needed to yield the correct form of the Stokes–Einstein relation.

Having obtained and discussed the ERRA, we would obviously like to solve it for some problems of interest. Perhaps the best such problem is calculation of the VCF for a tagged member of a pure fluid. Alder and co-workers[12a,b] found a fascinating, rich structure in their computer calculation of the VCF at liquid densities, which has yet to be reproduced quantitatively from a theory. Although our theory is not designed for liquid density, it does contain a lot of fluid structure, and we would very much like to determine its predictions for liquids. Unfortunately, the extreme complexity of the ERRA has stymied our attempts to use it to obtain the complete VCF. Thus, we turn to simpler problems. If the calculation is restricted to very long times or very large, heavy (Brownian) particles, the ERRA becomes tractable; our results are reported in the next two sections.

3. THE LONG-TIME TAIL OF THE VCF

In this section we wish to extract from the ERRA equations the asymptotic long-time behavior of the VCF, or alternatively the small z form of $C(z)$. Apart from the inherent interest in this effect, the calculation should provide a further check upon the quality of the approximations made, for the answer should agree with that obtained from the very careful analysis of Dorfman and Cohen.[13]

In order to do do this calculation, it is convenient to use operators and variables that are defined over the whole of space, rather than just the space exterior to the collision sphere. This is because we later wish to introduce a Fourier representation, which requires a knowledge of the relevant quantities for all $\mathbf{r}$. Instead of $\boldsymbol{\theta}$, we work from here on with the quantity, $[w(12)\boldsymbol{\theta}(12)]$, which vanishes for $|\mathbf{r}_{12}| < a_1$ as opposed to being ill defined. Since $\boldsymbol{\Phi}$ is determined by $\boldsymbol{\theta}$ as $|\mathbf{r}_{12}|$ approaches a_1 from the outside, $[w\boldsymbol{\theta}]$ is interchangeable with $\boldsymbol{\theta}$ for the purpose of obtaining the VCF. We define the operator, $\overline{\mathscr{R}\mathscr{R}}$, which determines $[w\boldsymbol{\theta}]$, by the relation

$$\overline{\mathscr{R}\mathscr{R}}^{-1}(12)\left[w(12)\boldsymbol{\theta}(12)\right] = w(12)\mathscr{R}\mathscr{R}^{-1}\boldsymbol{\theta}(12) \tag{24a}$$

where $\overline{\mathscr{R}\mathscr{R}}$ is also well defined for all space; according to the discussion before Eq. (24a), $\overline{\mathscr{R}\mathscr{R}}$ now replaces $\mathscr{R}\mathscr{R}$ in Eq. (21). Combination of Eqs. (13b, c), (20), and (24a) readily gives $\overline{\mathscr{R}\mathscr{R}}^{-1}$; some of the T's acting on $\boldsymbol{\theta}$ in Eq. (13c) must be changed to $\bar{T}$'s to compensate for the new terms which arise when $\boldsymbol{\nabla}_1$ or $\boldsymbol{\nabla}_2$ act on $w(12)$ on the left-hand side of Eqs. (24a) and (13b).

We next follow the procedure of Van Beijeren[21] and make a frequency expansion of all the functions and the operators. Thus

$$\boldsymbol{\Phi}(1) = \boldsymbol{\Phi}^{(0)}(1) + \boldsymbol{\Phi}^{(1)}(1) \tag{24b}$$

and

$$\overline{\mathscr{R}\mathscr{R}}(12) = \overline{\mathscr{R}\mathscr{R}}^{(0)}(12) + \overline{\mathscr{R}\mathscr{R}}^{(1)}(12) \tag{24c}$$

where the superscript zero indicates the $z = 0$ limit of the quantity. In three dimensions, we expect that $\boldsymbol{\Phi}^{(0)}$ is finite, and that $\boldsymbol{\Phi}^{(1)} \sim z^{1/2}$ for small z, so terms of order z or higher may be neglected at small z, that is, in the determination of the tail. In two dimensions, $\boldsymbol{\Phi}^{(0)}$ should not exist, since the tail here is t^{-1}, corresponding to a $\ln z$ dependence. Under these circumstances, Eq. (24b) may not make much sense. Nevertheless, as will be seen, our method does yield well-behaved results for $d = 2$, because $\boldsymbol{\Phi}^{(0)}$ ultimately appears in conjunction with some operators in a well-behaved combination. Probably the method could be formally justified here by working with wave-vector (k) dependent quantities and setting $k = 0$ as the last step in the calculation. For the moment, however, we shall concentrate on $d=3$, and simply note that we also obtain a sensible result in $d=2$, even if some intermediate steps are questionable there.

We introduce $\overline{\mathscr{R}\mathscr{R}}$ into Eq. (21), as indicated, and expand as in Eqs. (24), with the results

$$\begin{aligned}
&-\rho G(a_1)\int d2\,\phi_0(2)T_+(12)\mathbf{\Phi}^{(0)}(1)\\
&\quad-\rho^2G^2(a_1)\int d2\,\phi_0(2)\bar{T}_+(12)\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)T_+(12)\mathbf{\Phi}^{(0)}(1)\\
&\quad-\rho^2G(a_1)\int d2\,d3\,\phi_0(2)\phi_0(3)\left[G(123)-G(12)G(13)\right]\\
&\quad\times\bar{T}_+(13)\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)T_+(12)\mathbf{\Phi}^{(0)}(1)=\mathbf{v}_1
\end{aligned}\tag{25a}$$

and

$$\begin{aligned}
&-\rho G(a_1)\int d2\,\phi_0(2)T_+(12)\mathbf{\Phi}^{(1)}(1)\\
&\quad-\rho G^2(a_1)\int d2\,\phi_0(2)\bar{T}_+(12)\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)T_+(12)\mathbf{\Phi}^{(1)}(1)\\
&\quad-\rho^2G(a_1)\int d2\,d3\,\phi_0(2)\phi_0(3)\left[G(123)-G(12)G(13)\right]\\
&\quad\times\bar{T}_+(13)\overline{RR}^{(0)}(12)T_+(12)\mathbf{\Phi}^{(1)}(1)\\
&=\rho G^2(a_1)\int d2\,\phi_0(2)\bar{T}_+(12)\overline{\mathscr{R}\mathscr{R}}^{(1)}(12)T_+(12)\mathbf{\Phi}^{(0)}(1)\\
&\quad+\rho^2G(a_1)\int d2\,d3\,\phi_0(2)\phi_0(3)\left[G(123)-G(12)G(13)\right]\\
&\quad\times\bar{T}_+(13)\overline{\mathscr{R}\mathscr{R}}^{(1)}(12)T_+(12)\mathbf{\Phi}^{(0)}(1)
\end{aligned}\tag{25b}$$

where, in Eq. (25b), we have worked only to lowest order in $z^{1/2}$. If we now take the scalar product of Eq. (25a) with $\phi_0(1)\mathbf{\Phi}^{(1)}(1)$, and take the scalar product of Eq. (25b) with $\phi(1)\mathbf{\Phi}^{(0)}(1)$, integrate both equations over $\mathbf{v}_1$, and subtract one from the other, we end up with the result

$$\begin{aligned}
C^{(1)}(z)&=\langle\mathbf{v}_1\cdot\mathbf{\Phi}^{(1)}(1)\rangle\\
&=\rho G(a_1)\langle\mathbf{\Phi}^{(0)}(1)\\
&\qquad\cdot\left[G(a_1)\bar{T}_+(12)+\rho\left[G(123)-G(12)G(13)\right]\bar{T}_+(13)\right]\\
&\qquad\times\overline{\mathscr{R}\mathscr{R}}^{(1)}(12)T_+(12)\mathbf{\Phi}^{(0)}(1)\rangle
\end{aligned}\tag{26}$$

where $C^{(1)}(z)$ is the small z form of the VCF, and the angled brackets denote a scalar product, to be found by multiplying the function inside by the Maxwellian distribution function for all the particles involved, and then integrating over all the coordinates of the particles. In order to obtain this result, we used the fact that the operators on the left-hand side of Eqs. (25a) and (25b) were symmetric, a result most easily seen by using the Mori equations, Eqs. (10a) and (10b), and the symmetries of the matrix elements.

In order to analyze the operator $\overline{\mathscr{R}\mathscr{R}}^{(1)}$ (12) more fully, we introduce the operator, $\overline{\mathscr{R}}(12)$, defined by

$$\overline{\mathscr{R}}^{-1}(12) = \lim_{|\mathbf{r}_{12}|\to\infty} \overline{\mathscr{R}\mathscr{R}}^{-1}(12) \tag{27}$$

Thus $\overline{\mathscr{R}}^{-1}(12)$ is the far field operator, and is given explicitly by

$$\begin{aligned}
&\overline{\mathscr{R}}^{-1}(12)\boldsymbol{\theta}(12)\\
&\quad = z\boldsymbol{\theta}(12) + \rho z\int d3\,\phi_0(3)h(23)\boldsymbol{\theta}(13) - (\mathbf{v}_1\cdot\nabla_1 + \mathbf{v}_2\cdot\nabla_2)\boldsymbol{\theta}(12)\\
&\qquad -\rho\int d3\,\phi_0(3)\left[G(a_1)T_+(13) + g(a)T_+(23)(1+P_{23})\right]\boldsymbol{\theta}(12)\\
&\qquad +\rho g(a)\int d3\,\phi_0(3)\mathbf{v}_3\cdot\nabla_3 w(23)\boldsymbol{\theta}(13) - \rho\int d3\,\phi_0(3)h(23)\mathbf{v}_1\cdot\nabla_1\boldsymbol{\theta}(13)\\
&\qquad - \rho^2\int d3\,d4\,\phi_0(3)\phi_0(4)G(14)h(23)T_+(14)\boldsymbol{\theta}(13)
\end{aligned}\tag{28}$$

where $h(23) = h(r_{23}) = g(r_{23}) - 1$.

We may therefore write

$$\overline{\mathscr{R}\mathscr{R}}^{-1}(12) = \overline{\mathscr{R}}^{-1}(12) - \bar{S}(12), \tag{29}$$

where $\bar{S}(12)$ is that part of $\overline{\mathscr{R}\mathscr{R}}^{(1)}(12)$ that is only nonzero for values of $|\mathbf{r}_{12}|$ close to a_1. It is then easy to show that

$$\overline{\mathscr{R}\mathscr{R}}^{(1)}(12) = \left[1 + \overline{\mathscr{R}\mathscr{R}}(12)\bar{S}^{(0)}(12)\right]\overline{\mathscr{R}}^{(1)}(12)\left[1 + \bar{S}^{(0)}(12)\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)\right] \tag{30}$$

to lowest order in z, where $\bar{S}^{(0)}(12)$ is the zero-frequency part of $\bar{S}(12)$, and $\overline{\mathscr{R}}^{(1)}(12)$ is the low-frequency part of the operator $\overline{\mathscr{R}}(12)$. The point of all these manipulations is that if, to lowest order in the frequency, we can replace the $\overline{\mathscr{R}\mathscr{R}}(12)$ operator on the right-hand side of Eq. (30) by its zero-frequency form, $\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)$, then substitution of Eq. (30) into Eq. (26) yields an expression for the small-z form of $C(z)$ involving the relatively simple ring operator $\overline{\mathscr{R}}^{(1)}(12)$ instead of the complex operator $\overline{\mathscr{R}\mathscr{R}}^{(1)}(12)$.

From now on, the methods used will be very similar to those used by DC.[13] The Fourier transform of an operator, $\hat{O}(12)$, is denoted by $\hat{O}_{\mathbf{k}_1\mathbf{k}_2}(12)$ and is defined by

$$\hat{O}_{\mathbf{k}_1\mathbf{k}_2}(12) = \int d\mathbf{r}_{12}\,e^{-i\mathbf{k}_1\cdot\mathbf{r}_{12}}\hat{O}(12)e^{i\mathbf{k}_2\cdot\mathbf{r}_{12}} \tag{31a}$$

where the integral over $\mathbf{r}_{12}$ goes over all space. We then have the inverse relation

$$\int d\mathbf{r}_{12}\,\delta(\mathbf{r}-\mathbf{r}_{12})\hat{O}(12)\delta(\mathbf{r}_{12}-\mathbf{r}') = (2\pi)^{-2d}\int d\mathbf{k}_1\,d\mathbf{k}_2\,e^{i\mathbf{k}_1\cdot\mathbf{r}}\hat{O}_{\mathbf{k}_1\mathbf{k}_2}(12)e^{-i\mathbf{k}_2\cdot\mathbf{r}'} \tag{31b}$$

where d is the dimensionality of the system. When $\hat{O}(12)$ is taken to be $\overline{\mathscr{R}}^{(1)}(12)$ in Eq. (29a), it is found that $\overline{\mathscr{R}}^{(1)}_{\mathbf{k}_1\mathbf{k}_2}(12)$ is diagonal—that is, it is of the form

$$\overline{\mathscr{R}}^{(1)}_{\mathbf{k}_1\mathbf{k}_2}(12) = (2\pi)^d\delta(\mathbf{k}_1-\mathbf{k}_2)\overline{\mathscr{R}}^{(1)}_{k_2}(12) \tag{32}$$

We now made a spectral decomposition of $\overline{\mathscr{R}}^{(1)}_{\mathbf{k}_2}(12)$, by expanding it in terms of the left and right eigenfunctions of the operator $\overline{\mathscr{R}}^{(0)}_{\mathbf{k}_2}(12)$, which we denote by $\mathscr{E}^L_{i,\mathbf{k}_2}(12)$ and $\mathscr{E}^R_{i,\mathbf{k}_2}(12)$, respectively, for the ith eigenfunction. Thus we write

$$\overline{\mathscr{R}}^{(1)}_{\mathbf{k}_2}(12) = \sum_i \mathscr{E}^R_{i,\mathbf{k}_2}(12)\langle\mathscr{E}^L_{i,\mathbf{k}_2}(12)\overline{\mathscr{R}}^{(1)}_{\mathbf{k}_2}(12)\mathscr{E}^R_{i,\mathbf{k}_2}(12)\rangle\mathscr{E}^L_{i,\mathbf{k}_2}(12) \tag{33}$$

Use of Eqs. (31)–(33) in Eq. (30), with substitution of the result into Eq. (26), yields

$$\begin{aligned}
C^{(1)}(z) = \frac{\rho G(a_1)}{(2\pi)^d}\int d\mathbf{k}\sum_i \Big\{ &\langle\mathbf{\Phi}^{(0)}_\alpha(1)\big[G(a_1)\overline{T}_+(12) \\
&+\rho\big[G(123)-G(12)G(13)\big]\overline{T}_+(13)\big] \\
&\times\big(1+\overline{\mathscr{R}\mathscr{R}}(12)\overline{S}^{(0)}(12)\big)e^{i\mathbf{k}\cdot\mathbf{r}_{12}}\mathscr{E}^R_{i,k}(12)\rangle \\
&\times\langle\mathscr{E}^L_{i,\mathbf{k}}(12)\overline{\mathscr{R}}^{(1)}_{\mathbf{k}}\mathscr{E}^R_{i,\mathbf{k}}(12)\rangle \\
&\times\langle\mathscr{E}_{i,\mathbf{k}}(12)e^{-i\mathbf{k}\cdot\mathbf{r}_{12}} \\
&\times\big(1+\overline{S}^{(0)}(12)\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)\big)T_+(12)\mathbf{\Phi}^{(0)}_\alpha(1)\rangle\Big\}
\end{aligned} \tag{34}$$

where the subscript α denotes a Cartesian component of a vector. The small z form of the right-hand side of Eq. (34) arises from the hydrodynamic eigenfunctions of the operator $\overline{\mathscr{R}}^{(1)}_{\mathbf{k}}(12)$—the nonhydrodynamic eigenfunctions give contributions to the VCF that decay away roughly exponentially in time over the period of a few mean collision times. Furthermore the long-time tails arise from the small-k portion of the $\mathbf{k}$ integral, so the value of $C^{(1)}(z)$ may be obtained simply from the small-k values of the hydrodynamic eigenfunctions and eigenvalues of the operator $\overline{\mathscr{R}}_{\mathbf{k}}^{(1)}(12)$. The hydrodynamic eigenfunctions consist of products of a diffusive mode for particle 1 with fluid hydrodynamic modes for particle 2, and they may be calculated for small k by the methods described by DC[13] and Résibois and De Leener.[2] The dominant long-time tail of the VCF comes simply from the product of the fluid shear modes with the diffusive mode. Thus the only eigenfunction needed, which we call $\mathscr{E}_{\mathbf{k}}^{L}(12)$, is given by

$$\mathscr{E}_{\mathbf{k}}^{L}(12) = \mathscr{E}_{\mathbf{k}}^{R}(12) = (\beta m)^{1/2}(1 - \hat{k}\hat{k}) \cdot \mathbf{v}_2 + O(k) \tag{35a}$$

and

$$\begin{aligned}\langle \mathscr{E}_{\mathbf{k}}^{L}(12)\overline{\mathscr{R}}_{\mathbf{k}}^{(1)}(12)\mathscr{E}_{\mathbf{k}}^{R}(12)\rangle &= \left[z + k^2(D_E + \nu_E) + O(k^4)\right]^{-1} \\ &\quad - \left[k^2(D_E + \nu_E) + O(k^4)\right]^{-1}\end{aligned} \tag{35b}$$

where $\beta = (k_B T)^{-1}$, with T being the absolute temperature and k_B Boltzmann's constant, $\overleftrightarrow{1}$ is the unit tensor, $\hat{k}$ is a unit vector parallel to $\mathbf{k}$, D_E is the Enskog value of the diffusion constant, and $\nu_E = \eta_E/\rho m$, where η_E is the Enskog value of the shear viscosity. Explicit expressions for D_E and η_E in terms of the fluid properties are given in Ref. 2. We expect the expansions in Eqs. (35a) and (35b) to be valid for $|\mathbf{k}| < k_c$, where k_c is a cut-off wave vector, of the order of an inverse mean free path of the fluid particles. We thus obtain $C^{(1)}(z)$ from the expression

$$\begin{aligned}C^{(1)}(z) = \frac{\rho G(a_1)}{(2\pi)^d} \int_{|\mathbf{k}|<k_c} d\mathbf{k}\, f_1^{\alpha}(\mathbf{k}, z) f_2^{\alpha}(\mathbf{k}) \Big\{ \left[z + k^2[D_E + \nu_E] + O(k^4)\right]^{-1} \\ - \left[k^2[D_E + \nu_E] + O(k^4)\right]^{-1} \Big\}\end{aligned} \tag{36a}$$

where

$$\begin{aligned}f_1^{\alpha}(\mathbf{k}, z) = \langle \Phi_{\alpha}^{(0)}(1)\left[G(a_1)\overline{T}_{+}(12) + \rho\left[G(123) - G(12)G(13)\right]\overline{T}_{+}(13)\right] \\ \times \left(1 + \overline{\mathscr{R}\mathscr{R}}(12)\overline{S}^{(0)}(12)\right) e^{i\mathbf{k}\cdot\mathbf{r}_{12}} \mathscr{E}_{\mathbf{k}}^{R}(12)\rangle\end{aligned} \tag{36b}$$

and

$$f_2^{\alpha}(\mathbf{k}) = \langle \mathscr{E}_{\mathbf{k}}^{L}(12) e^{i\mathbf{k}\cdot\mathbf{r}_{12}}\left[1 + \overline{S}^{(0)}(12)\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)\right] T_{+} \Phi_{\alpha}^{(0)}(1)\rangle \tag{36c}$$

Because $\overline{S}^{(0)}(12)$ contains only contributions from values of $|\mathbf{r}_{12}|$ close to a_1, and vanishes as $|\mathbf{r}_{12}| \to \infty$, the Fourier transform, $\bar{S}^{(0)}_{\mathbf{k}_1,\mathbf{k}_2}(12)$, contains no term proportional to $\delta(\mathbf{k}_1 - \mathbf{k}_2)$. It is then possible to show that, for small values of z, the operator $\overline{\mathscr{R}\mathscr{R}}(12)$ may be replaced by $\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)$, the correction, $\overline{\mathscr{R}\mathscr{R}}^{(1)}(12)$, only contributing to higher order in z. Then, in order to obtain the long-time tail of the VCF, we replace $f_1^\alpha(\mathbf{k}, z)$ by $f_1^\alpha(\mathbf{k}, 0) \equiv f_1^\alpha(\mathbf{k})$, and take the inverse Laplace transform of the quantity in curly brackets in Eq. (36a). Upon expanding $f_1^\alpha(\mathbf{k})$ and $f_2^\alpha(\mathbf{k})$ in powers of $|\mathbf{k}|$, and carrying out the $\mathbf{k}$ integral, we obtain the result for the long-time tail of the VCF, denoted by $C_\infty(t)$, in the form

$$
\begin{aligned}
C_\infty(t) = \langle \mathbf{\Phi}^{(0)}(1) \cdot \Big[G(a_1)\bar{T}_+(12) + \rho\big[G(123) - G(12)G(13)\big]\bar{T}_+(13)\Big] \\
\times \Big(1 + \overline{\mathscr{R}\mathscr{R}}^{(0)}(12)\bar{S}^{(0)}(12)\Big)\mathbf{v}_2\rangle \frac{\rho G(a_1)\beta m}{108}\big((\nu_E + D_E)\pi t\big)^{-3/2} \\
\times \langle \mathbf{v}_2 \cdot \Big(1 + \bar{S}^{(0)}(12)\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)\Big) T_+(12)\mathbf{\Phi}^{(0)}(1)\rangle \qquad (37)
\end{aligned}
$$

where we have specialized to the case of three dimensions. From the definition of $\bar{S}^{(0)}(12)$ [Eqs. (13b), (13c), (20), (24a), (29)], we see that

$$
\bar{S}^{(0)}(12)\mathbf{v}_2 = G(a_1)\bar{T}_+(12)\mathbf{v}_2 \qquad (38a)
$$

and a little algebra shows that

$$
\begin{aligned}
\overline{\mathscr{R}\mathscr{R}}^{(0)}(r)\bar{S}^{(0)}(12)\mathbf{v}_2 &= \overline{\mathscr{R}\mathscr{R}}^{(0)}(12)G(a_1)T_+(12)\mathbf{v}_2 + (1 - w(12))\mathbf{v}_2 \\
&= -\left(\frac{m_1}{m}\right)G(a_1)\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)T_+(12)\mathbf{v}_1 + (1 - w(12))\mathbf{v}_2 \qquad (38b)
\end{aligned}
$$

where we have made use of Eqs. (7a) and (7b). Hence

$$
\begin{aligned}
&\langle \mathbf{\Phi}^{(0)}(1) \cdot \Big\{ G(a_1)\bar{T}_+(12) + \rho\big[G(123) - G(12)G(13)\big]\bar{T}_+(13)\Big\} \\
&\quad\times \Big(1 + \overline{\mathscr{R}\mathscr{R}}^{(0)}(12)\bar{S}^{(0)}(12)\Big)\mathbf{v}_2\rangle \\
&\quad= -\left(\frac{m_1}{m}\right)\langle \mathbf{\Phi}^{(0)}(1) \cdot \Big\{ G(a_1)\bar{T}_+(12) \\
&\qquad\qquad + \Big[G(a_1)\bar{T}_+(12) \\
&\qquad\qquad\qquad + \rho\big(G(123) - G(12)G(13)\big)\bar{T}_+(13)\Big] \\
&\qquad\qquad \times \overline{\mathscr{R}\mathscr{R}}^{(0)}(12)\bar{S}^{(0)}(12)\Big\}\mathbf{v}_1\rangle \\
&\quad= -(3/\beta m\rho) \qquad (39)
\end{aligned}
$$

where we have used the result $T_+(12)(1 - w(12))\mathbf{v}_2 = 0$ to obtain the first equality, and have used the symmetry of the operator and Eq. (25a) to obtain the second. Similarly it may also be shown that

$$\langle \mathbf{v}_2 \cdot \left(1 + \bar{S}^{(0)}(12)\overline{\mathscr{R}\mathscr{R}}^{(0)}(12)\right)T_+(12)\mathbf{\Phi}^{(0)}(1)\rangle = -(3/\beta m)(\rho G(a_1))^{-1} \tag{40}$$

Combining Eqs. (39) and (40) with Eq. (37) yields the final result

$$C_\infty(t) = (12\beta m\rho)^{-1}\left[\pi(v_E + D_E)t\right]^{-3/2} \tag{41}$$

the same answer as obtained by DC in three dimensions. In two dimensions, a similar analysis yields once again the results of DC with a t^{-1} tail, subject to the caveats discussed at the beginning of this section.

To summarize the results of this calculation, we have shown that our RRA equations, Eqs. (13a)–(13c), yield an asymptotic long-time tail, given by Eq. (41), for the VCF for a particle of arbitrary mass and size. This result is the same as that obtained by DC from "a single iterate" of their ring equation,[14] for the case of self-diffusion. So firstly, this gives us some confidence about the quality of our approximations made in deriving Eqs. (13a)–(13c). Secondly, because we have calculated the asymptotic long-time behavior and the answer agrees with that obtained from a single iterate of the ring equation, this calculation illustrates the cancellation that takes place between higher-order iterated rings and repeated rings—a fact pointed out by Van Beijeren.[22] Thirdly, we note that in two dimensions the true asymptotic long-time behavior of the VCF is proportional to $t^{-1}(\log t)^{1/2}$, not t^{-1}.[22,23] In terms of kinetic theory, this enhancement of the long-time tail is due to "ring within ring" and higher-order collision sequences, terms which are hidden in the memory function in our formalism. Finally, mode coupling approaches[24,25] and very systematic kinetic theory approaches[22,26] indicate that Eq. (41) remains true at arbitrary fluid densities, provided v_E and D_E are replaced by the true fluid kinematic viscosity and the true diffusion constant, respectively. In a subsequent paper, we show how this result may be obtained by retaining the memory function in the kinetic equations and then employing the methods just described.

4. THE STOKES–EINSTEIN RELATION

As we said in the Introduction, one requirement of a good kinetic theory is that it should give the Stokes–Einstein relation for the diffusion constant of a Brownian particle. For the case of a Brownian particle in a dilute gas, the work of Van Beijeren *et al.*[5] and Cukier *et al.*[15] showed that the RRA had this desired property. We now examine the Brownian limit of the ERRA equations.

Firstly, we use the boundary conditions, Eq. (13c), to rewrite Eq. (13a) in the form

$$z\boldsymbol{\Phi}(1) + \rho G(a_1)\int d2\,(\mathbf{v}_{12}\cdot\nabla_1 W(12))\boldsymbol{\theta}(12)\phi_0(2)$$
$$+\rho\int d2\,(\mathbf{v}_1\cdot\nabla_1[G(12) - G(a_1)W(12)])\boldsymbol{\theta}(12)\phi_0(2) = \mathbf{v}_1 \quad (42)$$

As we discussed elsewhere,[9c] in order to obtain the VCF from Eq. (42) to lowest order in (m/m_1), as is required for the Brownian particle case, $\boldsymbol{\theta}(12)$ is required both to zeroth and first order in $(m/m_1)^{1/2}$. This would prove to be rather a difficult calculation, but luckily it is possible[9c] to rewrite Eq. (42) in a form that only requires $\boldsymbol{\theta}(12)$ to lowest order in $(m/m_1)^{1/2}$. To do this, we rewrite the boundary conditions in the form

$$G(a_1)[\boldsymbol{\Phi}(\mathbf{v}_1') + \boldsymbol{\theta}(\mathbf{v}_1', \mathbf{v}_2', \mathbf{r}_{12}) - \boldsymbol{\Phi}(\mathbf{v}_1) - \boldsymbol{\theta}(\mathbf{v}_1, \mathbf{v}_2, \mathbf{r}_{12})]$$
$$+\rho\int d3\,\phi_0(3)(G(123) - G(12)G(13))[\boldsymbol{\theta}(\mathbf{v}_1', \mathbf{v}_3, \mathbf{r}_{13}) - \boldsymbol{\theta}(\mathbf{v}_1, \mathbf{v}_3, \mathbf{r}_{13})]$$
$$= 0, \qquad |\mathbf{r}_{12}| = a_1 \quad (43)$$

where $\mathbf{v}_1', \mathbf{v}_2'$ are the postcollision velocities, given by Eqs. (7). If this equation is multiplied by $\mathbf{v}_1\mathbf{v}_2\phi_0(1)\phi_0(2)$ and integrated over the velocities, we obtain the result

$$\int d\mathbf{v}_1\,d\mathbf{v}_2\,\phi_0(1)\phi_0(2)(\hat{r}_{12}\cdot\mathbf{v}_{12})(\mathbf{v}_1\cdot\boldsymbol{\theta}(12))$$
$$= (m/m_1)\int d\mathbf{v}_1\,d\mathbf{v}_2\,(\mathbf{v}_2\cdot\hat{r}_{12})^2(\hat{r}_{12}\cdot\boldsymbol{\theta}(12))\phi_0(1)\phi_0(2)$$
$$+ O(m/m_1)^2, \qquad |\mathbf{r}_{12}| = a_1 \quad (44)$$

If we now take the scalar product of Eq. (42) with $\mathbf{v}_1\phi_0(1)$ and integrate over $\mathbf{v}_1$, we obtain after using Eq. (44), the result

$$zC(z) + \rho G(a_1)(m/m_1)\int d1\,d2\,\phi_0(2)\phi_0(1)(\hat{r}_{12}\cdot\mathbf{v}_2)^2(\hat{r}_{12}\cdot\boldsymbol{\theta}(12))\delta(|\mathbf{r}_{12}| - a_1)$$
$$+\rho(k_BT/m_1)\int d1\,d2\,\phi_0(2)\phi_0(1)[\boldsymbol{\theta}(12)\cdot\nabla_1(G(12) - G(a_1)w(12))$$
$$= 3k_BT/m_1(1 + O(m/m_1)) \quad (45)$$

Clearly, $\boldsymbol{\theta}(12)$ is only required to lowest order in $(m/m_1)^{1/2}$ in order to obtain $C(z)$ in this equation. We may further manipulate this equation by multiplying Eq. (43) by $\mathbf{v}_2\mathbf{v}_2\phi_0(1)\phi_0(2)$ and integrating over $\mathbf{v}_1$ and $\mathbf{v}_2$, and using the resulting equality to reexpress Eq. (45) as

$$zC(z) + \rho G(a_1)(m/m_1)\int d1\,d2\,\phi_0(1)\phi_0(2)\delta(|\mathbf{r}_{12}| - a_1)(\hat{r}_{12}\cdot\mathbf{v}_2)(\mathbf{v}_2\cdot\boldsymbol{\theta}(12))$$
$$+\rho(k_BT/m_1)\int d1\,d2\,\phi_0(1)\phi_0(2)(\boldsymbol{\theta}(12)\cdot\boldsymbol{\nabla}_1[G(12) - G(a_1)W(12)])$$
$$= 3k_BT/m_1 \tag{46}$$

The second term now looks more like the integral of the normal component of the stress tensor over the surface of the collision sphere. The third term may be regarded as an extra contribution due to an integral of a number density multiplied by the gradient of the potential of mean force.

We now return to the Brownian limit of Eq. (13b). In this limit,

$$(m_1/m \gg 1, a_1/a \gg 1 \text{ and } a^2/m \gg a_1^2/m_1)$$

we obtain, to lowest order in $(m/m_1)^{1/2}$,

$$zG(12)\boldsymbol{\theta}(12) + z\rho\int d3\,\phi_0(3)[G(123) - G(12)G(13)]\boldsymbol{\theta}(13)$$
$$- G(12)\mathbf{v}_2\cdot\boldsymbol{\nabla}_2\boldsymbol{\theta}(12) - \rho\int d3\,\phi_0(3)G(123)T_+(23)(1 + P_{23})\boldsymbol{\theta}(12)$$
$$-\rho\int d3\,\phi_0(3)[G(12)G(13)\boldsymbol{\nabla}_3W(13) - G(123)\boldsymbol{\nabla}_3W(123)]\cdot\mathbf{v}_3\boldsymbol{\theta}(13)$$
$$= 0, \qquad |\mathbf{r}_{12}| > a_1 \tag{47}$$

For large values of $|\mathbf{r}_{12}|$, where the fluid equilibrium structure is uneffected by the presence of the Brownian particle, we may use the Chapman–Enskog procedure to find the form of $\boldsymbol{\theta}(12)$ both to zeroth and first order in powers of (l/a_1). That is to say $\boldsymbol{\theta}(12)$ will be given by the hydrodynamic solution, which will vary slowly in space provided the frequency, z, is of order $[(\beta m)^{1/2}a_1]^{-1}$ or less. When, however, $|\mathbf{r}_{12}|$ is just in a few molecular diameters away from the surface of the collision sphere, the static distribution functions, present in Eq. (47), which describe the influence of the Brownian particle upon the equilibrium fluid structure, will vary rapidly over the dimensions of a fluid particle. We may regard this region, extending several molecular diameters away from the surface of the collision sphere, as a static boundary layer. Within this layer the Chapman–Enskog expansion of $\boldsymbol{\theta}(12)$ will fail, and the hydrodynamic form of $\boldsymbol{\theta}(12)$ will not be a solution.

We thus appear to have a problem. In order to use the boundary conditions, Eq. (43), or to use Eq. (45) to obtain the VCF, we require knowledge of the form of $\boldsymbol{\theta}(12)$ within this static boundary layer. Unfortunately, though, we are only able to solve Eq. (47) for $\boldsymbol{\theta}(12)$ outside of this region, and have little knowledge about the form of solution inside, apparently where it is most urgently required. In order to make further progress, we must attempt to reexpress Eq. (45) so that it only involves the far-field, hydrodynamic solution of $\boldsymbol{\theta}(12)$, and we must try to extract boundary conditions that this function must obey exterior to the static boundary layer.

Let us introduce the microscopic length ζ, such that $\zeta/a_1 \ll 1$, and such that for $|\mathbf{r}_{12}| \geqslant a_1 + \zeta$, $G(12) = 1$ and $G(123) = G(13) + h(23)$. Thus ζ is large enough so that all effects of the tagged particle upon the fluid static structure have vanished a distance of ζ from the particle's surface. We may take ζ to be several mean free paths, or several fluid particle diameters, whichever is larger. We then have from Eq. (47) the equation

$$\begin{aligned} &z\boldsymbol{\theta}(12) + z\rho\int d3\,\phi_0(3)h(23)\boldsymbol{\theta}(13) \\ &\quad -\mathbf{v}_2\cdot\boldsymbol{\nabla}_2\boldsymbol{\theta}(12) - \rho g(a)\int d3\,\phi_0(3)T_+(23)(1+P_{23})\boldsymbol{\theta}(12) \\ &\quad +\rho a^2 g(a)\int d3\,d\hat{\sigma}\,\phi_0(3)\delta(\mathbf{r}_{23}-a\hat{\sigma})(\hat{\sigma}\cdot\mathbf{v}_3)\boldsymbol{\theta}(13) = 0, \qquad |\mathbf{r}_{12}| \geqslant a_1 + \zeta \end{aligned} \tag{48}$$

In the Brownian particle limit, the required solution of Eq. (48) is the hydrodynamic solution, denoted by $\boldsymbol{\theta}_H(12)$. This may be obtained by projecting $\boldsymbol{\theta}(12)$ onto the hydrodynamic eigenfunctions of the kinetic operator to $O(l/a_1)$, but, as pointed out by Van Beijeren *et al.*,[5] it is much more convenient to project onto linear combinations of these eigenfunctions—the so-called normal forms. For this particular operator, we therefore seek a solution of the form

$$\begin{aligned} \boldsymbol{\theta}_H^\alpha(12) = \mathbf{f}_n^\alpha(\mathbf{r}) &+ (\beta m)^{1/2}\left\{\mathbf{v}_2^\beta + \left(1+\frac{2b^E}{5}\right)\frac{B(v_2^2)}{\rho g(a)}\right. \\ &\qquad \left.\times\left[\mathbf{v}_2^\beta\mathbf{v}_2^\gamma - (v_2^2/3)\delta_{\beta\gamma}\right]\boldsymbol{\nabla}^\gamma\right\}\overleftrightarrow{f}_v^{\beta\alpha}(\mathbf{r}) \\ &+ \left(\frac{2}{3}\right)^{1/2}\left\{\left(\frac{\beta m v_2^2}{2} - \frac{3}{2}\right) + \left(1+\frac{3b^E}{5}\right)\frac{A(v_2^2)}{\rho g(a)}\mathbf{v}_2^\beta\boldsymbol{\nabla}^\beta\right\}\mathbf{f}_T^\alpha(\mathbf{r}) \end{aligned} \tag{49}$$

where $\boldsymbol{\nabla} \equiv \boldsymbol{\nabla}_1$ and $\mathbf{r} \equiv \mathbf{r}_{12}$. In this equation, $\mathbf{f}_n$, $\overleftrightarrow{f}_v$, and $\mathbf{f}_T$ are functions of $\mathbf{r}$ that are yet to be found, b^E is given by

$$b^E = 2\pi\rho a^3 g(a)/3 \tag{50}$$

and the functions $A(v_2^2)$ and $B(v_2^2)$ are the same as those used by Van Beijeren *et al.*[5] and are defined by

$$\lambda_B(\mathbf{v}_2)\phi_0(2)A(v_2^2)\mathbf{v}_2 = (\beta m v_2^2/2 - 5/2)\mathbf{v}_2\phi_0(2) \tag{51a}$$

and

$$\lambda_B(\mathbf{v}_2)\phi_0(2)B(v_2^2)\left[\mathbf{v}_2^\alpha\mathbf{v}_2^\beta - (v_2^2/3)\delta_{\alpha\beta}\right] = \left[\mathbf{v}_2^\alpha\mathbf{v}_2^\beta - (v_2^2/3)\delta_{\alpha\beta}\right]\phi_0(2) \quad (51b)$$

where $\lambda_B(\mathbf{v}_2)$ is the linearized Boltzmann operator. These functions have the additional properties

$$\int d\mathbf{v}_2\,\phi_0(2)v_2^4B(v_2^2) = -15\eta^B/\beta m^2 \quad (52a)$$

$$\int d\mathbf{v}_2\,\phi_0(2)v_2^2A(v_2^2) = 0 \quad (52b)$$

and

$$\int d\mathbf{v}_2\,\phi_0(2)\left(\frac{\beta m v_2^2}{2} - \frac{5}{2}\right)v_2^2A(v_2^2) = -3\lambda^B/k_B \quad (52c)$$

where η^B and λ^B are the Boltzmann values of the shear viscosity and thermal conductivity of the fluid, respectively. Substitution of Eq. (49) into Eq. (48), followed by multiplication by $\phi_0(1)\phi_0(2)$, $\mathbf{v}_2\phi_0(1)\phi_0(2)$ and $(\beta m v_2^2/2 - 3/2)\phi_0(1)\phi_0(2)$, respectively, and integrating over $\mathbf{v}_2$ and $\mathbf{v}_1$, yields the following coupled equations for $\mathbf{f}_n$, $\overleftrightarrow{f}_v$ and $\mathbf{f}_T$:

$$zS(0)\mathbf{f}_n^\alpha(\mathbf{r}) + (\beta m)^{-1/2}\nabla^\beta\cdot\overleftrightarrow{f}_v^{\beta\alpha}(\mathbf{r}) = 0 \quad (53a)$$

$$z\overleftrightarrow{f}_v^{\alpha\beta}(\mathbf{r}) + (\beta m)^{-1/2}\nabla^\alpha\mathbf{f}_n^\beta(\mathbf{r}) + (2/3)^{1/2}(\beta m)^{-1/2}(1+b_E)\nabla^\alpha\mathbf{f}_T^\beta(\mathbf{r})$$
$$- (\eta^E/\rho m)\nabla^2\overleftrightarrow{f}_v^{\alpha\beta} - (1/\rho m)(\eta^E/3 + \zeta^E)\nabla^\alpha\nabla^\gamma\overleftrightarrow{f}_v^{\gamma\beta}(\mathbf{r}) = 0 \quad (53b)$$

and

$$z\mathbf{f}_T^\alpha(\mathbf{r}) + (2/3)^{1/2}(\beta m)^{-1/2}(1+b_E)\nabla^\beta\overleftrightarrow{f}_v^{\beta\alpha}(\mathbf{r}) - (2\lambda^E/3\rho k_B)\nabla^2\mathbf{f}_T^\alpha(\mathbf{r}) = 0,$$
$$|\mathbf{r}_{12}| \gtrsim a_1 + \zeta \quad (53c)$$

Here η^E, λ^E, and ζ^E are the full Enskog transport coefficients of the shear viscosity, thermal conductivity, and bulk viscosity of the fluid. They are given explicitly by

$$\eta^E = (1 + 2b^E/5)^2\eta^B/g(a) + 3\tilde{\omega}/5 \quad (54a)$$

$$\lambda^E = (1 + 3b^E/5)^2\lambda^B/g(a) + 3k_B\tilde{\omega}/2m \quad (54b)$$

and

$$\zeta^E = \tilde{\omega} \quad (54c)$$

where

$$\tilde{\omega} = \frac{(b^E)^2(mk_BT)^{1/2}}{g(a)a^2\pi^{3/2}} \quad (54d)$$

Lastly, the quantity $S(0)$ in Eq. (53a) is the zero-k limit of the structure factor of the fluid, $S(k) = 1 + \rho h(k)$.

Clearly Eqs. (53) are closely related to the normal, linearized hydrodynamic equations. In order to make this more explicit, we note the following results, true for a hard-sphere fluid:

$$\left.\frac{\partial P}{\partial T}\right)_\rho = \rho k_B(1 + b^E) \tag{55a}$$

$$\left.\frac{\partial P}{\partial \rho}\right)_T = k_B T/S(0) \tag{55b}$$

and

$$C_v = 3k_B/2 \tag{55c}$$

where P denotes the pressure and C_v the specific heat per particle at constant volume. If we now take the scalar product of Eq. (53) with a constant vector, which we call $\mathbf{U}(z)$ and define

$$\delta n(\mathbf{r}, z) = S(0)\mathbf{f}_n(\mathbf{r}) \cdot \mathbf{U}(z) \tag{56a}$$

$$\rho v_\beta(\mathbf{r}, z) = (\beta m)^{-1/2} \overleftrightarrow{f}_v^{\beta\alpha}(\mathbf{r}) \cdot \mathbf{U}^\alpha(z) \tag{56b}$$

and

$$\delta T(\mathbf{r}, z) = (2/3)^{1/2}(T/\rho)\mathbf{f}_T(\mathbf{r}) \cdot \mathbf{U}(z) \tag{56c}$$

then these quantities obey the normal linearized hydrodynamic equations, appropriate for solving for the fluid fields around a sphere whose frequency-dependent velocity is $\mathbf{U}(z)$.

These calculations have thus given us the form of $\boldsymbol{\theta}(12)$ for large values of $|\mathbf{r}_{12}|$, but as pointed out previously, this cannot yet be used to determine the VCF because Eqs. (43) and (46) require knowledge of $\boldsymbol{\theta}(12)$ for $a_1 \leqslant |\mathbf{r}_{12}| < a_1 + \zeta$, and within this region $\boldsymbol{\theta}(12) \neq \boldsymbol{\theta}_H(12)$ because of the effects of the rapidly varying static distribution functions in Eq. (47). The next steps are to reexpress Eq. (46) so that it involves only the far-field solution, $\boldsymbol{\theta}_H(12)$, and then to obtain boundary conditions on the functions $\mathbf{f}_n$, $\overleftrightarrow{f}_v$ and $\mathbf{f}_T$ at $|\mathbf{r}_{12}| = a_1 + \zeta$. To do this, we return to the full equation for $\boldsymbol{\theta}(12)$, and consider the conservation equations. That is, we multiply Eq. (47) through by $\phi_0(1)\phi_0(2)$, $\mathbf{v}_2\phi_0(1)\phi_0(2)$ and $(\beta m v_2^2/2 - 3/2)\phi_0(1)\phi_0(2)$, respectively, and integrate over the velocities. We then obtain the equations

$$zG(12)\langle\langle \boldsymbol{\theta}^\alpha(12)\rangle\rangle + z\rho\int d\mathbf{r}_3 \left[G(123) - G(12)G(13)\right]\langle\langle \boldsymbol{\theta}^\alpha(13)\rangle\rangle$$
$$- G(12)\nabla_2^\gamma \langle\langle \mathbf{v}_2^\gamma \boldsymbol{\theta}^\alpha(12)\rangle\rangle = 0 \tag{57a}$$

$$zG(12)\langle\langle \mathbf{v}_2^\alpha \boldsymbol{\theta}^\beta(12)\rangle\rangle - G(12)\nabla_2^\gamma \cdot \langle\langle \mathbf{v}_2^\alpha \mathbf{v}_2^\gamma \boldsymbol{\theta}^\beta(12)\rangle\rangle$$
$$-\rho\int d\mathbf{r}_3\, G(123)\langle\langle \mathbf{v}_2^\alpha T_+(23)(1 + P_{23})\boldsymbol{\theta}^\beta(12)\rangle\rangle = 0 \tag{57b}$$

and

$$zG(12)\left\langle\left\langle\left(\frac{\beta m v_2^2}{2}-\frac{3}{2}\right)\boldsymbol{\theta}^{\alpha}(12)\right\rangle\right\rangle$$
$$-G(12)\nabla_2^{\gamma}\left\langle\left\langle \mathbf{v}_2^{\gamma}\left(\frac{\beta m v_2^2}{2}-\frac{3}{2}\right)\boldsymbol{\theta}^{\alpha}(12)\right\rangle\right\rangle$$
$$-\rho\int d\mathbf{r}_3\, G(123)\left\langle\left\langle\left(\frac{\beta m v_2^2}{2}-\frac{3}{2}\right)T_+(23)(1+P_{23})\boldsymbol{\theta}^{\alpha}(12)\right\rangle\right\rangle=0 \tag{57c}$$

where $\langle\langle\cdots\rangle\rangle$ means multiply through by the Maxwellian distribution functions of all the particles involved, and then integrate over all velocities.

These results may be used to rewrite Eq. (46) so that it only requires knowledge of $\boldsymbol{\theta}_H(12)$, and not $\boldsymbol{\theta}(12)$ for $|\mathbf{r}_{12}|<a_1+\zeta$ about which we know very little. To do this, we integrate Eq. (57b) over the volume (V) between two concentric spheres, the inner of radius a_1, the outer of radius $a_1+\zeta$. For $|\mathbf{r}_{12}|=a_1+\zeta$ thereabouts, or $\boldsymbol{\theta}(12)=\boldsymbol{\theta}_H(12)$ and all influence of the Brownian particle upon the fluid's static structure has vanished. Then, using the explicit form for $\boldsymbol{\theta}_H(12)$ given in Eq. (49), the hard-sphere YBG equations, Eq. (12), and finally Eq. (46), we find

$$zC(z)+(\rho k_B T/m_1)\int d\mathbf{r}_2\,\delta(|\mathbf{r}_{12}|-a_1-\zeta)\hat{r}_{12}^{\alpha}$$
$$\cdot\Big\{\mathbf{f}_n^{\alpha}(\mathbf{r}_{12})+(2/3)^{1/2}(1+b^E)\mathbf{f}_T^{\alpha}(\mathbf{r}_{12})$$
$$-(\beta m)^{1/2}(2\eta^E/\rho m)\hat{r}_{12}^{\gamma}\hat{r}_{12}^{\epsilon}\nabla_{\epsilon}\overleftrightarrow{f}_v^{\alpha\gamma}(\mathbf{r}_{12})$$
$$-(\beta m)^{1/2}((\zeta^E-2\eta^E/3)/\rho m)\nabla_{\gamma}\overleftrightarrow{f}_v^{\gamma\alpha}(\mathbf{r}_{12})\Big\}=3k_B T/m_1 \tag{58}$$

Note that the factor of $G(a_1)$ in front of the integral over $\boldsymbol{\theta}$ has disappeared in going from Eq. (46) to (58); a spurious $G(a_1)$ would be obtained were the boundary layer ignored. This again points out the ease with which deviant $G(a_1)$'s can enter moderate-density kinetic theory. To obtain this result, we have required that the term $z\int_V d\mathbf{r}_2\, G(12)\langle\langle \mathbf{v}_2^{\alpha}\boldsymbol{\theta}^{\beta}(12)\rangle\rangle$ be small compared to the integrals of the other terms in Eq. (57b). Because so little is known about the behavior of $\boldsymbol{\theta}(12)$ within this volume, we cannot estimate terribly precisely the value for z required to make this term sufficiently small to be negligible. However, if we assume that $\langle\langle \mathbf{v}_2^{\alpha}\boldsymbol{\theta}^{\beta}(12)\rangle\rangle$ is not too drastically different in magnitude from $\langle\langle \mathbf{v}_2^{\alpha}\boldsymbol{\theta}_H^{\beta}(12)\rangle\rangle$ (that is, $|\langle\langle \mathbf{v}_2^{\alpha}\boldsymbol{\theta}^{\beta}(12)\rangle\rangle| \ll (a_1/\zeta|\langle\langle \mathbf{v}_2^{\alpha}\boldsymbol{\theta}_H^{\beta}(12)\rangle\rangle|)$, then if $z \lesssim 0\ \ ((\beta m)^{1/2}a_1)^{-1})$ this term will only affect Eq. (58) to higher order in powers of (ζ/a_1). The form of the second term of Eq. (58) is now very similar to the hydrodynamic form for the force upon a sphere as a fluid flows past. The first two terms correspond to the integral of the pressure over the surface, the first term corresponding to that part of the pressure caused by number density fluctuations, the second corresponding to that part coming from temperature fluctuations. The third and fourth terms correspond to the dissipative part of the hydrodynamic stress tensor—that part coming directly from the fluid's velocity field.

All that now remains is to "transfer" the boundary conditions given by Eq. (43) at $|\mathbf{r}_{12}| = a_1$, to the surface of a sphere of radius $|\mathbf{r}_{12}| = a_1 + \zeta$. To do this we use methods that are rather similar to those used by Ronis *et al.*[18] in their investigation of hydrodynamic boundary conditions, and Van Beijeren *et al.*[5] in their investigation of the extended Boltzmann equation for a diffusely reflecting sphere. Firstly we consider Eq. (57a). We take the scalar product with $\hat{r}_{12}$, divide through by $G(12)$, and then integrate over the volume V defined previously. Following the arguments outlined in the last paragraph, we can drop the first two terms of Eq. (57a) provided that z is sufficiently small, and we are left with the result that

$$\begin{aligned}\int d\mathbf{r}_2\, \delta(|\mathbf{r}_{12}| - a_1)\hat{r}_{12}^{\alpha}\hat{r}_{12}^{\gamma}\langle\langle \mathbf{v}_2^{\gamma}\boldsymbol{\theta}^{\alpha}(12)\rangle\rangle \\ = \int d\mathbf{r}_2\, \delta(|\mathbf{r}_{12}| - a_1 - \zeta)\hat{r}_{12}^{\alpha}\hat{r}_{12}^{\gamma}\langle\langle \mathbf{v}_2^{\gamma}\boldsymbol{\theta}^{\alpha}(12)\rangle\rangle \\ - \int_V d\mathbf{r}_2\, \langle\langle \mathbf{v}_2^{\gamma}\boldsymbol{\theta}^{\alpha}(12)\rangle\rangle \frac{(\delta_{\alpha\gamma} - \hat{r}_{12}^{\alpha}\hat{r}_{12}^{\gamma})}{|r_{12}|}\end{aligned} \tag{59}$$

Again, provided that $\langle\langle \mathbf{v}_2^{\gamma}\boldsymbol{\theta}^{\alpha}(12)\rangle\rangle$ does not differ too drastically from $\langle\langle \mathbf{v}_2^{\gamma}\boldsymbol{\theta}_H^{\alpha}(12)\rangle\rangle$ within the volume V, then it is clear that the second term on the right-hand side of Eq. (59) is of $O(\zeta/a_1)$ times the other terms, and hence may be neglected. Furthermore, at $|\mathbf{r}_{12}| = a_1 + \zeta$, we may replace $\boldsymbol{\theta}(12)$ by $\boldsymbol{\theta}_H(12)$. Finally, we may use Eq. (43) to obtain the left-hand side of Eq. (59), by taking the scalar product of Eq. (43) with $\mathbf{v}_1\phi_0(1)\phi_0(2)$ and integrating over all velocities. This procedure finally yields

$$\int d\mathbf{r}_2\, \delta(|\mathbf{r}_{12}| - a_1)\frac{C(z)}{3} = (\beta m)^{1/2}\int d\mathbf{r}_2\, \delta(|\mathbf{r}_{12}| - a_1 - \zeta)\hat{r}_{12}\cdot \overleftrightarrow{f}_v(\mathbf{r}_{12})\cdot \hat{r}_{12} \tag{60a}$$

to lowest order in (ζ/a_1), or more straightforwardly

$$C(z)/3 = (\beta m)^{-1/2}\hat{r}_{12}\cdot \overleftrightarrow{f}_v(\mathbf{r}_{12})\cdot \hat{r}_{12}, \qquad |\mathbf{r}_{12}| = a_1 + \zeta \tag{60b}$$

This is the equivalent of the hydrodynamic normal velocity boundary condition.

A similar procedure may now be applied to the remaining conservation equations. Thus if Eq. (47b) is multiplied through by $(\delta_{\alpha\beta} - \hat{r}_{12}^{\alpha}\hat{r}_{12}^{\beta})$ and the result integrated over the volume V, and similar assumptions are made as discussed previously about the magnitude of moments of $\boldsymbol{\theta}(12)$ within this volume, we obtain the equivalent of the zero tangential stress boundary condition, which may be written

$$\left[\hat{r}_{12}^{\gamma}(\hat{r}_{12}^{\alpha}\hat{r}_{12}^{\epsilon} - \delta_{\alpha\epsilon}) + \hat{r}_{12}^{\epsilon}(\hat{r}_{12}^{\alpha}\hat{r}_{12}^{\gamma} - \delta_{\alpha\gamma})\right]\nabla_1^{\epsilon}\overleftrightarrow{f}_v^{\alpha\beta}(\mathbf{r}_{12}) = 0, \qquad |\mathbf{r}_{12}| = a_1 + \zeta \tag{61}$$

again to lowest order in (ζ/a_1). If instead one were to multiply Eq. (47b) by $\hat{r}_{12}^{\alpha}\hat{r}_{12}^{\beta}$ and integrate, one would then simply regain the equality used to convert Eq. (46) into Eq. (58). Finally if Eq. (47c) is multiplied by $\hat{r}_{12}^{\alpha}$ and integrated, the normal temperature flux boundary condition is obtained in the form

$$\hat{r}_{12} \cdot \nabla \mathbf{f}_T(\mathbf{r}_{12}) = 0, \qquad |\mathbf{r}_{12}| = a_1 + \zeta \tag{62}$$

Thus, provided that the required moments of the functions $\boldsymbol{\theta}(12)$ do not grow too excessively as one moves from the bulk fluid into the volume V, that is, for example, $|\langle\langle \mathbf{v}_2 \cdot \boldsymbol{\theta}(12)\rangle\rangle| \ll (a_1/\zeta)|\langle\langle \mathbf{v}_2 \cdot \boldsymbol{\theta}_H(12)\rangle\rangle|$, then we have succeeded in showing that the VCF may be obtained from the solution of the linearized hydrodynamic equations, Eq. (53) subject to hydrodynamic slip boundary conditions at the surface of a sphere of radius $a_1 + \zeta$, that is, boundary conditions exterior to the static boundary layer. These solution may then be substituted into Eq. (58), which then yields the Stokes–Einstein form for the VCF, with Enskog transport coefficients.

To be more explicit, we now consider the $z = 0$ limit of the preceding equations. Solution of Eq. (53), subject to the boundary conditions given in Eqs. (60b), (61), and (62), yields

$$\mathbf{f}_n(\mathbf{r}) = (\beta m)\frac{\eta^E}{\rho m} a_1 D \frac{\hat{r}}{r^2} \tag{63a}$$

$$f_v^{\alpha\beta}(r) = \frac{(\delta_{\alpha\beta} + \hat{r}_\alpha \hat{r}_\beta)}{r}(\beta m)^{1/2} D \frac{a_1}{2} \tag{63b}$$

and

$$\mathbf{f}_T(r) = 0 \tag{63c}$$

Substitution of these quantities into Eq. (58) yields the Stokes–Einstein result for slip-boundary conditions, i.e.,

$$D = k_B T / 4\pi\eta_E a_1 \tag{64}$$

where we have replaced $(a_1 + \zeta)$ by a_1 in these last four equations, as $\zeta/a_1 \ll 1$.

In summary, then, it appears that the ERRA equations do yield the Stokes–Einstein relationship with Enskog transport coefficients. We now shall briefly consider the simpler ERRA theory proposed by Mehaffey and Cukier,[15] contained in Eqs. (15) and (17). In the Brownian particle limit, because their boundary conditions differed from ours, they would not have the third term on the left-hand side of Eq. (46). The hydrodynamic solution for $\boldsymbol{\theta}(12)$ would be given by Eqs. (49)–(53), for all $|\mathbf{r}_{12}| \geqslant a_1$, as their equations do not contain the effects of the static distribution functions describing the disruption of the bulk fluid structure due to the presence of the tagged particle. The boundary conditions would be identical to Eqs. (60b)–(61), and, at $z = 0$, would lead to the same hydrodynamic solutions given by Eqs. (63a–c). However, when the hydrodynamic $\boldsymbol{\theta}(12)$ is substituted into their version of Eq. (46), the Stokes–Einstein result is not recovered. Firstly, the spurious $G(a_1)$ is present. Secondly, although the pressure contribution to the friction coefficient is given correctly, the contribution due to $\overleftrightarrow{f}v$ is given incorrectly—it contains instead of an Enskog shear viscosity, a "semi-Enskog" viscosity, given by $(1 + 2b^E/5)\eta^B/g(a)$. Furthermore, the correctness of the pressure contribution is partly fortuitous; the $(\partial P/\partial T)$ term is incorrect, but in Stokes' problem, $\delta T = 0$. Clearly, then, the extra detail contained in the ERRA Eqs. (13) is necessary in order to obtain the correct form of the stress tensor, Eq. (58), and hence to obtain the correct, Stokes–Einstein relation for the VCF of a Brownian particle. It is important to note, in this context, that the normal solutions of the Enskog equation are not produced from their Boltzmann cousins by simply changing "B" subscripts to "E" subscripts in parameters—if this were true, the MC approach would give a result containing η^E. Equations (49) and (54a) show, however, that the "parts" of η^E enter $\boldsymbol{\theta}_H$ in a seemingly disorganized fashion, and they must be carefully reconstructed in the calculation of D before anything looking like η^E appears. This reconstruction requires the new features of the ERRA at $r_{12} = a$ and $r_{12} \gtrsim a$. Although the physical meaning of all this is not transparent to us, consider that one part of $\eta^E(\tilde{\omega})$ arises from "collisional transport" of momentum, which occurs only when two gas molecules touch. This effect surely must be altered when the touching pair is further constrained to be near the tagged particle. So, it makes some sense that care must be taken in the boundary regime if the contribution of $\tilde{\omega}$ to D (missing in MC) is to be obtained correctly.

5. DISCUSSION

In the preceding sections we have obtained a repeated-ring kinetic equation for the VCF of a particle by using Mori's generalized Langevin equation for hard spheres and neglecting the "memory term." We argued that this memory term only contained dynamical events more complex than rings or repeated rings and then showed that the proposed equations yielded an asymptotic long-time tail for the VCF in agreement with that obtained by Dorfman and Cohen,[13] and also yielded the Stokes–Einstein relation with Enskog transport coefficients when the tagged particle was a Brownian particle. We believe that this is good evidence that our proposed ERRA equations are at least sensible, and suggests that use of Mori theory is a relatively painless way of generating such kinetic equations.

The outstanding problems would appear to be firstly how one might obtain good, numerical solutions to those complex, coupled equations, and secondly, how might one set about improving these equations so they might deal with diffusion of a very light tagged particle (the Lorentz gas limit) and also with diffusion at liquid densities.

To deal with the first point, as we said in the Introduction we believe that use of Cercignani's variational principle is a promising way of obtaining the VCF of a tagged particle from the low-density RRA equations. It would therefore be logical to attempt to apply a version of this method to the ERRA equations, but so far we unfortunately have made little progress. As for the second point, we can offer some speculations as to how the ERRA equations may be improved. As we said, they work best for a massive tagged particle in a moderately dense gas. They cannot describe diffusion in a liquid because the ERRA equations require that the surrounding fluid be well described by the modified Enskog theory.[17,27] One way of systematically improving the calculations would be to introduce a third variable, $C(\bar{1}\bar{2}\bar{3})$, into the Mori formalism where $C(\bar{1}\bar{2}\bar{3})$ would be a three-particle term. If this were included, and if the new memory function were to be thrown away, then a kinetic theory containing all ring-within-ring and repeated-ring-within-repeated-ring collision sequences would emerge, again the binary collision operators "dressed" with the required static distribution functions. Clearly even more complex equations may be obtained by introducing four, five, six, etc. body terms into the Mori formalism and dropping the memory term, but the problem with this approach would be firstly that one might have to introduce very many variables in order to obtain an accurate liquid state theory, even assuming the procedure converged, and secondly the resulting coupled equations would be horrendously complicated and intractable. Another, possibly more promising approach is to approximate the memory function in some way, rather than simply neglect it. Thus, as we shall show in a subsequent paper the effect of the memory term in Eqs. (5d) is to replace the Enskog transport coefficients by the true, fluid coefficients both in the long-time tail calculation and in the Stokes–Einstein relation. This is because far away from the tagged particle we know that the fluid obeys the "true" kinetic equation, as opposed to the approximate modified Enskog kinetic equation. An attractive possibility, therefore, is to propose a self-consistent repeated-ring approximation, where the far field Enskog operators are replaced by the true fluid and tagged-particle kinetic operators. Previous work on the Lorentz gas[9b,28] and on pure fluids[11] suggests that these self-consistent theories are superior to non-self-consistent theories—for instance, when the Lorentz gas scatterers are allowed to overlap, the self-consistent theories correctly predict a critical density of scatterers at which the diffusion constant vanishes, whereas the non-self-consistent theories do not show this behavior. This self-consistent approach in kinetic theory is originally due to Götze et al.[28]

Of course one problem with a self-consistent theory is that although the large $|\mathbf{r}_{12}|$ form of the operator may be known, as are the boundary conditions on the collision sphere, it is unclear how best to approximate the kinetic operator inside the boundary layer region. In spite of this, self-consistent theories seem so far to be the best candidates for a successful kinetic theory for diffusion in dense fluids.

NOTE ADDED IN PROOF

After this paper was submitted, two closely related articles by Sung and Dahler [*J. Chem. Phys.* **78**:6280; 6264 (1983)] appeared. The method of derivation of the kinetic equations is basically the same. In the Stokes–Einstein law calculation, their treatment of the second equation (analogue to Eq. 9b) is almost identical to ours. They obtain Enskog normal solutions in which the hydrodynamic fields are given by solutions to Enskog hydrodynamic equations, with slip boundary conditions. They state that the slip Stokes–Einstein law immediately follows (discussion after their Eq. 3.21). While this is true in a hydrodynamic calculation, a fully Kinetic theory of diffusion should be based upon substitution of the solution of the second equation into the first repeated ring equation (analogue of Eq. 9a). This would be straightforward if the normal solution were the true solution at the surface of the collision sphere. However, such is not the case, and the straightforward procedure gives the wrong answer. We suggest that the analysis presented here shows that finding the correct way to use the normal solution in the first equation is an important step in solving the coupled repeated ring equations.

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