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The Long Time and Brownian Limits for Tagged Particle Motion in Liquids[1]

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Formally exact theories of tagged particle motion in liquids are developed, based upon kinetic theory for hard spheres and mode coupling for smooth potentials. It is shown that the resulting equations are tractable in the long time and Brownian limits. The coefficient of the long time tail of the velocity correlation function is seen to differ from its low-density form by only the replacement of the low-density viscosity and diffusion constant by the true viscosity and diffusion constant. In the Brownian limit, the slip Stokes–Einstein law is obtained, with the true viscosity. The relation to other work is discussed.

KEY WORDS: Kinetic theory; mode coupling; long time tails; Brownian limits; Stokes–Einstein law.

1. INTRODUCTION

Consider the motion of a tagged particle through a hard-sphere fluid with mean free path l; the tagged-fluid and fluid–fluid collision radii are a_1 and a, respectively. If the fluid is a dilute gas, and if $a_1 \ll l$, the motion is described by the Lorentz–Boltzmann equation.[1,2]

This equation, however, fails either if the fluid is made denser, so that a becomes comparable to l, or else if the fluid remains a dilute gas but the tagged particle is increased in size so that $a_1 \simeq l$ or $a_1 \gg l$. In the second instance there is very good evidence that the required kinetic equation is the repeated ring approximation (RRA)[3-6], provided that the tagged particle is sufficiently massive. This equation correctly yields the Stokes–Einstein relation for the tagged particle in the Brownian particle limit,[7,8] with the

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transport coefficients of the fluid given by their low-density Boltzmann values. Furthermore, this equation predicts that the velocity correlation function (VCF) of the tagged particle exhibits a positive asymptotic $t^{-3/2}$ long time tail in three dimensions[9,10] the coefficient again involving the Boltzmann values of transport coefficients. The presence of such a long time tail in the VCF had previously been observed in computer simulations.[11,12]

The RRA equation assumes that the fluid far away from the tagged particle obeys the linearized Boltzmann equation. As the fluid is made denser, so that the condition $a/l \ll 1$ no longer holds true, the Boltzmann equation fails to give an adequate description of its behavior and the RRA equation for tagged particle motion also fails. Recently in papers published first by Sung and Dahler[13a] and later by ourselves[13b] (this paper henceforth to be called I), Mori's generalized Langevin equation[14] for a system of hard, specularly reflecting spheres was used to write down a formally exact kinetic equation for the tagged particle's motion. An approximate kinetic theory was then obtained by dropping the "memory function" in the exact equation. The resulting equation had the form of an RRA equation, but contained in it a lot of information about the equilibrium static structure of the fluid particles around the tagged particle. Then both Sung and Dahler and ourselves showed that the equation yielded the Stokes–Einstein relationship in the Brownian particle limit, but this time the fluid transport coefficients being given by their Enskog values.[1,2] We note, though, that our method of analysis in this limit differed considerably from that used by Sung and Dahler. These differences are discussed briefly in a note added in proof to I. We further showed[13b] that the equation predicted an asymptotic long time tail for the VCF in agreement with the very careful "ring" calculation of Dorfman and Cohen,[15] again with the transport coefficients taking on their Enskog values. It was concluded that this equation, which we called an Enskog repeated ring approximation (ERRA) (and called the two-fluid mean field approximation, or MFA, by Sung and Dahler), required that the fluid far away from the tagged particle obeyed the linearized modified Enskog equation.[3] Although the modified Enskog equation seems to work remarkably well over a wide range of fluid densities, it does fail at liquid densities. Thus the ERRA is a theory for tagged particle motion in a moderately dense gas, but cannot be expected to apply to diffusion in a liquid. In order to describe this, one must go beyond the ERRA and retain the memory term in the true kinetic equation. Of course, in order to have any hope of solving such an equation for a tagged particle of arbitrary mass and size, this memory function must be approximated in some way. It is possible, though, to make some progress with the exact

[3] This has been derived by many authors, including those listed in Ref. 16.

kinetic equation in some limiting cases. In this paper we consider the long time behavior of the VCF and also the Brownian particle limit. These limits provide tests that may be applied to approximate, high density theories in order to check their possible validity.

Much attention has already been given to both of these limiting cases. Mode coupling calculations upon the long time tail of the VCF have been made by Ernst *et al.*[17] and by several others.[18] Their results involved the true fluid transport coefficients, and reduced to the RRA (or ERRA) results if the transport coefficients were given their Boltzmann (or Enskog) values. Pomeau and Resibois[19] also obtained a long time tail involving full transport coefficients on the basis of kinetic theory. More recently a very thorough analysis of the hard sphere fluid has been given by Van Beijeren and Ernst,[20] which confirmed the previous mode coupling results. These results also show excellent agreement with computer simulations.[11,12] It would therefore seem that the question of the long time behavior of the VCF has been settled. All that we hope to do in this paper is to show how this well-known result may be obtained very simply both for hard-sphere systems and also for systems in which the particles interact through short-ranged, continuous and central potentials, but without having to make the assumptions commonly made in mode-coupling theories.

The second problem, that of a molecular theory of Brownian motion and the Stokes–Einstein relationship, has also been considered by many workers. Keyes and Oppenheim[21] used mode-coupling methods to obtain the correct function form of the Stokes–Einstein relation, but they obtained an incorrect value for the constant of proportionality (5π instead of either 4π or 6π). Masters and Madden[22] later showed how the correct form of the Stokes–Einstein relation could be obtained by avoiding the Gaussian approximation commonly made in mode-coupling calculations, which was shown to allow fluid to get inside the Brownian particle. Several approximations were still made in that calculation, however, about how the fluid behaved nearby the Brownian particle. In this paper we attempt to analyze the problem more deeply, both for hard-sphere systems and also for a system with short-range, continuous potentials of interaction, hopefully giving a more fundamental derivation of the Stokes–Einstein relationship, involving the true shear viscosity, in both cases.

2. THE LONG-TIME TAIL AND THE STOKES–EINSTEIN BEHAVIOR FOR A HARD-SPHERE SYSTEM

A detailed account of the derivation of the exact hard-sphere kinetic equation is given in I, so we shall give only a very brief recap of the methods used here.

We introduced the variables $A(\bar{1})$ and $B(\bar{1}\bar{2})$, defined by

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

and

$$B(\bar{1}\bar{2}) = \delta(\bar{\mathbf{v}}_1 - \mathbf{v}_1) \left\{ \sum_{i>1} \delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1i})\, \delta(\bar{\mathbf{v}}_2 - \mathbf{v}_i) - \rho G(\bar{1}\bar{2})\, \varnothing_0(\bar{2}) \right\}, \qquad |\bar{\mathbf{r}}_{12}| \geqslant a_1 \tag{1b}$$

where the barred variables are field variables and the unbarred dynamical variables. The Maxwellian velocity distribution function for particle j is given by $\varnothing_0(j)$, ρ is the number density of the fluid, and $G(12 \cdots R)$ is the R-body distribution function for fluid particles around the tagged particle. Since any average involving B will vanish if particles overlap, the restriction, $|r_{12}| > a_1$, is needed if the average, $\langle BB \rangle^{-1}$, required in the Mori[14] approach we will use, is to exist. This restriction involves no loss of information, since the hard spheres cannot overlap in reality.

We then applied Mori's generalized Langevin equation[14] to these variables for all possible values of the field variables, and thereby obtained two coupled equations for two functions denoted by $\mathbf{\Phi}(1)$ and $\mathbf{\theta}(12)$. The Laplace transform of the VCF, $C(z)$, is then given by

$$C(z) = \int d\bar{1}\, \varnothing_0(\bar{1}) \mathbf{v}_1 \cdot \mathbf{\Phi}(\bar{1}) \tag{2}$$

where $d\bar{1} \equiv d\bar{v}_1$. We later on use the notation $d\bar{2} \equiv d\bar{\mathbf{v}}_2\, d\bar{\mathbf{r}}_2$, and so on. The coupled equations for $\mathbf{\Phi}$ and $\mathbf{\theta}$ were given by

$$z\mathbf{\Phi}(1) - \rho G(a_1) \int d2\, \varnothing_0(2)\, T_+(12)\, \mathbf{\Phi}(1) - \rho G(a_1) \int d2\, \varnothing_0(2)\, \bar{T}_+(12)\, \mathbf{\theta}(12)$$

$$- \rho^2 \int d2\, d3\, \varnothing_0(2)\, \varnothing_0(3) (G(123) - G(12)\, G(13))\, \bar{T}_+(13)\, \mathbf{\theta}(12) = \mathbf{v}_1 \tag{3a}$$

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

$$zG(12)\, \mathbf{\theta}(12) + z\rho \int d3\, \varnothing_0(3) [G(123) - G(12)\, G(13)]\, \mathbf{\theta}(13)$$

$$- G(12) [\mathbf{v}_1 \cdot \mathbf{\nabla}_1 + \mathbf{v}_2 \cdot \mathbf{\nabla}_2]\, \mathbf{\theta}(12) - G(a_1)\, T_+(12)\, \mathbf{\theta}(12)$$

$$- \rho \int d3\, \varnothing_0(3) [G(123) - G(12)\, G(13)]\, T_+(12)\, \mathbf{\theta}(13)$$

$$-\rho \int d3\, \varnothing_0(3)\, G(123)[T_+(13) + T_+(23)(1 + P_{23})]\, \theta(12)$$

$$-\rho \int d3\, \varnothing_0(3)[G(123) - G(12)\, G(13)][\mathbf{v}_1 \cdot \nabla_1 + \mathbf{v}_3 \cdot \nabla_3]\, \theta(13)$$

$$-\rho^2 \int d3\, d4\, \varnothing_0(3)\, \varnothing_0(4)[G(1234) - G(12)\, G(134)]\, T_+(34)\, \theta(13)$$

$$-\rho^2 \int d3\, d4\, \varnothing_0(3)\, \varnothing_0(4) \left[G(1234) - \frac{G(124)\, G(134)}{G(14)}\right] T_+(14)\, \theta(13)$$

$$-\frac{1}{\rho} \cdot \theta(1'3)^* M(1'3; 12) = G(a_1)\, T_+(12)\, \Phi(1) \tag{3b}$$

where all the variables are field variables and we have dropped the overbars for convenience. In these equations $G(a_1)$ is the value of the radial distribution function at contact for fluid around the tagged particle, P_{23} is a permutation operator that exchanges indices 2 and 3, $T_+(ij)$ and $\bar{T}_+(ij)$ are binary collision operators,[23] and $M(1'3; 12)$ is the memory function, defined by

$$M(1'3; 12) = \langle \{i\mathscr{L}_+[z - Qi\mathscr{L}_+]^{-1} Qi\mathscr{L}_+ B(1'3)\}\, B(12) \rangle \tag{4}$$

where Q is the Mori projection operator that projects a dynamical variable orthogonal to the variables $A(1)$ and $B(12)$, and $i\mathscr{L}$ is the pseudo-Liouville operator that propagates a variable either forward (+) or backwards (−) in time, and is given by

$$i\mathscr{L}_\pm = \sum_{i=1} \mathbf{v}_1 \cdot \nabla_1 \pm \tfrac{1}{2} \sum_{i=1} \sum_{\substack{j=1 \\ i \neq j}} T_\pm(ij) \tag{5}$$

Finally the star in Eq. (3b) means integrate over all value of $\mathbf{v}_1'$ and $\mathbf{v}_3$, and all values of $\mathbf{r}_3$ such that $|\mathbf{r}_3 - \mathbf{r}_1'| \geqslant a_1$.

Equations (3a) and (3b) are formally exact kinetic equations. If they could be solved, the exact VCF could be obtained from Eq. (2). In I we made the approximation of dropping the memory term in Eq. (3b) which is appropriate if we restrict ourselves to studying diffusion in a moderately dense gas. As we wish to study diffusion in fluids of arbitrary density in this paper, we must retain this term as it becomes important at liquid densities.

We shall now consider the long time behavior of the VCF, which may be obtained from the form of $C(z)$ for small z. We proceed by using the methods described in I. Firstly, we rewrite Eq. (3b) in the form

$$\theta(12) = RR(12)\, G(a_1)\, T_+(12)\, \Phi(1), \qquad |\mathbf{r}_{12}| \geqslant a_1 \tag{6a}$$

where $RR(12)$ is the operator such that the left-hand side of Eq. (3b) is given by $RR^{-1}(12)\,\boldsymbol{\theta}(12)$. At this point, we must mention some hard-sphere arcana. Owing to our use of T in the pseudo-streaming operator, $\boldsymbol{\theta}$ is nonzero and physically meaningless for $|r_{12}| < a_1$. This presents no difficulty so long as we work in real space, since we only need θ in the physically relevant regime, $|r_{12}| \geqslant a_1$. In the tail calculation, however, we Fourier-transform some quantities, which should then have their correct value, zero, for $|r_{12}| < a_1$. We thus introduce the operator, $\widehat{RR}$, which has the required properties, via the relation

$$W(12)\,RR^{-1}\theta(12) = \widehat{RR}^{-1}(W(12)\,\theta(12)) \tag{6b}$$

where

$$W(r_{12}) = \begin{matrix} 1, & |\mathbf{r}_{12}| \geqslant a_1 \\ 0, & |\mathbf{r}_{12}| < a_1 \end{matrix}$$

The transformation from RR to $\widehat{RR}$ is the reverse of a procedure used by[7] van Beijern and Dorfman. They began using $\bar{T}$'s and thus had functions which vanished for $|r_{12}| < a_1$, and, by replacing the analog of θ with $W\theta$, obtained functions nonzero and unphysical inside the overlapping region, governed with operators containing T's.

Use of this operator allows us to define the problem over all space. It is easy to obtain $\widehat{RR}^{-1}$ by combining Eqs. (3b), (a), and (6b). Some of the $T(12)$'s in Eq. (3b) are converted to $\bar{T}(12)$'s.[13] One might also note that $G(12...)$ in RR^{-1} can be regarded as having been replaced by $\tilde{G}(12\ldots)$ in $\widehat{RR}^{-1}$, where $\tilde{G}$ is not zero, but has some smooth continuation for $|\mathbf{r}_{12}| < a_1$, and thus presents no obstacles to inversion. We will leave this latter point implicit in the following.

Proceeding, we note $\bar{T}\theta = \bar{T}W\theta$, so combination of Eqs. (6) and (3a) yields

$$\begin{aligned} &z\boldsymbol{\Phi}(1) - \rho G(a_1) \int d2\, \varnothing_0(2)\, T_+(12)\, \boldsymbol{\Phi}(1) \\ &\quad - \rho G^2(a_1) \int d2\, \varnothing_0(2)\, \bar{T}_+(12)\, \widehat{RR}(12)\, T_+(12)\, \boldsymbol{\Phi}(1) \\ &\quad - \rho^2 G(a_1) \iint d2\, d3\, \varnothing_0(2)\, \varnothing_0(3) (G(123) \\ &\quad - G(12)\, G(13))\, \bar{T}_+(13)\, \widehat{RR}(12)\, T_+(12)\, \boldsymbol{\Phi}(1) = \mathbf{v}_1 \end{aligned} \tag{7}$$

We now follow Van Beijeren[24] and make a frequency expansion of $\mathbf{\Phi}(1)$ and of $\widehat{RR}(12)$. Thus we write

$$\mathbf{\Phi}(1) = \mathbf{\Phi}^{(0)}(1) + \mathbf{\Phi}^{(1)}(1) + \cdots \tag{8a}$$

and

$$\widehat{RR}(12) = \widehat{RR}^{(0)}(12) + \widehat{RR}^{(1)}(12) \tag{8b}$$

where the superscript 0 indicates the $z = 0$ limit of the quantity, and the superscript 1 indicates the first-order correction. Thus we expect that in three dimensions $\mathbf{\Phi}^{(1)}(1) \propto z^{1/2}$. Substitution of Eqs. (8a) and (8b) into Eq. (7) yields the two equations

$$\begin{aligned}
&-\rho G(a_1) \int d2\, \varnothing_0(2)\, T_+(12)\, \mathbf{\Phi}^{(0)}(1) - \rho G^2(a_1) \int d2\, \varnothing_0(2)\, \bar{T}_+(12)\, \widehat{RR}^{(0)}(12) \\
&\quad \times T_+(12)\, \mathbf{\Phi}^{(0)}(1) - \rho^2 G(a_1) \int d2\, d3\, \varnothing_0(2)\, \varnothing_0(3)(G(123) - G(12)\, G(13)) \\
&\quad \times \bar{T}_+(13)\, \widehat{RR}^{(0)}(12)\, T_+(12)\, \mathbf{\Phi}^{(0)}(1) = \mathbf{v}_1
\end{aligned} \tag{9a}$$

and

$$\begin{aligned}
&-\rho G(a_1) \int d2\, \varnothing_0(2)\, T_+(12)\, \mathbf{\Phi}^{(1)}(1) - \rho G^2(a_1) \int d2\, \varnothing_0(2)\, \bar{T}_+(12) \\
&\qquad \times \widehat{RR}^{(0)}(12)\, T_+(12)\, \mathbf{\Phi}^{(1)}(1) - \rho^2 G(a_1) \int d2\, d3\, \varnothing_0(2)\, \varnothing_0(3) \\
&\qquad (G(123) - G(12)\, G(13))\, \bar{T}_+(13)\, \widehat{RR}^{(0)}(12)\, T_+(12)\, \mathbf{\Phi}^{(1)}(1) \\
&\quad = \rho G^2(a_1) \int d2\, \varnothing_0(2)\, \bar{T}_+(12)\, \widehat{RR}^{(1)}(12)\, T_+(12)\, \mathbf{\Phi}^{(0)}(1) \\
&\qquad + \rho^2 G(a_1) \int d2\, d3\, \varnothing_0(2)\, \varnothing_0(3)(G(123) - G(12)\, G(13)) \\
&\qquad \times \bar{T}_+(13)\, \widehat{RR}^{(1)}(12)\, T_+(12)\, \mathbf{\Phi}^{(0)}(1)
\end{aligned} \tag{9b}$$

where we have ignored terms that yield contributions of $O(z)$ to $\mathbf{\Phi}^{(1)}(1)$ in Eq. (9b). We now take the scalar products of Eq. (9a) and (9b) with $\varnothing_0(1)\, \mathbf{\Phi}^{(1)}(1)$ and $\varnothing_0(1)\, \mathbf{\Phi}^{(0)}(1)$, respectively. After integrating both the resulting equations over $\mathbf{v}_1$ and comparing the results, we obtain the equality

$$\begin{aligned}
\langle \mathbf{v}_1 \cdot \mathbf{\Phi}^{(1)}(1) \rangle &= \rho G(a_1) \langle \mathbf{\Phi}^{(0)}(1) \cdot [G(a_1)\, \bar{T}_+(12) \\
&\quad + \rho(G(123) - G(12)\, G(13))\, \bar{T}_+(13)]\, \widehat{RR}^{(1)}(12)\, T_+(12)\, \mathbf{\Phi}^{(0)}(1) \rangle
\end{aligned} \tag{10}$$

where $\langle\cdots\rangle$ means multiply what is inside the angled brackets by the Maxwellian velocity distribution functions of all the particles involved and then integrate over all the coordinates of those particles. In order to obtain this result we have used the fact that the operators on the left-hand side of Eqs. (9a) and (9b) are symmetric. The left-hand side of Eq. (10) clearly directly gives the small z form of $C(z)$ and hence the long time tail of the VCF. It therefore remains to analyze the rather complex term on the right-hand side of that equation. To do this, we introduce the simpler operator, $\hat{R}(12)$, defined by

$$\hat{R}^{-1}(12) = \lim_{|\mathbf{r}_{12}|\to\infty} \widehat{RR}^{-1}(12) \tag{11}$$

We then write

$$\widehat{RR}^{-1}(12) = \hat{R}^{-1}(12) - \hat{S}(12) \tag{12}$$

where the operator $\hat{S}(12)$ contains all the complicated behavior that occurs in the vicinity of the tagged particle. As in I, we then have the operator identity,

$$\widehat{RR}^{(1)}(12) = [1 + \widehat{RR}^{(0)}(12)\,\hat{S}^{(0)}(12)]\,\hat{R}^{(1)}(12)[\hat{S}^{(0)}(12)\,\widehat{RR}^{(0)}(12) + 1] \\ + \text{higher-order terms in } z \tag{13}$$

The superscripts 0 and 1 on the operators $\hat{R}(12)$ and $\hat{S}(12)$ have the same meaning as given after Eq. (8b). Also, again as in I, the operators $\hat{R}(12)$, $\hat{S}(12)$, etc. are defined for all $|\mathbf{r}_{12}|$. In order to obtain Eq. (13) we used the fact that terms involving $\hat{S}^{(1)}(12)$ are of higher order in z than the term written out. This is not immediately obvious, for it might be though that the memory function, $M(1'3;12)$ in Eq. (3b), could give a contribution to $\hat{S}^{(1)}(12)$ that could in turn contribute to the $z^{1/2}$ term in $\varnothing(1)$. Although we shall not give a detailed proof that these terms do not contribute, we sketch out an argument in Appendix A which supports this contention. Furthermore, as in I, one can show that terms involving $\widehat{RR}^{(1)}\hat{S}^{(0)}\hat{R}^{(1)}$ are of higher order in z, by using the fact that the Fourier transform of $\hat{S}$ [i.e., $\hat{S}_{k_1k_2}$; see Eq. (16)] contains no part proportional to $\delta(\mathbf{k}_1 - \mathbf{k}_2)$.

If we accept Eq. (13), we have reduced the problem of analyzing the complicated operator $\widehat{RR}^{(1)}(12)$ to that of analyzing the considerably simpler operator $\hat{R}^{(1)}(12)$. The action of the operator $\hat{R}^{-1}(12)$ upon a function $\chi(12)$ is given by

$$\hat{R}^{-1}(12)\chi(12) = z\chi(12) + \rho z \int d3\, \varnothing_0(3)\, h(23)\, \chi(13)$$

$$- [\mathbf{v}_1 \cdot \boldsymbol{\nabla}_1 + \mathbf{v}_2 \cdot \boldsymbol{\nabla}_2]\, \chi(12) - \rho G(a_1) \int d3\, \varnothing_0(3)\, T_+(13)\, \chi(13)$$

$$- \rho g(a) \int d3\, \varnothing_0(3)\, T_+(23)(1 + P_{23})\, \chi(12)$$

$$+ \rho g(a) \int d3\, \varnothing_0(3)(\boldsymbol{\nabla}_3 W(23) \cdot \mathbf{v}_3)\, \chi(13)$$

$$-\rho \int d3\, \varnothing_0(3)\, h(23) \mathbf{v}_1 \cdot \boldsymbol{\nabla}_1 \chi(13)$$

$$- \rho^2 G(a_1) \int d3\, d4\, \varnothing_0(3)\, \varnothing_0(4)\, h(23)\, T_+(14)\, \chi(13)$$

$$- \hat{K}(12)\, \chi(12) \tag{14}$$

where $g(23) \equiv g(r_{23})$, the pure fluid radial distribution function, and $h(23) = g(23) - 1$. The function $W(23)$ is unity unless particles 2 and 3 overlap, whereupon it is zero, and $g(a)$ is the value of the fluid radial distribution function at contact. Lastly the operator $\hat{K}(12)$ is given by

$$\hat{K}(12)\, \chi(12) = 1/\rho \lim_{|\mathbf{r}_{12}| \to \infty} \chi(1'3) * M(1'3; 12) \tag{15}$$

For large values of $|\mathbf{r}_{12}|$, it is clear that the decay of fluctuations of the fluid variables are uncorrelated with the motion and position of the tagged particle. Thus the Mori projection operator, Q, in the memory function, will, in this limit, project all fluid variables orthogonal to the variable $(\sum_{i>1} \delta(\bar{\mathbf{r}}_2 - \mathbf{r}_i)\, \delta(\bar{\mathbf{v}}_2 - v_i) - \varnothing_0(2)\rho)$, for all values of $\mathbf{r}_2$ and $\mathbf{v}_2$, and it will project all tagged particle variables orthogonal to the variable $\delta(\bar{\mathbf{v}}_1 - \mathbf{v}_1)\, \delta(\bar{\mathbf{r}}_1 - \mathbf{r}_1)$, for all $\bar{\mathbf{v}}_1$ and $\bar{\mathbf{r}}_1$. Thus the operator $\hat{R}^{-1}(12)$ says that for large $|\mathbf{r}_{12}|$, functions of the fluid variables or of the tagged particle variables obey the true equations of motion for the pure fluid or for the tagged particle, respectively.

In order to further analyze $\hat{R}^{(1)}(12)$, we follow I, and introduce the Fourier transform of an operator, $\hat{O}(12)$, defined by

$$\hat{O}_{\mathbf{k}_1, \mathbf{k}_2}(12) = \int d\mathbf{r}_{12} e^{i\mathbf{k}_1 \cdot \mathbf{r}_{12}}\, \hat{O}(12)\, e^{i\mathbf{k}_2 \cdot \mathbf{r}_{12}} \tag{16}$$

where the integration goes over all values of $\mathbf{r}_{12}$. The operator $\hat{R}(12)$ is diagonal in this representation, that is to say, in three dimensions,

$$\hat{R}_{\mathbf{k}_1, \mathbf{k}_2}(12) = (2\pi)^3\, \delta(\mathbf{k}_1 + \mathbf{k}_2)\, \hat{R}_{\mathbf{k}_2}(12) \tag{17}$$

We thus have the result, using Eqs. (10), (13), (16), and (17), that

$$\begin{aligned}\langle \mathbf{v}_1 \cdot \mathbf{\Phi}^{(1)}(1)\rangle = \rho G(a_1)(2\pi)^{-3} \int d\mathbf{k} \langle \mathbf{\Phi}^{(0)}(1) \\ \times [G(a_1)\,\bar{T}_+(12) + (G(123) - G(12)\,G(13))\,\bar{T}_+(13)] \\ \times [1 + \widehat{RR}^{(0)}(12)\,\hat{S}^{(0)}(12)]\,e^{-i\mathbf{k}\cdot\mathbf{r}_{12}}\hat{R}^{(1)}_{\mathbf{k}}(12)\,e^{i\mathbf{k}\cdot\mathbf{r}_{12}} \\ \times [\hat{S}^{(0)}(12)\,\widehat{RR}^{(0)}(12) + 1]\,T_+(12)\,\mathbf{\Phi}^{(0)}(1)\rangle \end{aligned} \tag{18}$$

It therefore remains to analyze $\hat{R}^{(1)}_{\mathbf{k}}(12)$. This operator contains contributions both from the first two terms of Eq. (14) and also from the z-dependent memory function, $\hat{K}^{(1)}(12)$. In Appendix A we sketch out an argument that shows that $\hat{K}^{(1)}(12)$ only gives rise to contributions of higher order in z than $z^{1/2}$ in $\mathbf{\Phi}^{(1)}(1)$. For our purposes, therefore, we may replace $\hat{K}(12)$ by $\hat{K}^{(0)}(12)$ in Eq. (14) and also in the operator $\hat{R}^{(1)}(12)$. We now expand $\hat{R}^{(1)}(12)$ in terms of the eigenfunctions and eigenvalues of the operator $\hat{R}^{(0)}(12)$. As discussed by Dorfman and Cohen,[15] the long time tail arises solely from the small $|\mathbf{k}|$ portion of the $\mathbf{k}$ integral in Eq. (18), and also comes only from the hydrodynamic modes.

In this case the only mode that contributes is the product of a fluid shear mode and the tagged particle's diffusive mode. If we denote this eigenfunction by $\boldsymbol{\varepsilon}_{\mathbf{k}}(12)$, we have

$$\boldsymbol{\varepsilon}_{\mathbf{k}}(12) = (\beta m)^{1/2}(1 - \hat{k}\hat{k})^*\mathbf{v}_2 + O(\mathbf{k}) \tag{19a}$$

and

$$\begin{aligned}&\langle \boldsymbol{\varepsilon}_{\mathbf{k}}(12) \cdot \hat{R}^{(1)}_{k}(12)\,\boldsymbol{\varepsilon}_{\mathbf{k}}(12)\rangle \\ &\quad = 2\left[\frac{1}{z + k^2(D + \eta/\rho m) + O(k^4)} - \frac{1}{k^2(D + \eta/\rho m) + O(k^4)}\right]\end{aligned} \tag{19b}$$

where D is the full diffusion constant for the tagged particle, η is the full shear viscosity of the fluid, m is the mass of a fluid molecule, and $\beta = (k_B T)^{-1}$, where k_B is Boltzmann's constant and T the absolute temperature. We thus obtain the result

$$\langle \mathbf{v}_1 \cdot \mathbf{\Phi}^{(1)}(1)\rangle = \frac{\rho G(a_1)}{9(2\pi)^3} \int d\mathbf{k}\, f_1(k)\, f_2(k) \langle \boldsymbol{\varepsilon}_{\mathbf{k}}(12) \cdot \hat{R}^{(1)}_{\mathbf{k}}(12)\,\boldsymbol{\varepsilon}_{\mathbf{k}}(12)\rangle, \quad |\mathbf{k}| < k_c \tag{20}$$

where k_c is a cutoff wave vector, on the order of an inverse fluid correlation length. The functions $f_1(k)$ and $f_2(k)$ are given by

$$\begin{aligned}f_1(k) = \langle \mathbf{\Phi}^{(0)}(1)[G(a_1)\,\bar{T}_+(12) + (G(123) - G(12)\,G(13))\,\bar{T}_+(13)] \\ \times (1 + \widehat{RR}^{(0)}(12)\,\hat{S}^{(0)}(12))\,e^{-i\mathbf{k}\cdot\mathbf{r}_{12}}\mathbf{v}_2\rangle\end{aligned} \tag{21a}$$

and

$$f_2(k) = \langle \mathbf{v}_2 \cdot e^{i\mathbf{k}\cdot\mathbf{r}_{12}}(1 + \hat{S}^{(0)}(12)\,\widehat{RR}^{(0)}(12))\,T_+(12)\,\Phi^{(0)}(1)\rangle \tag{21b}$$

As in I, only the zero–k limits of $f_1(k)$ and $f_2(k)$ contribute to the long time tail. We then obtain the long time tail of the VCF by inverse Laplace transforming Eq. (20), which leads to

$$\lim_{t\to\infty} C(t) = \frac{2\rho G(a_1)}{9(2\pi)^3}\, 4\pi f_1(0)\, f_2(0) \cdot \frac{\sqrt{\pi}}{4}\left(\left[\frac{\eta}{\rho m} + D\right] t\right)^{-3/2} \tag{22}$$

where $C(t)$ is the inverse Laplace transform of $C(z)$, that is, the time-dependent VCF. We also have the results

$$\begin{aligned}\frac{f_1(0)}{G(a_1)} &= f_2(0)\\ &= \frac{1}{\rho G(a_1)} \cdot \frac{3k_B T}{m}\end{aligned} \tag{23}$$

where we have used Eq. (9a) and the symmetry of the operator on the left-hand side of that equation. We further used the result, derived in the Appendix B

$$v_3 * (\hat{M}(1'3;12) - \hat{K}(1'3;12)) = 0 \tag{24}$$

the part of $\hat{M}$ confined to the boundary layer, $\hat{M} - \hat{K}$, enters $\hat{S}$. More details of the procedures used to get Eq. (23) are given in I. We therefore have the final result in three dimensions that

$$\lim_{t\to\infty} C(t) = (k_B T/m)[\pi(\eta/\rho m + D)t]^{-3/2}(1/4\rho) \tag{25}$$

—a result in full agreement with the previous mode-coupling results[17,18] and that of the analysis of Van Beijeren and Ernst.[20] As we said in the Introduction, all that we have attempted to do here is to give a derivation of this well-known result that is both straightforward and also fairly careful.

Why does the use of a kinetic equation far more complicated than the Ring[9,10] equation result in nothing but replacement of the Boltzmann viscosity and diffusion constant by the true viscosity and diffusion constant in the coefficient of the tail? Within our formalism, this arises from the simplicity of the products, $G(a_1)f_{1,2}(0)$. Now, the f's contain complicated combinations of operators and $\Phi^{(0)}$. If, however, in, e.g., f_1, $\hat{S}^0$ can be replaced by $G(a_1)T$, f_1 is trivially obtained from Eq. (9a) upon use of the adjoint properties of the T's. In other words, given the cooperative behavior of $\hat{S}^0$, the operators acting on $\Phi^{(0)}$ in f are just the ones appearing in the basic equation obeyed by $\Phi^{(0)}$; this is why our results are so simple. We established the good properties of $\hat{S}^0$ without the memory function in I, and introduction of M does not change f (even if it changes $\hat{S}^0$) because of Eq. (24).

It is possible to apply the method just discussed to two dimensions, but the analysis is more complicated and we prefer not to discuss two dimensions here.

The second problem to be considered is that of the Brownian particle limit. In this limit $a_1/\xi \gg 1$, $m_1/m \gg 1$, where m_1 is the mass of the tagged particle and ξ is of the order of several fluid correlation lengths and also $\eta/\rho m D \gg 1$. To solve this problem, it is most convenient to rewrite Eq. (3b) as an equation valid for $|\mathbf{r}_{12}| > a_1$, supplemented by boundary conditions at $|\mathbf{r}_{12}| = a_1$. Then, as in I, we can rewrite the equations to be solved in the form

$$zC(z)+\frac{m\rho}{m_1}G(a_1)\int d1\,d2\,\varnothing_0(1)\,\varnothing_0(2)(\nabla_1 W(12)\cdot\mathbf{v}_2)(\mathbf{v}_2\cdot\boldsymbol{\theta}(12))+\rho(k_BT/m_1)$$
$$\times\int d1\,d2\,\varnothing_0(1)\,\varnothing_0(2)[\nabla_1(G(12)-G(a_1)\,W(12))\cdot\boldsymbol{\theta}(12)]=3k_BT/m_1 \qquad \text{(26a)}$$

$$zG(12)\,\boldsymbol{\theta}(12)+z\rho\int d3\,\varnothing_0(3)[G(123)-G(12)\,G(13)]\,\boldsymbol{\theta}(13)$$
$$-G(12)\mathbf{v}_2\cdot\nabla_2\boldsymbol{\theta}(12)-\rho\int d3\,\varnothing_0(3)\,G(123)\,T_+(23)(1+P_{23})\,\boldsymbol{\theta}(12)$$
$$-\rho\int d3\,\varnothing_0(3)[G(12)\,G(13)\,\nabla_3 W(13)-G(123)\,\nabla_3 W]123)]\cdot\mathbf{v}_3\boldsymbol{\theta}(13)$$
$$-1/\rho\,\boldsymbol{\theta}(1'3)^*M_B(1'3;\,12)=0 \qquad |\mathbf{r}_{12}|>a_1 \qquad \text{(26b)}$$

and

$$G(a_1)\,T_+(12)[\boldsymbol{\theta}(12)+\Phi(1)]+\rho\int d3\,\varnothing_0(3)[G(123)-G(12)\,G(13)]$$
$$\times T_+(12)\,\boldsymbol{\theta}(13)=0 \qquad \text{(26c)}$$

where $M_B(1'3;\,12)$ is the Brownian particle limit of $M(1'3;\,12)$. As in I, we introduce the microscopic length, ξ, of the order of several fluid correlation lengths, such that $(a_1/\xi) \gg 1$, and such that for $|\mathbf{r}_{12}| \geqslant a_1 + \xi$, the effect of the disruption upon the fluid's structure and dynamics due to the presence of the

Brownian particle is negligible. For $|\mathbf{r}_{12}| \geqslant a_1 + \xi$, $\boldsymbol{\theta}(12)$ is given by its hydrodynamic form, $\boldsymbol{\theta}_H$ (12), which may be obtained from the Chapman–Enskog procedure. For $|\mathbf{r}_{12}| < a_1 + \xi$, however, the Chapman–Enskog expansion fails owing to the rapid variation of the fluid properties in the vicinity of the Brownian particle, and so, in this region $\boldsymbol{\theta}(12) \neq \boldsymbol{\theta}_H(12)$. Unfortunately, Eqs. (26a) and (26c) require knowledge of $\boldsymbol{\theta}(2)$ in just this region where the form of the function is unknown. In order to circumvent this problem we shall use the same stategy described in I, where we reexpressed Eq. (26a) in terms of the far field solution $\boldsymbol{\theta}_H(12)$ and we used Eqs. (26b) and (26c) to obtain boundary conditions upon $\boldsymbol{\theta}_H(12)$ on a sphere of radius $a_1 + \xi$.

Firstly we must investigate the form of $\boldsymbol{\theta}_H(12)$. The equation that is satisfies is

$$z\boldsymbol{\theta}_4(12) + z\rho \int d3\, \varnothing_0(3)\, h(23)\, \boldsymbol{\theta}_H(13) - \mathbf{v}_2 \cdot \boldsymbol{\nabla}_2 \boldsymbol{\theta}_H(12)$$

$$- \rho g(a) \int d3\, \varnothing_0(3)\, T_+(23)(1 + P_{23})\, \boldsymbol{\theta}_H(12) + \rho g(a) \int d3\, \varnothing_0(3)\, \boldsymbol{\nabla}_3 W(23)$$

$$\cdot\, \mathbf{v}_3 \theta(13) - 1/\rho\, \boldsymbol{\theta}_H(1'3)^* M_{B,\infty}(1'3;\, 12) = 0, \qquad |\mathbf{r}_{12}| \geqslant a_1 + \xi \qquad (27)$$

where $M_{B,\infty}$ is the large $|\mathbf{r}_{12}|$ limit of $M_B(1'3;\, 12)$. As discussed beneath Eq. (15), for large $|\mathbf{r}_{12}|$ the projection operator Q projects a function of fluid particle variables orthogonal to the variable $\{\sum_{i>1} \delta(\mathbf{r}_2 - \mathbf{r}_i)\, \delta(\mathbf{v}_2 - \mathbf{v}_i) - \rho\varnothing_0(2)\}$ for all $\mathbf{r}_2$ and $\mathbf{v}_2$, and hence gives rise to true transport coefficients for the fluid. Furthermore, because we require that $z \approx 0[(a_1(\beta m)^{1/2})^{-1}]$ in the Brownian limit, we may set $z = 0$ in the memory function $M_{B,\infty}(1'3;\, 12)$, because the fluid fluctuations decay on a molecular as opposed to a Brownian particle time scale. Henceforth, we shall ignore the z dependence of $M_{B,\infty}(1'3;\, 12)$.

It is now convenient to expand the operators occurring in Eq. (27) in powers of the gradient operator. We thus write Eq. (24) in the form

$$z\boldsymbol{\theta}_H(12) + \rho z \int d3\, \varnothing_0(3)\, h(23)\, \boldsymbol{\theta}_H(13)$$

$$- \{[e_0(\mathbf{v}_2) + M_0(\mathbf{v}_2)] + [\mathbf{v}_2 + \mathbf{e}_1(\mathbf{v}_2) + \mathbf{M}_1(\mathbf{v}_2)] \cdot \boldsymbol{\nabla}_2$$

$$+ [\mathsf{e}_2(\mathbf{v}_2) + \mathsf{M}_2(\mathbf{v}_2)] : \boldsymbol{\nabla}_2 \boldsymbol{\nabla}_2 + O(\nabla_2^3)\}\, \boldsymbol{\theta}_H(12) = 0 \qquad (28)$$

where the operators are given by

$$e_0(\mathbf{v}_2)\, \chi(\mathbf{r}_{12}, \mathbf{v}_2) = \rho g(a) \int d3\, \varnothing_0(3)\, T_+(23)(x(\mathbf{r}_{12}, \mathbf{v}_2) + \chi(\mathbf{r}_{12}, \mathbf{v}_3)) \qquad (29a)$$

$$\mathbf{e}_1(\mathbf{v}_2)\,\chi(\mathbf{r}_{12},\mathbf{v}_2)=\rho g(a)\int d3\ \varnothing_0(3)\,\mathbf{r}_{23}[T_+(23)-(\nabla_3 W(23)\cdot\mathbf{v}_3)]\,\chi(\mathbf{r}_{12},\mathbf{v}_3) \tag{29b}$$

$$\mathsf{e}_2(\mathbf{v}_2)\,\chi(\mathbf{r}_{12},\mathbf{v}_2)=\frac{\rho g(a)}{2}\int d3\ \varnothing_0(3)\,\mathbf{r}_{23}\mathbf{r}_{23}\,T_+(23)\,\chi(\mathbf{r}_{12},\mathbf{v}_3) \tag{29c}$$

$$M_0(\mathbf{v}_2)\,\chi(\mathbf{r}_{12},\mathbf{v}_2)=\frac{1}{\rho}\int d1'\ d3M_{B,\infty}(1'3;\,12)\,\chi(\mathbf{r}_{12},\mathbf{v}_3) \tag{29d}$$

$$\mathbf{M}_1(\mathbf{v}_2)\,\chi(\mathbf{r}_{12},\mathbf{v}_2)=\frac{1}{\rho}\int d1'\ d3\ \mathbf{r}_{23}M_{B,\infty}(1'3;\,12)\,\chi(\mathbf{r}_{12},\mathbf{v}_3) \tag{29e}$$

and

$$\mathsf{M}_2(\mathbf{v}_2)\,\chi(\mathbf{r}_{12},\mathbf{v}_2)=1/2\rho\int d1'\ d3\ \mathbf{r}_{23}\mathbf{r}_{23}\,M_{B,\infty}(1'3;\,12)\,\chi(\mathbf{r}_{12},\mathbf{v}_3) \tag{29f}$$

for an arbitrary function $\chi(\mathbf{r}_{12},\mathbf{v}_2)$. We may now find the form of $\boldsymbol{\theta}_H(12)$ by projecting it onto the hydrodynamic eigenfunctions of the gradient operator, but as pointed out by Van Beijeren and Dorfman[7] it is much simpler to project instead upon the normal forms which are linear combinations of the eigenfunctions. Thus we seek a solution for $\boldsymbol{\theta}_H(12)$ of the form

$$\begin{aligned}\boldsymbol{\theta}_H^{\alpha}(12)&=\mathbf{f}_n^{\alpha}(\mathbf{r}_{12})+(\beta m)^{1/2}\{\mathbf{v}_2^{\beta}+\mathsf{B}_{\beta\gamma}(\mathbf{v}_2)\nabla_1^{\gamma}\}\,\mathsf{f}_v^{\beta\alpha}(\mathbf{r}_{12})\\&\quad+\left(\frac{2}{3}\right)^{1/2}\left\{\left(\frac{\beta m v_2^2}{2}-\frac{3}{2}\right)+\mathbf{A}_{\beta}(\mathbf{v}_2)\cdot\nabla_1^{\beta}\right\}\mathbf{f}_T^{\alpha}(\mathbf{r}_{12})\end{aligned} \tag{30}$$

where $\mathbf{f}_n$, f_v, and $\mathbf{f}_T$ are functions yet to be determined, the Greek subscripts and superscripts indicate Cartesian components, and the functions $\mathbf{A}(\mathbf{v}_2)$ and $\mathsf{B}(\mathbf{v}_2)$ are solutions of the equations

$$\begin{aligned}[e_0(\mathbf{v}_2)+M_0(\mathbf{v}_2)]\,\mathbf{A}(\mathbf{v}_2)&=(1+3b^E/5)(\beta m v_2^2/2-5/2)\mathbf{v}_2\\&\quad+\mathbf{M}_1(\mathbf{v}_2)(\beta m v_2^2/2-3/2)\end{aligned} \tag{31a}$$

and

$$\begin{aligned}[e_0(\mathbf{v}_2)+M_0(\mathbf{v}_2)]\,\mathsf{B}_{\alpha\beta}(\mathbf{v}_2)&=(1+2b^E/5)(\mathbf{v}_2^{\alpha}\mathbf{v}_2^{\beta}-(1/3)v_2^2\,\delta_{\alpha\beta})\\&\quad+\mathbf{M}_1^{\alpha}(\mathbf{v}_2)\mathbf{v}_2^{\beta}\end{aligned} \tag{31b}$$

where $b^E=2\pi\rho a^3 g(a)/3$. We now substitute Eq. (30) into Eq. (28), multiply through in turn by $\varnothing_0(1)\,\varnothing_0(2)$, $\varnothing_0(1)\,\varnothing_0(2)\mathbf{v}_2$ and $\varnothing_0(1)\,\varnothing_0(2)$

$(\beta m v_2^2/2 - 3/2)$, respectively, and then integrate over $\mathbf{v}_1$ and $\mathbf{v}_2$. This leads to the coupled equations

$$zs(0)\,\mathbf{f}_n^\alpha(\mathbf{r}_{12}) + (\beta m)^{-1/2}\nabla_1^\beta \cdot \mathrm{f}_v^{\beta\alpha}(\mathbf{r}_{12}) = 0 \tag{32a}$$

$$z\mathrm{f}_v^{\alpha\beta}(\mathbf{r}_{12}) + (\beta m)^{-1/2}\nabla_1^\alpha \mathbf{f}_n^\beta(\mathbf{r}_{12}) + (2/3)^{1/2}(\beta m)^{-1/2}(1+b^E)\nabla^\alpha \mathbf{f}_T^\beta(\mathbf{r}_{12}) - \eta/\rho m\,\nabla^2 \mathrm{f}_v^{\alpha\beta}(\mathbf{r}_{12}) - 1/\rho m(\eta/3+\eta_B)\,\nabla_1^\alpha \nabla_1^\gamma \mathrm{f}_v^{\gamma\beta}(\mathbf{r}_{12}) = 0 \tag{32b}$$

and

$$z\mathbf{f}_T^\alpha(\mathbf{r}_{12}) + (2/3)^{1/2}(\beta m)^{-1/2}(1+b^E)\nabla_1^\beta \cdot \mathrm{f}_v^{\beta\alpha}(\mathbf{r}_{12}) - \frac{2\lambda}{3\rho k_B}\nabla_1^2 \mathbf{f}_T^\alpha(\mathbf{r}_{12}) = 0 \tag{32c}$$

where η, η_B, and λ are the full coefficients of the shear viscosity, bulk viscosity, and thermal conductivity, respectively. In order to get these equations we have used the following results obtained from the Chapman–Enskog procedure:

$$\int d\mathbf{v}_2\, \varnothing_0(2)\mathbf{v}_2 \cdot \mathbf{A}(\mathbf{v}_2) = 0 \tag{33a}$$

$$\int d\mathbf{v}_2\, \varnothing_0(2)\, \mathrm{B}(\mathbf{v}_2) = 0 \tag{33b}$$

$$(\beta m)\int d\mathbf{v}_2\, \varnothing_0(2)\, \mathbf{v}_2^\alpha[(\mathbf{v}_2^\gamma + \mathbf{e}_1^\gamma(\mathbf{v}_2) + \mathbf{M}_1^\gamma(\mathbf{v}_2))\,\mathrm{B}^{\delta\varepsilon}(\mathbf{v}_2) - (\mathrm{e}_2^{\gamma\varepsilon}(\mathbf{v}_2) + \mathrm{M}_2^{\gamma\varepsilon}(\mathbf{v}_2))\mathbf{v}_2^\delta]\,\nabla_1^\gamma\nabla_1^\varepsilon \mathrm{f}_v^{\delta\beta}(\mathbf{r}_{12}) = -(\rho m)^{-1}[\eta\nabla_1^2 \mathrm{f}_v^{\alpha\beta}(\mathbf{r}_{12}) + (\eta/3+\eta_B)\,\nabla_1^\alpha\nabla_1^\gamma \mathrm{f}_v^{\gamma\beta}(\mathbf{r}_{12})] \tag{33c}$$

and

$$\int d\mathbf{v}_2\, \varnothing_0(2)\left(\frac{\beta m v_2^2}{2} - \frac{3}{2}\right)\left\{[\mathbf{v}_2^\gamma + \mathbf{e}_1^\gamma(\mathbf{v}_2) + \mathbf{M}_1^\gamma(\mathbf{v}_2)]\,\mathbf{A}^\varepsilon(\mathbf{v}_2) - [\mathrm{e}_2^{\gamma\varepsilon}(\mathbf{v}_2) + \mathrm{M}_2^{\gamma\varepsilon}(\mathbf{v}_2)]\left(\frac{\beta m v_2^2}{2} - \frac{3}{2}\right)\right\} = \frac{-\lambda}{\rho k_B}\delta_{\varepsilon\gamma} \tag{33d}$$

Lastly, the quantity denoted by $s(0)$ in Eq. (32a) is the zero–k limit of the fluid structure factor, $s(k)$. It is given by

$$s(0) = 1 + \rho\int d\mathbf{r}_3 h(23)$$

Equations (32a–c) are exactly the same equations obtained in I, except that here we have the full fluid transport coefficients instead of the Enskog values. As discussed in I, by means of a change of variables, these equations can be made to be identical to the usual linearized hydrodynamic equations.

We now must return to the problem of reexpressing Eq. (26a) in terms of $\boldsymbol{\theta}_H(12)$, and also to the problem of obtaining boundary conditions upon the functions $\mathbf{f}_n, \mathbf{f}_v$, and $\mathbf{f}_T$. To do this we consider the conservation equations. As in I, we multiply Eq. (26b) though by $\varnothing_0(1)\,\varnothing_0(2)$, $\varnothing_0(1)\,\varnothing_0(2)\mathbf{v}_2$ and $\varnothing_0(1)\,\varnothing_0(2)(\beta m v_2^2/2 - 3/2)$, respectively, and integrate over $\mathbf{v}_1$ and $\mathbf{v}_2$. We then get the following equations, for $|\mathbf{r}_{12}| > a_1$:

$$zG(12)\langle\langle\boldsymbol{\theta}_\alpha(12)\rangle\rangle + z\rho\int d\mathbf{r}_3(G(123) - G(12)\,G(13))\langle\langle\boldsymbol{\theta}_\alpha(13)\rangle\rangle$$
$$- G(12)\,\nabla_2^\beta \cdot \langle\langle \mathbf{v}_2^\beta \boldsymbol{\theta}_\alpha(12)\rangle\rangle = 0 \tag{34a}$$

$$zG(12)\langle\langle\mathbf{v}_2^\beta\boldsymbol{\theta}_\alpha(12)\rangle\rangle - G(12)\,\nabla_2^\gamma \cdot \langle\langle\mathbf{v}_2^\gamma\mathbf{v}_2^\beta\boldsymbol{\theta}_\alpha(12)\rangle\rangle$$
$$-\rho\int d\mathbf{r}_3\, G(123)\langle\langle\mathbf{v}_2^\beta T_+(23)(1+P_{23})\,\boldsymbol{\theta}_\alpha(12)\rangle\rangle$$
$$- 1/\rho\langle\langle\mathbf{v}_2^\beta[\boldsymbol{\theta}_\alpha(1'3)^*M_B(1'3;\,12)]\rangle\rangle = 0 \tag{34b}$$

and

$$zG(12)\left\langle\left\langle\left(\frac{\beta m v_2^2}{2} - \frac{3}{2}\right)\boldsymbol{\theta}_\alpha(12)\right\rangle\right\rangle - G(12)\,\nabla_2^\beta$$
$$\cdot\left\langle\left\langle\left(\frac{\beta m v_2^2}{2} - \frac{3}{2}\right)\boldsymbol{\theta}_\alpha(12)\right\rangle\right\rangle$$
$$-\rho\int d\mathbf{r}_3 G(123)\left\langle\left\langle\left(\frac{\beta m v_2^2}{2} - \frac{3}{2}\right)T_+(23)(1+P_{23})\,\boldsymbol{\theta}_\alpha(12)\right\rangle\right\rangle$$
$$- 1/\rho\left\langle\left\langle\left(\frac{\beta m v_2^2}{2} - \frac{3}{2}\right)[\boldsymbol{\theta}_\alpha(1'3)^*M_B(1'3;\,12)]\right\rangle\right\rangle = 0 \tag{34c}$$

In these equations, $\langle\langle\cdots\rangle\rangle$ means multiply what is inside the brackets by the Maxwellian velocity distribution functions for all the particles involved, and then integrate over all the velocities. In order to get Eq. (4a), we used the relation

$$\langle\langle\boldsymbol{\theta}_\alpha(1'3)^*M_B(1'3;\,12)\rangle\rangle = 0$$

which arises from the alternative expression for $M(1'3;\,12)$, given by

$$M(\bar{1}'\bar{3};\,\bar{1}\bar{2}) = -\langle\{[z - Qi\mathscr{L}_+]^{-1}Qi\mathscr{L}_+B(\bar{1}'\bar{3})\}\,Qi\mathscr{L}\_B(\bar{1}\bar{2})\rangle \tag{35}$$

and from the fact that $\int d\bar{\mathbf{v}}_2 Qi\mathscr{L}_- B(\bar{1}\bar{2}) = 0$, from the definition of Q. We now integrate Eq. (34b) over the volume V between concentric spheres of radius a_1 and $(a_1 + \xi)$. The only term that is different from the equation studied in I is the memory term. To deal with this, we first note the result that in the Brownian limit,

$$Qi\mathscr{L}_- B(\bar{1}\bar{2}) = Q \left\{ \sum_{i>j>1} T_-(ij)\, B(\bar{1}\bar{2}) \right\} \tag{36a}$$

The reason for this is that Q projects out all purely two-body terms, so that there are no terms involving free streaming terms or binary collision operators involving the tagged particle. For clarity we have here returned to the overbar convention for field variables. If we now multiply Eq. (36a) though by $\bar{\mathbf{v}}_2$ and integrate over $\bar{\mathbf{v}}_2$, we obtain the result that

$$\begin{aligned} \int d\bar{\mathbf{v}}_2 \bar{\mathbf{v}}_2 Qi\mathscr{L}_- B(\bar{1}\bar{2}) &= Q \sum_{i>j>1} T_-(ij) \sum_{k>1} \delta(\bar{\mathbf{r}}_{12} - \bar{\mathbf{r}}_{1k}) \mathbf{v}_k \\ &= Q \sum_{i>j>1} \tfrac{1}{2} T_-(ij) \mathbf{v}_i [\delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1i}) - \delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1j})] \end{aligned} \tag{36b}$$

where we have used $T_-(ij) = T_-(ji)$. If we now integrate this over the volume V, we see that the result is only nonzero if one of the particles out of i and j is inside the volume and the other one outside. As, however, the $T_-(ij)$ operator requires that these particles be in contact, it is clear that the whole of the integral comes from values of $|\bar{\mathbf{r}}_{12}|$ very close to $a_1 + \xi$. These results therefore show that the whole of the integral of the memory term in Eq. (34b) comes from $|\bar{\mathbf{r}}_{12}| \simeq a_1 + \xi$. But, from the definition of ξ, $\boldsymbol{\theta}(12) = \boldsymbol{\theta}_H(12)$ out there, and the memory function simply describes the pure fluid dynamics—that is, M_B can be replaced by $M_{B,\infty}$. It is also important for this argument that the pure fluid memory function also gives no contributions to the integral over V unless $|\mathbf{r}_{12}| \sim a + \xi$, so no totally spurious contributions arise from the interior region when $M \neq M_\infty$. By using these facts, the results already found in I, and Eqs. (30), (33c), and (33d), we find that we may rewrite Eq. (23a) in the form

$$\begin{aligned} zC(z) + \frac{k_B T p}{m_1} \int d\mathbf{r}\, \delta(|\mathbf{r}| - a_1 - \xi) \hat{r}^\alpha \cdot \Bigg\{ \mathbf{f}_n^\alpha(\mathbf{r}) + \left(\frac{2}{3}\right)^{1/2} (1 + b^E)\, \mathbf{f}_T^\alpha(\mathbf{r}) \\ - (\beta m)^{1/2} \left[\frac{2\eta}{\rho m} \hat{r}_\gamma \hat{r}_\varepsilon \nabla_\varepsilon \mathbf{f}_v^\alpha(\mathbf{r}) + \frac{(\eta_B - 2\eta/3)}{\rho m} \nabla_\gamma \mathbf{f}_v^{\gamma\alpha}(\mathbf{r}) \right] \Bigg\} = 3k_B T/m_1 \end{aligned} \tag{37}$$

where, as discussed in I, this form may directly be related to the surface integral of the hydrodynamic stress tensor. In this equation, $\hat{r}$ is a unit vector.

Finally, we must attempt to transfer the boundary condition upon (12) to the surface of a sphere of radius $(a_1 + \xi)$. The same methods used in I may be used to do this, except that the arguments outlined after Eq. (36a) are required to deal with the memory terms. Thus, by taking scalar productions of Eq. (34a) and (34c) with $\hat{r}_{12}$, and Eq. (34b) with $(1 - \hat{r}_{12}\hat{r}_{12})$, integrating over the volume V, and then making use of Eq. (26c), we obtain the slip hydrodynamic boundary conditions, given by

$$\hat{r} \cdot \mathrm{f}_v(\mathbf{r}) \cdot \hat{r} = (\beta m)^{1/2} C(z)/3 \tag{38a}$$

$$[\hat{r}_\gamma(\hat{r}_\alpha \hat{r}_\varepsilon - \delta_{\alpha\varepsilon}) + \hat{r}_\varepsilon(\hat{r}_\alpha \hat{r}_\gamma - \delta_{\alpha\gamma})]\, \nabla_\varepsilon \mathrm{f}_v^{\alpha\beta}(\mathbf{r}) = 0 \tag{38b}$$

and

$$\hat{r} \cdot \nabla \mathrm{f}_T(\mathbf{r}) = 0 \tag{38c}$$

all for $|\mathbf{r}| = a_1 + \xi$. The assumptions made here were that z was $O(1/a_1(\beta m)^{1/2})$, and that $\theta(12)$ did not behave too strangely for $|\mathbf{r}_{12}| < a_1 + \xi$—that is, that the average values of certain moments of $\theta(12)$ inside the boundary layer were not of $O(a_1/\xi)$ times their values just outside. Thus for small z, and also with the above assumption concerning the mgnitude of $\theta(12)$ inside the boundary layer, we have reduced the problem of finding $C(z)$ to that of solving the hydrodynamic equations Eqs. (29a)–(29c) subject to the slip boundary conditions given by Eqs. (38a)–(28c). This is equivalent to saying that the VCF of the Brownian particle shows Stokes–Einstein behavior. For completeness, for $z = 0$ it is straightforward to solve these equations, which leads to the Stokes–Einstein result,

$$D = k_B T/4\pi\eta a_1 \tag{39}$$

where, because $\xi/a_1 \ll 1$, we have replaced $(a_1 + \xi)$ by a_1.

In conclusion, we have indicated in this section how one may obtain the long time tail of the VCF and the VCF in the Brownian particle limit for a particle moving in a fluid of hard spheres of arbitrary density. The methods used have essentially been methods based upon kinetic theory, and they have required that all the interactions be hard-sphere interactions. Although the entire point of this paper is to carry out the indicated derivations with a maximum of simplicity and a minimum of assumptions, our results still cannot be called "proofs." The tail calculation requires that M contribute no $z^{1/2}$ term, which is very nearly nearly certain, as discussed in the Appendix, but can be questioned. If we just define D in terms of $C(z = 0)$, then our arguments about the size of z in the Stokes–Einstein calculation of D are unnecessary. We still require that the fluid fields in the boundary layer do not differ too drastically from their hydrodynamic forms—again, highly plausible but not certain. One might even question whether $\theta = \theta_H$ for $|\mathbf{r}_{12}| \gg a_1$ even though this is a standard assumption. So, our derivations could be wrong. The facts needed to disprove them, however, would be surprising indeed.

3. THE LONG TIME TAIL AND STOKES–EINSTEIN RELATION FOR CONTINUOUS POTENTIALS OF INTERACTION

In the previous section, we first wrote down a kinetic equation, and then obtained both the long time tail of the VCF and the Brownian particle behavior by means of a hydrodynamic analysis. In this section, where we are considering a system of particles interacting via a continuous potential, we use a more direct approach and directly couple the tagged particle's motion to the hydrodynamic modes of the surrounding fluid. Thus, whereas the previous section used a kinetic theory approach, the approach in this section will be more closely akin to the mode-coupling methods used by Keyes and Oppenheim[21] and Masters and Madden.[22] The main difference will be that much of the following analysis will be conducted in real space instead of in k space, as was also done by Cukier *et al.*[8] in their analysis of Brownian particle motion is a dilute gas of hard spheres.

By using Mori's generalized Langevin equation,[14] we may express $C(z)$ in the form

$$C(z) = \frac{3k_B T/m_1}{z + \nu(z)} \tag{40a}$$

where $\nu(z)$, the friction coefficient, is given by

$$\nu(z) = (3m_1 k_B T)^{-1} \langle \{ [z - Q_i i\mathscr{L}]^{-1} \mathbf{F}_1 \} \cdot \mathbf{F}_1 \rangle \tag{40b}$$

where $\mathbf{F}_1$ is the force exerted upon the tagged particle, $i\mathscr{L}$ is the Liouville operator, Q_1 is the Mori projection operator that projects a variable orthogonal to $\mathbf{v}_1$, and we are working in three dimensions. In order to obtain the long time behavior of the VCF of the Stokes–Einstein relation, we must couple $\mathbf{F}_1$ to the conserved variables of the fluid. Thus we introduce the following variables, describing the local fluctuations of the fluid's number density, momentum density, and energy density at a given distance away from the tagged particle:

$$a_n(\mathbf{r}) = \sum_{i>1} \delta(\mathbf{r} - \mathbf{r}_{1i}) - \rho G(r) \tag{41a}$$

$$\mathbf{a}_v(\mathbf{r}) = \sum_{i>1} \mathbf{v}_i\, \delta(\mathbf{r} - \mathbf{r}_{1i}) \tag{41b}$$

and

$$a_\varepsilon(\mathbf{r}) = \sum_{i>1} \left[\frac{1}{2} m v_i^2 + \frac{1}{2} \sum_{\substack{j \neq i \\ j>1}} u(ij) + u_1(1i) \right] \delta(\mathbf{r} - \mathbf{r}_{1i}) \quad (41c)$$

In Eq. (41c), $u(ij) = u(\mathbf{r}_{ij})$ and $u_1(1i) = u_1(\mathbf{r}_{1i})$, are the potentials of interaction between particles i and j and the tagged particle, respectively. In the subsequent analysis we take these potentials to be short ranged, central, and continuous, with a harshly repulsive potential wall as the particles get very close. Furthermore we take these potentials to be finite (except possibly at $|\mathbf{r}_{ij}| = 0$), so there is a finite probability of finding the particles at any distance apart. Thus, unlike the hard spheres in Section 2, $|\mathbf{r}|$ may take on all possible values in Eqs. (41a)–(41c). These variables are very simply related to the variables used in previous mode-coupling calculations.[18,21,22] Thus if Eqs. (41a)–(41c) are Fourier transformed, we end up with bilinear products of a Fourier component of the tagged particle number density with a Fourier component of the density of a fluid conserved variable. It is clearly completely equivalent to work with the variables defined above, for all values of $|\mathbf{r}|$, or to work with all the Fourier components of these variables, but we make the former choice here because the physical content of many of the later transformations are then clearer. For the subsequent analysis, it proves convenient to work with a variable called $a_T(\mathbf{r})$ rather than $a_\varepsilon(\mathbf{r})$, where $a_T(\mathbf{r})$ is a fluctuating quantity [as are $a_n(\mathbf{r})$ and $a_v(\mathbf{r})$], and is orthogonal to $a_n(\mathbf{r}')$ for all values of $\mathbf{r}'$. We call the variable $a_T(\mathbf{r})$ because it is closely related to local temperature fluctuations in the fluid. It is given by

$$a_T(\mathbf{r}) = a_\varepsilon(\mathbf{r}) - \langle a_\varepsilon(\mathbf{r}) \rangle - \int d\mathbf{r}'\, d\mathbf{r}'' \langle a_\varepsilon(\mathbf{r})\, a_n(\mathbf{r}') \rangle A_{nn}^{-1}(\mathbf{r}', \mathbf{r}'')\, a_n(\mathbf{r}'') \quad (42)$$

where the spatial integrals are over all space and $A_{nn}^{-1}(\mathbf{r}', \mathbf{r}'')$ is the inverse to $\langle a_n(\mathbf{r})\, a_n(\mathbf{r}') \rangle$ so that

$$\int d\mathbf{r}' \langle a_n(\mathbf{r})\, a_n(\mathbf{r}') \rangle A_{nn}^{-1}(\mathbf{r}', \mathbf{r}'') = \delta(\mathbf{r} - \mathbf{r}'') \quad (43)$$

We note in passing that unlike $a_\varepsilon(\mathbf{r})$, $a_T(\mathbf{r})$ contains no term involving the potential energy of interaction between a fluid particle and the tagged particle. This is because such a term is given by $\int d\mathbf{r}\, u_1(\mathbf{r})\, a_n(\mathbf{r})$, and hence is projected out in Eq. (2).

We now analyze $v(z)$ using the Mori theory,[14] taking $a_n(\mathbf{r})$, $a_v(\mathbf{r})$ and $a_T(\mathbf{r})$ as variables for all values of $\mathbf{r}$. Firstly $\mathbf{F}_1$ is given exactly as an integral over $a_n(\mathbf{r})$, so that

$$\mathbf{F}_1 = -\int d\mathbf{r}\, \nabla u_1(\mathbf{r})\, a_n(\mathbf{r}) \quad (44a)$$

from which the useful relation

$$\langle \mathbf{F}_1 a_n(\mathbf{r})\rangle = \rho k_B T \nabla G(\mathbf{r}) \tag{44b}$$

may be derived. Using Eq. (44a), we have

$$\nu(z) = (3m_1 k_B T)^{-1} \int d\mathbf{r}\, d\mathbf{r}' \langle \mathbf{F}_1 a_n(\mathbf{r})\rangle \cdot RR_{nn}(\mathbf{r}, \mathbf{r}')\langle \mathbf{F}_1 a_n(\mathbf{r}')\rangle \tag{45}$$

where $RR_{nn}(\mathbf{r}, \mathbf{r}')$ is given by

$$\int d\mathbf{r}'\, RR_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, RR_{\beta\gamma}^{-1}(\mathbf{r}', \mathbf{r}') = \delta_{\alpha\gamma}\delta(\mathbf{r} - \mathbf{r}'') \tag{46a}$$

and $RR_{\beta\gamma}^{-1}(\mathbf{r}', \mathbf{r}'')$ is given by

$$RR_{\beta\gamma}^{-1}(\mathbf{r}', \mathbf{r}'') = z\langle a_\beta(\mathbf{r}')\, a_\gamma(\mathbf{r}'')\rangle - \langle Qi\mathscr{L} a_\beta(\mathbf{r}')\, a_\gamma(\mathbf{r}'')\rangle$$
$$+ \langle \{[z - Qi\mathscr{L}]^{-1} Qi\mathscr{L} a_\beta(\mathbf{r}')\}\, Qi\mathscr{L} a_\gamma(\mathbf{r}'')\rangle \tag{46b}$$

In these equations the Greek suffices take on the labels n, v, and T, and summation convention is used. Furthermore a repeated suffix also implies a scalar product when the suffix takes on the label v. The Mori projection operator Q projects a dynamical variable orthogonal to $\mathbf{v}_1$ and also to $a_\alpha(\mathbf{r})$ for all values of α and $\mathbf{r}$.

We shall now consider the long time behavior of the VCF, which we obtain from the small z form of $\nu(z)$. We use the same notation as in Section 2, where a superscript of zero or one indicates the $z = 0$ limit and leading small z correction to the quantity, respectively, to obtain from Eq. (45) the two equations

$$\nu^{(0)} = (3m_1 k_B T)^{-1} \int d\mathbf{r}\, d\mathbf{r}' \langle \mathbf{F}_1 a_n(\mathbf{r})\rangle \cdot RR_{nn}^{(0)}(\mathbf{r}, \mathbf{r}')\langle \mathbf{F}_1 a_n(\mathbf{r}')\rangle \tag{47a}$$

and

$$\nu^{(1)} = (3m_1 k_B T)^{-1} \int d\mathbf{r}\, d\mathbf{r}' \langle \mathbf{F}_1 a_n(\mathbf{r})\rangle \cdot RR_{nn}^{(1)}(\mathbf{r}, \mathbf{r}')\langle \mathbf{F}_1 a_n(\mathbf{r}')\rangle \tag{47b}$$

We now must investigate $RR_{\alpha\beta}^{(1)}(\mathbf{r}, \mathbf{r}')$. We introduce the far-field form of $RR_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$, which is given by

$$R_{\alpha\beta}^{-1}(\mathbf{r}, \mathbf{r}') = \lim_{|\mathbf{r}'| \to \infty} RR_{\alpha\beta}^{-1}(\mathbf{r}, \mathbf{r}') \tag{48}$$

We then write

$$RR_{\alpha\beta}^{-1}(\mathbf{r}, \mathbf{r}') = R_{\alpha\beta}^{-1}(\mathbf{r}, \mathbf{r}') - S_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \tag{49}$$

where $S_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ contains in it all the complexities arising from the behavior of the fluid close to the tagged particle. Because $u_1(\mathbf{r})$ is a short-ranged function, and because we also assume we are not at a critical point, $R_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ describes pure fluid and pure tagged particle dynamics, with no correlation between them as the processes are taking place far apart. For reasons similar to those discussed in the Appendix, we may replace $S_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ by $S^{(0)}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ in Eq. (49) because the z dependence of $S_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ has no effect upon the asymptotic long time tail of the VCF. If we do this, we get the result

$$\begin{aligned} RR^{(1)}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = {} & [\delta_{\alpha\varepsilon}\delta(\mathbf{r} - \mathbf{r}_2) + RR^{(0)}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}_1) * S^{(0)}_{\gamma\varepsilon}(\mathbf{r}_1, \mathbf{r}_2)] * R^{(1)}_{\varepsilon\mu}(\mathbf{r}_2, \mathbf{r}_3) \\ & * [S^{(0)}_{\mu\nu}(\mathbf{r}_3, \mathbf{r}_4) * RR^{(0)}_{\nu\beta}(\mathbf{r}_4, \mathbf{r}') + \delta_{\mu\beta}\delta(\mathbf{r}_3 - \mathbf{r}')] \end{aligned} \quad (50)$$

where the asterisks mean integration over repeated variables. Any extra terms are of higher order in z. We next introduce the Fourier transform of a quantity $A(\mathbf{r}, \mathbf{r}')$ defined by

$$A(\mathbf{k}, \mathbf{k}') = \int d\mathbf{r}\, d\mathbf{r}'\, e^{i\mathbf{k}\cdot\mathbf{r}} A(\mathbf{r}, \mathbf{r}') e^{i\mathbf{k}'\cdot\mathbf{r}'} \quad (51)$$

In this representation $R_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ is diagonal, so we write

$$R_{\alpha\beta}(\mathbf{k}, \mathbf{k}') = (2\pi)^3\, \delta(\mathbf{k} + \mathbf{k}')\, R_{\alpha\beta}(\mathbf{k}) \quad (52)$$

We therefore have the result

$$R^{(1)}_{\alpha\beta}(\mathbf{r}_2, \mathbf{r}_3) = \frac{1}{(2\pi)^3} \int d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{r}_2} R^{(1)}_{\alpha\beta}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}_3} \quad (53)$$

Substitution of Eq. (50) into Eq. (47b) followed by use of Eq. (53) yields an expression for $\nu^{(1)}$ involving an integral of $R^{(1)}_{\alpha\beta}(\mathbf{k})$ over $\mathbf{k}$. As before, the long time tail is determined by the small $|\mathbf{k}|$ portion of this integral, say, for $|\mathbf{k}| < k_c$, where k_c is a cutoff wave vector of the order of an inverse fluid correlation length. We now must evaluate $R^{(1)}_{\alpha\beta}(\mathbf{k})$ for small $|\mathbf{k}|$. As in Section 2 and as discussed in Appendix A, we can ignore the z dependence of the dissipative terms in Eq. (46b), where the dissipative terms are given by the third term on the right-hand side of the that equation. For small $|\mathbf{k}|$, it can then be readily seen that these dissipative terms contain full fluid and tagged particle transport coefficients. The reason for this is that because $R_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ is the large $|\mathbf{r}'|$ limit of $RR_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$, the Q operator in the dissipative term projects a function of fluid variables orthogonal to the conserved variables of the fluid, giving rise to full fluid transport coefficients, and projects a function of the tagged particle variables orthogonal to the tagged particle number density, yielding the full tagged particle diffusion constant. The asymptotic long time tail arises purely from the $R^{(1)}_{vv}(\mathbf{k})$ term, which is given for small $|\mathbf{k}|$ by

$$R^{(1)}_{vv}(\mathbf{k}) = (1 - \hat{k}\hat{k})(\beta m)\left[\frac{1}{z + k^2(\eta/\rho m + D)} - \frac{1}{k^2(\eta/\rho m + D)}\right] \tag{54}$$

where 1 is the unit tensor, the caret denotes a unit vector, and we have not written out the longitudinal modes, proportional to $\hat{k}\hat{k}$, because they do not contribute to the asymptotic long time tail.

These results give rise to an expression for $\nu^{(1)}$ given by

$$\nu^{(1)} = \frac{m}{3(k_B T)^2 m_1 (2\pi)^3}\int_{|\mathbf{k}|\leqslant k_c} d\mathbf{k}\, f_1(\mathbf{k})\, f_2(\mathbf{k})[1 - \hat{k}\hat{k}] \times \left\{\frac{1}{z + k^2(\eta/\rho m + D)} - \frac{1}{k^2(\eta/\rho m + D)}\right\} \tag{55a}$$

where

$$f_1(\mathbf{k}) = \langle \mathbf{F}_1 a_n(\mathbf{r})\rangle * RR^{(0)}_{n\alpha}(\mathbf{r}, \mathbf{r}_1) * S_{\alpha v}(\mathbf{r}_1, \mathbf{r}_2) * e^{-i\mathbf{k}\cdot\mathbf{r}_2} \tag{55b}$$

and

$$f_2(\mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{r}_3} * S^{(0)}_{v\beta}(\mathbf{r}_3, \mathbf{r}_4) * RR_{\beta n}(\mathbf{r}_4, \mathbf{r}') * \langle \mathbf{F}_1 a_n(\mathbf{r}')\rangle \tag{55c}$$

As before, the asymptotic long time tail arises from the $|\mathbf{k}| \to 0$ limit of $f_1(\mathbf{k})$ and $f_2(\mathbf{k})$. These limits are readily evaluated, because we have the results

$$\int d\mathbf{r}_2\, S^{(0)}_{\alpha v}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\delta_{\alpha n}}{m}\langle \mathbf{F}_1 a_n(\mathbf{r}_1)\rangle \tag{56a}$$

and

$$\int d\mathbf{r}_3\, S^{(0)}_{v\beta}(\mathbf{r}_3, \mathbf{r}_4) = \frac{\delta_{\beta n}}{m}\langle \mathbf{F}_1 a_n(\mathbf{r}_4) \tag{56b}$$

which leads to the result that

$$f_1(0) = -\frac{(3 m_1 k_B T)}{m}\nu^{(0)} = -f_2(0) \tag{57}$$

where we have used Eq. (47a).

Finally, in order to obtain the long time tail of the VCF, we return to Eq. (40a), which yields

$$C^{(1)}(z) = -\frac{3k_B T}{m_1} \frac{\nu^{(1)}}{[\nu^{(0)}]^2} \tag{58}$$

Substitution of Eq. (55a) into this result, followed by use of Eq. (57) and then followed by an inverse Laplace transform and the evaluation of the **k** integral leads us back to the same expression for the long time tail as given in Eq. (25), except that the transport coefficients here refer to a system interacting via continuous potentials.

This result came about through a coupling between the local density fluctuations of the fluid, that directly cause the force on the tagged particle, and local fluctuations of the shear modes of the fluid. In a pure, isotropic fluid this coupling cannot occur because of symmetry considerations, but in the region close to the tagged particle this symmetry is no longer present and the coupling is allowed. This point has previously been discussed by Michaels and Oppenheim.[25]

Just as in Section 2, we obtain very simple expressions for the tails because the potentially complicated quantities in $\nu^{(1)}$ are determined by the equation for $\nu^{(0)}$. For hard spheres, a precondition for the simplification was that $\hat{S}^0$ could be replaced by T in evaluating f; the analogous requirement here is that all contributions of S^0 to f involve $\langle \mathbf{F}_1 a_n \rangle$ [Eqs. (56)]. If any part of S^0 other than the $\langle \mathbf{F}_1 a_n \rangle$ terms entered f, we would be left with parts of the tail which could not be evaluated from Eq. (47a). Thus, a general argument for the pervasiveness of $\langle \mathbf{F}_1 a_n \rangle$ in f is desirable; fortunately, this is easily given. S^0 is that part of the hydrodynamic operator (in $\mathbf{r}, \mathbf{r}'$) confined to the boundary layer. The hydrodynamic equations describe both tagged particle-fluid and fluid–fluid interactions. The latter are of the usual form and, even in the boundary layer, contain at least one $\nabla_{r,r'}$; they consequently can contribute to $f(k)$ to $O(k)$ at best, giving tails weaker than $t^{-3/2}$. A nonzero $f(0)$ can only come from the "external force" (tagged-fluid) terms in the equations, and these appear as $\langle \mathbf{F}_1 a_n \rangle$ only.

Note that according to this argument, calculations of the tails in the Lorentz gas, where[26] $f \propto k$, $k \to 0$, and the tails decay as $t^{-5/2}$, should be much harder than in fluids. Such is indeed[27] the case.

We lastly come to the question of Brownian motion and the Stokes–Einstein relation. Firstly it is convenient to introduce the functions $f_\alpha(\mathbf{r})$ defined by

$$f_\alpha(\mathbf{r}) = \langle \mathbf{F}_1 a_n(\mathbf{r}') \rangle * RR_{n\alpha}(\mathbf{r}', \mathbf{r}) \tag{59}$$

Use of this definition and Eq. (44) leads to the result that

$$\nu(z) = \frac{\rho}{3m_1} \int d\mathbf{r}\, \mathbf{f}_n(\mathbf{r}) \cdot \nabla G(r) \tag{60}$$

and use of Eq. (45a) yields the following equations that these functions must obey:

$$f_\alpha(\mathbf{r}') * RR^{-1}_{\alpha\beta}(\mathbf{r}', \mathbf{r}) = \rho k_B T \nabla G(r)\, \delta_{\beta n} \tag{61}$$

In this Brownian particle limit, $RR^{-1}_{\alpha\beta}(\mathbf{r}', \mathbf{r})$ is simplified because we may ignore the motion of the tagged particle. We shall not give a detailed justification of this statement, but in the formalism used here it comes about because in the Brownian limit $\eta/\rho m \gg \mathrm{D}$ and because the projection operator Q_1 in Eq. (45b) ensures that one is always studying the decay of the tagged particle velocity multiplied by a fluctuation in a fluid property, and so the product fluctuation decays in a microscopic as opposed to a Brownian particle time scale.[22]

For large values of $|\mathbf{r}|$, it is straightforward to write out Eq. (61) explicitly by conducting a gradient expansion. This expansion will be valid because for large $|\mathbf{r}|$ the functions $f_\alpha(\mathbf{r})$ vary on a Brownian particle length scale. As in Section 2, however, this expansion will not work for smaller values of $|\mathbf{r}|$, because of the rapidly varying fluid properties close to the Brownian particle. Again our strategy will therefore be to reexpress Eq. (60) in terms of the far fields, and attempt, via Eqs. (61), to obtain boundary conditions on these far fields.

Let us, for definiteness, let a_1 be that distance at which the repulsive wall of $u_1(\mathbf{r})$ passes through zero. This gives us a measure of where the repulsive core starts. We next introduce the microscopic length, ξ, so that for $|\mathbf{r}| \geqslant a_1 + \xi$ the fluid does not feel any disruption due to the presence of the tagged particle. Hence $G(a_1 + \xi) = 1$, for instance. Thus for $|\mathbf{r}| \geqslant a_1 + \xi$, Eq. (61) yields the three coupled equations:

$$zs(0)\, \mathbf{f}^\alpha_n(\mathbf{r}) + \frac{\rho k_B T}{m} \nabla^\beta \mathbf{f}^{\alpha\beta}_v(\mathbf{r}) = 0 \tag{62a}$$

$$z\mathbf{f}^{\alpha\beta}_v(\mathbf{r}) + \nabla^\beta \mathbf{f}^\alpha_n(\mathbf{r}) + \left[\frac{(\gamma - 1) k_B T^2}{s(0) C_v}\right]^{1/2} \nabla^\beta \mathbf{f}^\alpha_T(\mathbf{r})$$
$$- \frac{1}{\rho m}\left[\eta \nabla^2 f^{\alpha\beta}_v(t) + \left(\eta_B + \frac{\eta}{3}\right) \nabla^\beta \nabla^\gamma \mathbf{f}^{\alpha\gamma}_v(\mathbf{r})\right] = 0 \tag{62b}$$

and

$$zmC_v \mathbf{f}^\alpha_T(\mathbf{r}) + \left[\frac{(\gamma - 1) k_B}{s(0) C_v}\right]^{1/2} \nabla^\beta \mathbf{f}^{\alpha\beta}_v(\mathbf{r}) - \frac{m\lambda}{\rho} \nabla^2 \mathbf{f}^\alpha_T(\mathbf{r}) = 0 \tag{62c}$$

where C_v is the specific heat at constant volume, γ is the ratio of the specific heats, the Greek superscripts here denote Cartesian components, and the other symbols are the same as those given under Eq. (32c). In order to get these equations, we needed the value of several, standard correlation functions, which are given, for example, by Hansen and MacDonald.[28] As in I, we may relate Eqs. (62a)–(62c) to the normal linearized hydrodynamic equations by making a change of variable and by noting the results

$$\left.\frac{\partial P}{\partial \rho}\right)_T = \frac{k_B T}{s(0)} \tag{63a}$$

and

$$\left.\frac{\partial P}{\partial T}\right)_\rho^2 = \frac{\rho^2 C_v}{T}(\gamma - 1)\left.\frac{\partial P}{\partial \rho}\right)_T \tag{63b}$$

where P is the pressure.

We now consider the problem of obtaining an expression for $v(z)$ in terms of these far-field variables. To do this we consider Eq. (61), setting $\beta = v$. We then integrate this equation over all the space inside a sphere of radius $(a_1 + \xi)$, which we denote as the volume V. We thus get the result

$$\begin{aligned}\int_V d\mathbf{r}\{\mathbf{f}_n(\mathbf{r}') * RR^{-1}_{nv}(\mathbf{r}', \mathbf{r}) + \mathbf{f}_v(\mathbf{r}') * RR^{-1}_{vv}(\mathbf{r}', \mathbf{r})\\ + \mathbf{f}_T(\mathbf{r}') * RR^{-1}_{Tv}(\mathbf{r}', \mathbf{r})\} = 0\end{aligned} \tag{64}$$

where we have explicitly written out the sum implied in Eq. (61). We now examine each term in turn. In the Brownian particle limit,

$$RR^{-1}_{nv}(\mathbf{r}', \mathbf{r}) = -\frac{\rho k_B T}{m} \nabla_{r'} \delta(\mathbf{r} - \mathbf{r}')\, G(\mathbf{r}') \tag{65}$$

there being no dissipative contribution. The next term, $RR^{-1}_{vv}(\mathbf{r}', \mathbf{r})$ is more complicated, because this time there is a dissipative term. We can make progress, though, by using similar arguments to those used in Section 2, after Eq. (36b). Thus, we have

$$\begin{aligned}Qi\mathscr{L}\mathbf{a}_v(\mathbf{r}) &= Q \sum_{i>1} \left\{\nabla \cdot \mathbf{v}_i \mathbf{v}_i\, \delta(\mathbf{r} - \mathbf{r}_{1i}) + \frac{1}{m} \sum_{\substack{j \neq 1\\ j>1}} \mathbf{f}_{ij}\, \delta(\mathbf{r} - r_1 i)\right\}\\ &= Q \sum_{i>1} \left\{\nabla \cdot \mathbf{v}_i \mathbf{v}_i\, \delta(\mathbf{r} - \mathbf{r}_{1i}) + \frac{1}{2m} \sum_{\substack{j \neq i\\ j>1}} \mathbf{f}_{ij}[\delta(\mathbf{r} - \mathbf{r}_{1i}) - \delta(\mathbf{r} - \mathbf{r}_{1j})]\right\}\end{aligned} \tag{66}$$

where $\mathbf{f}_{ij}$ is the force on particle i due to particle j, and we have used $\mathbf{f}_{ij} = -\mathbf{f}_{ji}$. Because Q projects a variable orthogonal to $a_n(\mathbf{r}')$, Eq. (66)

contains no term involving the force exerted on a fluid particle by the tagged particle. Thus when Eq. (66) is integrated over the volume V, the whole of the integral arises from values of $|\mathbf{r}|$ close to $a_1 + \xi$, because $\mathbf{f}_{ij}$ is taken to be a short-ranged force. Hence the integral over the volume V of the second term in Eq. (64) is also confined to the surface. An equivalent statement is that, in the absence of explicit "external force" terms, the right-hand side of the hydrodynamic equations look like $\nabla \cdot \mathbf{J}$, and integrals over V can be converted to outer surface integrals, provided z is small enough so that the integral over the Euler term proportional to z in Eq. (61) is negligible. However, for $|\mathbf{r}| \simeq a_1 + \xi$, we can evaluate $\mathbf{f}_v(\mathbf{r}') * RR_{vv}^{-1}(\mathbf{r}', \mathbf{r})$ by using the gradient expansion used previously, and we can therefore express this term as a surface integral of the far-field function $f_v(\mathbf{r})$. Lastly, the third term in Eq. (64) involves both Euler and dissipative contributions. An argument similar to that given above shows that the dissipative term makes a negligible contribution in this Brownian particle limit, that is, its contribution to the drag is $O(\xi/a_1)$ times the leading terms. The Euler term is given by

$$\begin{aligned} RR_{Tv}^{-1}(\mathbf{r}', \mathbf{r}) &= -\langle Q_1 i\mathscr{L} a_T(\mathbf{r}')\, \mathbf{a}_v(\mathbf{r})\rangle \\ &= \langle a_T(\mathbf{r}')\, i\mathscr{L} \mathbf{a}_v(\mathbf{r})\rangle \end{aligned} \qquad \text{(Euler)} \tag{67}$$

The quantity $i\mathscr{L}\mathbf{a}_v(\mathbf{r})$ is given by

$$\begin{aligned} i\mathscr{L}\mathbf{a}_v(\mathbf{r}) = \sum_{i>1} \Bigg\{ &\nabla \cdot \mathbf{v}_i \mathbf{v}_i\, \delta(\mathbf{r} - \mathbf{r}_{1i}) + \frac{\mathbf{f}_{i1}}{m} \delta(\mathbf{r} - \mathbf{r}_{1i}) \\ &+ \frac{1}{2} m \sum_{\substack{j \neq i \\ j > 1}} \mathbf{f}_{ij} [\delta(\mathbf{r} - \mathbf{r}_{1j}) - \delta(\mathbf{r} - \mathbf{r}_{1i})] \Bigg\} \end{aligned} \tag{68}$$

The second term is a linear function of the variable $a_n(\mathbf{r}')$, and hence by definition is orthogonal to $a_T(\mathbf{r})$. Thus the Euler term simply arises from the correlation function of $a_T(\mathbf{r})$ with the first and third terms of Eq. (68), and, for the same reasons discussed above, the integral over the volume V comes simply from values of $|\mathbf{r}|$ close to $a_1 + \xi$, where the Euler term may be evaluated by means of a gradient expansion. Combining together these results, we obtain from Eqs. (60) and (64) the result that

$$\begin{aligned} \nu(z) = \frac{\rho}{3m_1} \int d\mathbf{r}\, \delta(|\mathbf{r}| - a_1 - \xi) \Bigg\{ &\hat{r} \cdot \mathbf{f}_n(\mathbf{r}) + \left[\frac{(\gamma - 1) k_B T^2}{s(0) C_v} \right]^{1/2} \hat{r} \cdot \mathbf{f}_T(\mathbf{r}) \\ &- \frac{(\eta_B - 2/3\, \eta)}{\rho m} \hat{r}_\alpha \nabla_\gamma \mathrm{f}_v^{\alpha\gamma}(t) - \frac{2\eta}{\rho m} \hat{r}_\alpha \hat{r}_\beta \hat{r}_\gamma \nabla_\alpha \mathrm{f}_v^{\beta\gamma}(\mathbf{r}) \Bigg\} \end{aligned} \tag{69}$$

a result very closely related to the surface integral of the hydrodynamic stress tensor.

It now remains to obtain boundary conditions upon these far-field functions. Firstly, let us write out Eq. (61) setting $\beta = n$. We obtain

$$\mathbf{f}_n^\alpha(\mathbf{r}') * RR_{nn}^{-1}(\mathbf{r}', \mathbf{r}) + \frac{\rho k_B T}{m} \nabla^\beta [G(\mathbf{r})\, \mathrm{f}_v^{\alpha\beta}(\mathbf{r})] = \rho k_B T \nabla^\alpha G(r) \tag{70}$$

We then take the scalar product of this equation with $\hat{r}$ and integrate over the volume V. By using the fact that $G(r)$ is negligibly small for $|\mathbf{r}| < a_1$, and by requiring that in the Brownian limit $z \sim O(a_1(\beta m)^{1/2})^{-1}$, we obtain from Eq. (70) the boundary condition

$$\hat{r}_\alpha \cdot \mathrm{f}_v^{\alpha\beta}(\mathbf{r}) \cdot \hat{r}_\beta = m, \qquad |\mathbf{r}| = a_1 + \xi \tag{71}$$

where we have neglected terms of order (ξ/a_1) or smaller. To get these conditions we required that $|\mathrm{f}_v(\mathbf{r})|$ does not grow enormously for $a_1 < |\mathbf{r}| < a_1 + \xi$. That is we require that the ratio of $|\mathrm{f}_v(\mathbf{r})|$ to the hydrodynamic, far-field value of $|\mathrm{f}_v(\mathbf{r})|$ is much less than a_1/ξ. Equation (71) is the equivalent of the hydrodynamic normal velocity boundary condition. The other boundary conditions may be obtained in a similar way by setting $\beta = v$ and $\beta = T$ in Eq. (61), and integrating over the volume V. This procedure, combined with similar assumptions to those made above, shows that

$$\{\hat{r}_\varepsilon[\delta_{\delta\gamma} - \hat{r}_\delta \hat{r}_\gamma] + \hat{r}_\gamma[\delta_{\delta\varepsilon} - \hat{r}_\delta \hat{r}_\varepsilon]\} \nabla_\varepsilon f_v^{\alpha\gamma}(\mathbf{r}) = 0, \qquad |\mathbf{r}| = a_1 + \xi \tag{72a}$$

and

$$\hat{r} \cdot \nabla \mathbf{f}_T(\mathbf{r}) = 0, \qquad |\mathbf{r}| = a_1 + \xi \tag{72b}$$

the equivalents of the zero tangential stress and zero temperature gradient hydrodynamic slip boundary conditions.

A combination of Eqs. (62a)–(62c), (69), (71), and (72a), (72b) allows us to solve for the VCF of the Brownian particle interacting with the fluid particles by a continuous short ranged potential. For $z = 0$, these equations are readily solved to yield the slip form of the Stokes–Einstein results, given by Eq. (38).

Finally, we would like to make some brief comments relating to the results given in this section to previous work. Firstly, although the methods used are somewhat akin to mode-coupling methods,[18] we nowhere need to invoke concepts such as "bare" transport coefficients. One of the advantages of working in real as opposed to k space is that it is transparently clear that both the long time behavior of the VCF and the Stokes–Einstein relation arise from hydrodynamic fluid fields far from the tagged particle, and therefore that the full transport coefficients come in naturally to describe the behavior of these far fields. Furthermore the Gaussian approximation, commonly made in mode-coupling theories, may readily be shown in the example of the Stokes–Einstein relation to be equivalent to solving Eqs. (62a)–(62c) for all values of $|\mathbf{r}|$, and then substituting the solution into Eq. (60). This approximation clearly does not take into account the rapid variation of the fluid properties close to the tagged particle, which are essential to obtain the correct boundary conditions. We would also like to comment that the method used here of analyzing the problem in terms of the far fields and boundary conditions at the edge of the boundary layer, is similar in many ways to the approach used by Ronis *et al.*[29] in their work on hydrodynamic slip boundary conditions.

4. DISCUSSION

In the preceding sections we have indicated how one way investigate the long time tail of the VCF and the Stokes–Einstein limit both by kinetic theory techniques and by methods based upon generalized hydrodynamics. Although the results obtained were not new, we do hope that we have presented a direct and physically intuitive approach, while at the same time being fairly careful. We also hope that this work will also be of some help in an attempt to formulate a good, approximate, high-density theory of tagged particle motion.

Before finishing, we would like to mention that the methods described here can also be applied to correlation functions of collective variables. Thus within the kinetic theory approach, one may for instance start with the variables $\sum_i \delta(\mathbf{v}-\mathbf{v}_i)$ and $\sum_{i\neq j} \delta(\mathbf{v}-\mathbf{v}_i)\,\delta(\mathbf{v}'-\mathbf{v}_j)[[\delta(\mathbf{r}_{12}-\mathbf{r}_{ij})-\rho g(12)]$, and, using the same methods described in I and Section 2, investigate for example the long time tail of the stress autocorrelation function. Similarly the methods of Section 3 may be used to investigate the same thing for a system interacting via continuous potentials. In both cases the result for the long time tail is found to agree with earlier mode-coupling results[17] and the calculation of van Beijeren and Ernst.[20] The reason for the discrepancy between these results and the results of computer simulation[30] remains unclear, though the self-consistent mode-coupling approach of Leutheusser[31] does predict on enhancement of the long time tail coefficient over these previous theoretical results.

APPENDIX A

In this appendix, we wish to argue that the z dependence of the memory function $M(1'3; 12)$ in Eq. (3) is unimportant as regards the long time behavior of the VCF. We similarly would like to show that the z dependence of the dissipative terms in Eq. (45b) is again irrelevant. Before proceeding with the ensuing analysis, we note that this problem arises in "normal" mode-coupling approximation methods. In these methods, the small-z form of $C(z)$ comes from an integral of the form

$$C^{(1)}(z) \propto \int_{|k|<k_c} d\mathbf{k} \left\{ \frac{1}{z + k^2[\eta(k,z)/\rho m + D(k,z)} - \frac{1}{k^2[\eta(k,0)/\rho m + D(k,0)]} \right\} \tag{A1}$$

where $\eta(k,z)$ and $D(k,z)$ are the k- and z-dependent values of the shear viscosity and the diffusion constant. We therefore may rewrite Eq. (1) in the form

$$C^{(1)}(z) \propto \int_{|\mathbf{k}|<k_c} \frac{-[(\eta(k,z)-\eta(k,0))/\rho m + D(k,z) - D(k,0)]}{k^2[\eta(k,0)/\rho m + D(k,0)]^2} d\mathbf{k} + \int_{|\mathbf{k}|<k_c} \left\{ \frac{1}{z + k^2[\eta(k,0)/\rho m + D(k,0)]} - \frac{1}{k^2[\eta(k,0)/\rho m + D(k,0)} \right\} d\mathbf{k} \tag{A2}$$

The second term gives rise to the familiar result for the long time tail, written out in Eq. (25). The first term gives no contribution to the longtime tail. This is because, as shown by Keyes and Oppenheim,[21] the inverse Laplace transforms of $\eta(k,z)$ and $D(k,z)$ are both of the form $t^{-3/2}e^{-\Gamma k^2 t}$ at long time, where Γ is a constant. Carrying out the k integral in the first term shows that this term dies away as t^{-2} at long times, and hence is negligible compared to the second term. Thus, the z dependence of the transport coefficients, equivalent to the z dependence of the memory function, seems to be unimportant.

In order to argue within our formalism, we introduce the three-particle function $C(\bar{1}\bar{2}\bar{3})$, given by

$$C(\bar{1}\bar{2}\bar{3}) = Q \left\{ \sum_{i>1} \sum_{\substack{j<1 \\ j\neq i}} \delta(\bar{\mathbf{v}}_1 - \mathbf{v}_1)\, \delta(\bar{\mathbf{v}}_2 - \mathbf{v}_1)\, \delta(\bar{\mathbf{v}}_3 - \mathbf{v}_j)\, \delta(\bar{\mathbf{r}}_{12} - \mathbf{r}_{1i})\, \delta(\bar{\mathbf{r}}_{13} - \mathbf{r}_{1j}) \right\} \tag{A3}$$

where Q is defined after Eq. (4). We them may write $M(1'3; 12)$ schematically in the form

$$M = \langle (i\mathscr{L}_+ B) C \rangle * \widehat{RR}_{cc} * \langle C (i\mathscr{L}_+ B) \rangle \tag{A4}$$

where for brevity we have suppressed the arguments of the functions, and $\widehat{RR}_{cc}^{-1}$ is given by

$$\widehat{RR}_{cc}^{-1} = z\langle CC\rangle - \langle (i\mathscr{L}_+ C)C\rangle - \langle \{i\mathscr{L}_+ [z - Q'i\mathscr{L}]^{-1} Q' i\mathscr{L}_+ C\} C\rangle \quad \text{(A5)}$$

where Q' projects a variable orthogonal to the variables A, B, and C. Following the arguments used in the text, we obtain $M^{(1)}$ from a hydrodynamic analysis of the far field form of RR_{cc}, that is, when the field points $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$ are all far apart. Nonhydrodynamic modes are expected to decay away exponentially on the time scale of a typical molecular correlation time. If we then ignore the z dependence of the memory function in (A5) we find, schematically, that the dominant contribution of $M^{(1)}$ toward $C^{(1)}(z)$ is given by

$$C^{(1)}(z) \propto \iint_{|\mathbf{k}|, |\mathbf{k}| < k_c} d\mathbf{k}\, d\mathbf{k}' \left\{ \frac{1}{z + k^2\Gamma + |\mathbf{k} + \mathbf{k}'|^2 \Gamma'} - \frac{1}{k^2\Gamma + |\mathbf{k} + \mathbf{k}'|\,\Gamma'} \right\} \frac{1}{k^2} \quad \text{(A6)}$$

where Γ and Γ' are constants. Upon inverse Laplace transforming this we find, as suggested by Eq. (A2), that it gives rise to a t^{-2} tail, but does not contribute to the asymptotic $t^{-3/2}$ tail. The only problem remaining then is the neglect of the z dependence in the memory term of Eq. (A5). This effect may, in turn, be investigated by introducing four-particle variables, and conducting the hydrodynamic analysis, this time neglecting the z dependence of the four-particle memory function, and so on. It would seem that truncating this procedure at any finite level would lead to results that do not change the asymptotic long time tail of the VCF. Self-consistent calculations along the lines conducted by Keyes and Oppenheim[21] also strongly suggest that these memory effects do not contribute.

Lastly the arguments used here are essentially applicable to the neglect of the z dependence of the dissipative terms in Section 3, Eq. (45b). In this case, though, this dependence may be studied by coupling the bilinear variables to trilinear variables and conducting a hydrodynamic analysis. Again the results indicate that one can safely set $z = 0$ in the memory terms so far as the long time tail of the VCF is concerned. We would like to stress, though, that the foregoing analysis is only appropiate for a dimensionality of three or more. In two dimensions the z dependence of the memory functions does contribute to the long-time tail, and it is a more subtle calculation to extract its functional form and obtain neat expressions for the coefficients.

APPENDIX B

The relation between M and $\hat{M}$ which follows from Eq. (6b) is

$$W(1'3)\,\theta(1'3)*\hat{M}(1'3;12)=\theta(1'3)*M(1'3;12) \tag{B1}$$

Referring to Eq. (4) for M, the important quantity here is $Qi\mathscr{L}_+B(1'3)$, and

$$Qi\mathscr{L}_+B(1'3)=Q\sum_{\substack{j\neq i\\>1}}(T_+(1j)+T_+(ij))\sum_{i>1}\delta(\bar{\mathbf{v}}_1'-\bar{\mathbf{v}}_1)\,\delta(\bar{\mathbf{v}}_3-\mathbf{v}_i)$$
$$\times\,(\delta(\bar{\mathbf{r}}_{1'3}-\mathbf{r}_{1i})-\rho G(1'3)) \tag{B2}$$

Now the T's give the same results when acting on θ or $W\theta$, so $\hat{M}=M$. It follows that

$$v_3*\hat{M}(1'3;12)=v_3*M(1'3;12)$$
$$=\left\langle i\mathscr{L}_+[z-Qi\mathscr{L}_+]^{-1}\,Q\sum_{\substack{j\neq i,i>1\\j>1}}\sum T_+(ij)\,v_i\left(1-\rho\int dr\,G(r)\right)\right\rangle \tag{B3}$$

The essential feature of Eq. (B3) is the absence of the $T_+(1j)$ terms—those involving the interaction of the tagged particle and the bath. The reason for this is that Q removes all quantities which can be expressed in terms of the tagged-bath pair phase-space distribution function, and the $T_+(1j)$ terms are of this type. Then. $\sum T_+(ij)v_i=0$, being, in the absence of any 1's in the arguments of the T's, the statement of conservation of momentum in the fluid *unperturbed* by the tagged particle, and Eq. (24) follows. Identical arguments show that $v_3*\hat{K}(1'3;12)=0$.

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