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Mode coupling and tagged particle correlation functions: the Stokes–Einstein law

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In this paper a mode coupling theory for equilibrium tagged particle correlation functions in simple fluids is developed from molecular considerations. The mode coupling formalism developed in a previous paper [Physica A 181 (1992) 89] to describe equilibrium fluctuations in simple liquids is generalized to include tagged particle correlations. The mode coupling formalism and N ordering approximation scheme used in the previous paper allow a series for the generalized diffusion constant to be obtained which is exact in the thermodynamic limit. The Stokes–Einstein law for a slip Brownian particle is then derived from this series in a systematic fashion. The techniques applied here obviate the need to assume that the simple liquid is incompressible, and allow a self-consistent series of equations for the diffusion constant of the Brownian particle and transport coefficients of the fluid to be obtained which are useful in the study of supercooled liquids.

1. Introduction

The behavior of time dependent equilibrium correlation functions of single particle densities in simple fluids resembles the time evolution of equilibrium correlations of N particle densities in many ways. At long times, small wavevectors and away from any critical point, the behavior of both the single and N particle density correlation functions are determined by the slowly varying densities of the system. For systems with small gradients, the set of slowly varying densities includes the so-called hydrodynamic variables, which are the densities of conserved quantities of the system. The hydrodynamic variables for a system of N point particles are the microscopic number, energy and momentum densities, which we define to be

$$N(\boldsymbol{r}, X(t)) = \sum_{j=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_j(t)) ,$$

$$E(\boldsymbol{r}, X(t)) = \sum_{j=1}^{N} e_j(t)\, \delta(\boldsymbol{r} - \boldsymbol{r}_j(t)) ,$$
$$\boldsymbol{P}(\boldsymbol{r}, X(t)) = \sum_{j=1}^{N} \boldsymbol{p}_j(t)\, \delta(\boldsymbol{r} - \boldsymbol{r}_j(t)) , \tag{1.1}$$

where $\boldsymbol{r}_j$, e_j and $\boldsymbol{p}_j$ refer to the position, energy and momentum of particle j and $X(t) \equiv (\boldsymbol{r}^N(t), \boldsymbol{p}^N(t))$ is the phase point of the N particle system.

Single particle densities will be designated as properties of particle 0 in an $N+1$ particle system, and denoted by

$$C^s(\boldsymbol{r}, X(t)) \equiv c(X(t))\, \delta(\boldsymbol{r} - \boldsymbol{r}_0(t)) , \tag{1.2}$$

where $c(X(t))$ is an arbitrary function of the phase point $X(t)$ of the $N+1$ particle system. Examples of interesting single particle densities are the single particle number and momentum densities, which are given by

$$N_1(\boldsymbol{r}, \boldsymbol{r}_0(t)) = \delta(\boldsymbol{r} - \boldsymbol{r}_0(t)) ,$$
$$\boldsymbol{P}_1(\boldsymbol{r}, \boldsymbol{r}_0(t), \boldsymbol{p}_0(t)) = \boldsymbol{p}_0(t)\, \delta(\boldsymbol{r} - \boldsymbol{r}_0(t)) . \tag{1.3}$$

Observations of the macroscopic state of the equilibrium system are described by averaging the dynamical variables, which are functions of the phase point $X(t)$, over the grand canonical distribution function. The Hamiltonian for the system of interest is

$$H = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \tfrac{1}{2} \sum_{j=1} \sum_{l \neq j} u(|\boldsymbol{r}_{lj}|) + \frac{p_0^2}{2M} + \sum_{j=1}^{N} \phi(|\boldsymbol{r}_{j0}|) , \tag{1.4}$$

where $u(|\boldsymbol{r}_{lj}|)$ and $\phi(|\boldsymbol{r}_{j0}|)$ are short range interaction potentials between particles l and j and particle j and the tagged particle 0, respectively. The time evolution of a dynamical variable $A(\boldsymbol{r}, t)$ is determined classically by the Liouvillian, L, according to the classical equation of motion

$$\dot{A}(\boldsymbol{r}, t) = \mathrm{i}LA(\boldsymbol{r}, t) , \tag{1.5}$$

where

$$\mathrm{i}L = \sum_{j=0}^{N} \nabla \boldsymbol{p}_j H \cdot \nabla \boldsymbol{r}_j - \sum_{j=0}^{N} \nabla \boldsymbol{r}_j H \cdot \nabla \boldsymbol{p}_j .$$

These rules define the macroscopic state unequivocally.

Mode coupling equations for tagged particle correlation functions have been formulated in incomplete form for many years. Keyes and Oppenheim [2] first applied mode coupling techniques to calculate the autocorrelation function of the momentum density of a tagged particle. They found that the bilinear hydrodynamic modes nearly reproduced the Stokes–Einstein law for a large, massive Brownian particle immersed in a simple fluid. However, instead of obtaining the ordinary "slip" form of the Stokes–Einstein law in which $b = 4$ in

$$D = \frac{K_B T}{b\pi\eta R}, \tag{1.6}$$

where K_B is Boltzmann's constant, T is the temperature of the system, η is the transverse viscosity of the fluid system, R is the radius of the Brownian particle and D is the diffusion constant for the Brownian particle, they obtained $b = 5$. Similar problems were encountered by other investigators who attempted to derive the law from renormalized kinetic theory [3]. Madden and Masters [4] reexamined the work of Keyes and Oppenheim [2] using methods akin to mode coupling techniques and obtained the correct "slip" result. In this paper, we formulate a perturbation series for the diffusion constant of a tagged particle immersed in a simple fluid which is exact in the thermodynamic limit. From the perturbation series, the Stokes–Einstein law is shown to be an exact result to order (ξ/R), where ξ is defined to be the correlation length for fluid correlation functions in the absence of the tagged particle. The result is based upon an expansion of the off-diagonal (in wavevector) elements of a bilinear correlation function in powers of R. This expansion was motivated by an approximation in the work of Madden and Masters [4] which they did not justify, and exploits the fact that the pair distribution function for the Brownian (tagged) particle and a fluid particle is much longer ranged than the pair distribution function for fluid particles alone. The leading order term of the expansion of the off-diagonal bilinear correlation function in terms of R is exactly the approximation used by Madden and Masters [4] in their work.

This paper is organized as follows: The formal mode coupling hierarchy is presented in section 2. In section 3, the N ordering expansion is established for tagged particle correlation functions. A perturbation series is obtained for generalized transport coefficients of tagged particle correlations and subseries of the perturbation series are resummed to renormalize the propagators and establish self-consistent equations. In section 4, the special case of a macroscopic and massive Brownian particle immersed in a simple fluid is considered. The correct Stokes–Einstein law in the "slip" limit is obtained from the mode coupling series based upon an expansion of the vertices in powers of R. The nature of our results and its implications to models of the dynamics of supercooled simple liquids is discussed in section 5.

2. The mode coupling formalism

We define $B(\boldsymbol{r}, t)$ to be a column vector composed of the hydrodynamic densities $\hat{N}(\boldsymbol{r}, t)$, $\hat{E}(\boldsymbol{r}, t)$ and $\boldsymbol{P}(\boldsymbol{r}, t)$ of an $N+1$ particle system, where $\hat{C} \equiv C - \langle C \rangle$, and define $A(\boldsymbol{r}, t)$ to be a column vector composed of the slowly varying single particle and $N+1$ particle densities of the system. For systems with small gradients, at least the tagged particle number density $N_1(\boldsymbol{r}, t)$ and the hydrodynamic densities are slowly varying and hence in A. Finally, we define $A'(\boldsymbol{r}, t)$ to be a column vector whose components are the single or $N+1$ particle densities for the correlation function of interest and the slowly varying densities of the system which compose $A(\boldsymbol{r}, t)$. For example, if we are interested in describing the dynamics of the autocorrelation function of the tagged particle momentum density $\boldsymbol{P}_1(\boldsymbol{r}, t)$ defined in eq. (1.3), then $A'(\boldsymbol{r}, t)$ is defined to be composed of $\boldsymbol{P}_1(\boldsymbol{r}, t)$ and the slowly varying densities which compose the column vector $A(\boldsymbol{r}, t)$. The designation of A' is arbitrary in the formalism and explicit choices will be made at a later stage to investigate the diffusion constant for a Brownian particle in a simple fluid. It should be emphasized that the components of the column vector A are restricted to be the slowly varying linear densities of the system whereas the components of A' are unrestricted and can be quickly varying single or $N+1$ particle densities of the system. It should be noted that any linearly independent combination of the hydrodynamic densities defines B, A and A' equally well.

In order to form a complete set of slow variables, we define the infinite column vector Q to be

$$\begin{aligned}
&Q_0 = 1\,,\\
&Q_1(\boldsymbol{r}) = A'(\boldsymbol{r}) - \langle A'(\boldsymbol{r})\rangle \equiv \hat{A}'(\boldsymbol{r})\,,\\
&Q_2(\boldsymbol{r}, \boldsymbol{r}^1) = \hat{B}(\boldsymbol{r})\,\hat{A}(\boldsymbol{r}^1) - \langle(\hat{B}(\boldsymbol{r})\,\hat{A}(\boldsymbol{r}^1))\rangle\\
&\qquad\qquad - \langle \hat{B}(\boldsymbol{r})\,\hat{A}(\boldsymbol{r}^1)\,Q_1(\boldsymbol{r}_1)\rangle * K_{11}^{-1}(\boldsymbol{r}_1, \boldsymbol{r}_1') * Q_1(\boldsymbol{r}_1')\,,\\
&\quad\vdots\\
&Q_n(\boldsymbol{r}, \boldsymbol{r}^1, \ldots, \boldsymbol{r}^{n-1}) = \hat{B}(\boldsymbol{r})\,\hat{B}(\boldsymbol{r}^1)\cdots\hat{A}(\boldsymbol{r}^{n-1}) - \langle \hat{B}(\boldsymbol{r})\cdots\hat{A}(\boldsymbol{r}^{n-1})\rangle\\
&\qquad\qquad - \sum_{i=1}^{n-1} \langle \hat{B}(\boldsymbol{r})\cdots\hat{A}(\boldsymbol{r}^{n-1})\,Q_i(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i)\rangle\\
&\qquad\qquad * K_{ii}^{-1}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i, \boldsymbol{r}_i', \ldots, \boldsymbol{r}_i') * Q_i(\boldsymbol{r}_1', \ldots, \boldsymbol{r}_i')\,,
\end{aligned} \tag{2.1}$$

where $K_{ii}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i, \boldsymbol{r}_1', \ldots, \boldsymbol{r}_i') \equiv \langle Q_i(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i)\; Q_i(\boldsymbol{r}_1', \ldots, \boldsymbol{r}_i')\rangle$ and $*$ implies an integration of repeated spatial arguments over the volume of the system and a sum over the repeated labels in the matrix products at each order.

It should be noted that Q_i for $i \geqslant 2$ involves products of A's and B's only; A' appears in Q_i only in subtractions which make the Q components orthogonal in mode order. Furthermore, only one density of the tagged particle appears at each order, since the product of two linear tagged particle densities is a linear tagged particle density in Fourier space. Thus defined, Q contains all the slow modes of the system. In subsequent equations where multilinear densities are involved, the $*$ will also imply a sum over all mode orders. We also define the column vector

$$
\begin{aligned}
&\bar{Q}_0 = 1 , \\
&\bar{Q}_1(\boldsymbol{r}) = B(\boldsymbol{r}) - \langle B(\boldsymbol{r})\rangle \equiv \hat{B}(\boldsymbol{r}) , \\
&\bar{Q}_2(\boldsymbol{r}, \boldsymbol{r}^1) = \bar{Q}_1(\boldsymbol{r})\, \bar{Q}_1(\boldsymbol{r}^1) - \langle \bar{Q}_1(\boldsymbol{r})\, \bar{Q}_1(\boldsymbol{r}^1)\rangle \\
&\qquad - \langle \bar{Q}_1(\boldsymbol{r})\, \bar{Q}_1(\boldsymbol{r}^1)\, \bar{Q}_1(\boldsymbol{r}_1)\rangle * \bar{K}_{11}^{-1}(\boldsymbol{r}_1, \boldsymbol{r}_2) * \bar{Q}_1(\boldsymbol{r}_2) , \\
&\vdots \\
&\bar{Q}_n(\boldsymbol{r}, \boldsymbol{r}^1, \ldots, \boldsymbol{r}^{n-1}) = \bar{Q}_1(\boldsymbol{r})\, \bar{Q}_1(\boldsymbol{r}^1) \cdots \bar{Q}_1(\boldsymbol{r}^{n-1}) - \langle \bar{Q}_1(\boldsymbol{r}) \cdots \bar{Q}_1(\boldsymbol{r}^{n-1})\rangle \\
&\qquad - \sum_{i=1}^{n-1} \langle \bar{Q}_1(\boldsymbol{r}) \cdots \bar{Q}_1(\boldsymbol{r}^{n-1})\, \bar{Q}_i(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i)\rangle \\
&\qquad * \bar{K}_{ii}^{-1}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_i, \boldsymbol{r}'_1, \ldots, \boldsymbol{r}'_i) * \bar{Q}_i(\boldsymbol{r}'_1, \ldots, \boldsymbol{r}'_i) ,
\end{aligned}
\tag{2.2}
$$

where $\bar{K} \equiv \langle \bar{Q}_i \bar{Q}_i \rangle$. $\bar{Q}$ contains $N+1$ particle densities of conserved (hydrodynamic) quantities of the system only, and is contained in Q. As in ref. [1], a combinatorial factor must accompany each sum over repeated column indices in the multilinear variables in both Q and $\bar{Q}$ to avoid overcounting each particular multilinear product.

We shall assume that the slowly varying part of any dynamical density $C(\boldsymbol{r}, t)$ of the system is an analytic function of the densities of the slow variables which comprise the columns of A. We define two projection operators:

$$\tilde{\mathcal{P}} C = \langle C\hat{A}'\rangle * \langle \hat{A}'\hat{A}'\rangle^{-1} * \hat{A}' \quad \text{and} \quad \mathcal{P} C = \langle CQ\rangle * K^{-1} * Q . \tag{2.3}$$

Using standard operator identities, we obtain [1]

$$\dot{\hat{A}}'(t) = \int_0^t \tilde{M}(\tau) * \hat{A}'(t-\tau)\, \mathrm{d}\tau + f(t) , \tag{2.4}$$

$$\dot{Q}(t) = \int_0^t M(\tau) * Q(t-\tau)\, \mathrm{d}\tau + \phi(t) , \tag{2.5}$$

where

$$\tilde{M}(\tau) = 2\langle \dot{A}'\hat{A}'\rangle * \langle \hat{A}'\hat{A}'\rangle^{-1}\delta(\tau) - \langle f(\tau)\, f\rangle * \langle \hat{A}'\hat{A}'\rangle^{-1}\,, \tag{2.6}$$

$$M(\tau) = 2\langle \dot{Q}Q\rangle * K^{-1}\delta(\tau) - \langle \phi(\tau)\,\phi\rangle * K^{-1} \equiv N(\tau) * K^{-1} \tag{2.7}$$

and

$$f(t) = \mathrm{e}^{(1-\tilde{\mathscr{P}})\mathrm{i}Lt}(1-\tilde{\mathscr{P}})\dot{A}'\,, \tag{2.8}$$

$$\phi(t) = \mathrm{e}^{(1-\mathscr{P})\mathrm{i}Lt}(1-\mathscr{P})\dot{Q}\,. \tag{2.9}$$

The first term on the right hand side of (2.7) is generally called the Euler term and the second term is usually called the dissipative term since these terms correspond to the Euler and dissipative terms in the phenomenological hydrodynamic equations. Since $\langle f(\tau)\ A'\rangle = 0$ and $\langle \phi(\tau)\ Q\rangle = 0$ by construction, eqs. (2.4) and (2.5) imply

$$\langle \dot{A}'(t)\,\hat{A}'\rangle = \langle \dot{\hat{A}}'(t)\,\hat{A}'\rangle = \int_0^t \tilde{M}(\tau) * \langle \hat{A}'(t-\tau)\,\hat{A}'\rangle\,\mathrm{d}\tau\,, \tag{2.10}$$

$$\langle \dot{Q}(t)\,Q\rangle = \int_0^t M(\tau) * \langle Q(t-\tau)\,Q\rangle\,\mathrm{d}\tau\,, \tag{2.11}$$

which may be written in Laplace space as

$$\langle \hat{A}'(z)\,\hat{A}'\rangle = (zI - \tilde{M}(z))^{-1} * \langle \hat{A}'\hat{A}'\rangle\,, \tag{2.12}$$

$$\langle Q(z)Q\rangle = (zI - M(z))^{-1} * \langle QQ\rangle\,. \tag{2.13}$$

Since $Q_1 \equiv \hat{A}'$, it follows from the orthogonality of the components in the Q basis set that

$$(zI - \tilde{M}(z))^{-1} = (zI - M(z))^{-1}_{11}\,, \tag{2.14}$$

where $(zI - M(z))^{-1}_{11}$ is the one-one sub-block of the infinite dimensional matrix $(zI - M(z))^{-1}$.

Since any product of conserved densities can be written as a linear combination of the components of the column vector Q, it follows that any slowly varying component of an arbitrary dynamical density of the system $C(\boldsymbol{r})$ is projected out by $\mathcal{P}$, and therefore $(1-\mathcal{P})C(\boldsymbol{r}_1)$ is quickly varying in the sense that for any arbitrary density $D(\boldsymbol{r}_2)$ of the system,

$$\langle (\mathrm{e}^{(1-\mathcal{P})\mathrm{i}Lt}(1-\mathcal{P})\mathrm{i}LC(\boldsymbol{r}_1))\, D(\boldsymbol{r}_2)\rangle \to 0$$

for times longer than a microscopic timescale τ_{m} ($\sim 10^{-13}$ s). Since $f(t)$ has only linear densities projected out, $\langle f(t)\, f\rangle$ decays slowly whereas $\langle \phi(t)\, \phi\rangle$ decays on a microscopic timescale since all slowly varying behavior has been removed from $\phi(t)$. Thus we expect $\tilde{M}(z)$ to have a much stronger z dependence than $M(z)$.

3. N ordering and resummations of the hydrodynamic matrix

The N ordering scheme developed in ref. [1] can be applied to evaluate correlation functions of multilinear order in the densities. The N ordering analysis developed previously is easily generalized to apply to correlation functions involving single particle densities as well as N particle densities. Whereas in ref. [1] the N order of the Fourier transform of a cumulant factor (denoted by $\langle\!\langle \cdots \rangle\!\rangle$) of an N particle density correlation function was assigned order N,

$$\begin{aligned}\langle\!\langle \hat{N}(\boldsymbol{k})\, \hat{N}(\boldsymbol{k})^* \rangle\!\rangle &= \sum_{i,j=1}^{N} \langle \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j}\rangle \\ &= (\langle N\rangle + \langle N(N-1)\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)}\rangle) \sim \mathcal{O}(N)\,,\end{aligned}$$

the N order of a cumulant factor of a correlation function involving single particle densities must be $\mathcal{O}(1)$, since

$$\begin{aligned}\langle\!\langle \hat{N}_1(\boldsymbol{k})\, \hat{N}(\boldsymbol{k})^* \rangle\!\rangle &= \sum_{i=0}^{N} \langle \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_0}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}\rangle \\ &= (1 + \langle N\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_0-\boldsymbol{r}_1)}\rangle) \sim \mathcal{O}(1)\,,\end{aligned}$$

which is a factor of N lower than $\langle\!\langle \hat{N}(\boldsymbol{k})\, \hat{N}(\boldsymbol{k})^* \rangle\!\rangle$. This suggests the general rule that the N order of the Fourier transform of a correlation function involving a component of Q_i which contains a tagged particle density is at least a factor of N lower in order than the N order obtained by using $\bar{Q}_i$ in its place in the correlation function.

We shall apply the N ordering scheme to the hydrodynamic matrix

$$M_{\alpha\beta}(t) = \sum_{|\hat{\beta}|=0}^{\infty} [2\langle \dot{Q}_\alpha Q_{\hat{\beta}} \rangle \, \delta(t) - \langle \phi_\alpha(t) \, \phi^*_{\hat{\beta}} \rangle] * K^{-1}_{\hat{\beta}\beta} \equiv \sum_{|\hat{\beta}|=0}^{\infty} N_{\alpha\hat{\beta}}(t) * K^{-1}_{\hat{\beta}\beta} \,, \tag{3.1}$$

and formulate a perturbation series using the inverse system size as a small parameter. The subscripts like

$$\alpha \equiv \{b_1(\boldsymbol{k} - \boldsymbol{q}_1 - \cdots - \boldsymbol{q}_{|\alpha|-1}), \ldots, b_{|\alpha|-1}(\boldsymbol{q}_{|\alpha|-2}), a_1(\boldsymbol{q}_{|\alpha|-1})\}$$

denote sets of wavevector and hydrodynamic indices, where each b_i is a component of the column vector B, a_1 is one of the components of the column vector A, and $|\alpha|$ is an integer referring to the number of elements in the set and is the order of the mode. The N order of the hydrodynamic matrices depends upon the presence or absence of single particle densities in the sets α and β. If the component of A in the set α contains a single particle density, we denote the corresponding mode by a superscript s, Q^{s}_α; if this component is an $N+1$ particle density, the corresponding mode will be denoted by a superscript c, Q^{c}_α. Our task will be to determine the relative N orders of the hydrodynamic matrices $M^{\mathrm{ss}}_{\alpha\beta}$, $M^{\mathrm{sc}}_{\alpha\beta}$, $M^{\mathrm{cs}}_{\alpha\beta}$ and $M^{\mathrm{cc}}_{\alpha\beta}$, where the superscript ss implies that both sets α and β contain a single particle density, and so forth.

In order to determine this N orderings we present a detailed discussion of the N orders of the matrix $K_{\hat{\alpha}\alpha}$, where $|\hat{\alpha}| = |\alpha|$. Similar considerations apply to the matrices in the numerator in eq. (3.1). The results are

$$K^{\mathrm{cc}}_{\hat{\alpha}\alpha} = \langle Q^{\mathrm{c}}_{\hat{\alpha}} Q^{\mathrm{c}*}_\alpha \rangle \sim N^j \,, \tag{3.2}$$

where $1 \leq j \leq |\alpha|$ and j is the number of matched sets of wavevectors in α and $\hat{\alpha}$;

$$K^{\mathrm{sc}}_{\hat{\alpha}\alpha} = K^{\mathrm{cs}}_{\hat{\alpha}\alpha} \sim N^{j-1} \,, \tag{3.3}$$

$$K^{\mathrm{ss}}_{\hat{\alpha}\alpha} \sim N^{j-1} \,, \tag{3.4}$$

if the single particle densities in $\hat{\alpha}$ and α are in the same matched set and

$$K^{\mathrm{ss}}_{\hat{\alpha}\alpha} \sim N^{j-2} \,, \tag{3.5}$$

where $2 \leq j \leq |\alpha|$, if these single particle densities are in different sets. These results imply that the elements of the inverse matrix K^{-1} have the following N

orders:

$$K^{-1\,\mathrm{sc}}_{\hat{\alpha}\alpha},\ K^{-1\,\mathrm{cs}}_{\hat{\alpha}\alpha},\ K^{-1\,\mathrm{cc}}_{\hat{\alpha}\alpha} \sim N^{-2|\alpha|+j}, \qquad K^{-1\,\mathrm{ss}}_{\hat{\alpha}\alpha} \sim N^{-2|\alpha|+j+1}, \tag{3.6}$$

if the single particle densities in $\hat{\alpha}$ and α are in the same matched set and

$$K^{-1\,\mathrm{ss}}_{\hat{\alpha}\alpha} \sim N^{-2|\alpha|+j}, \tag{3.7}$$

if the single particle densities are in different sets. In our subsequent analysis, we shall add a superscript m to ss elements in which particle densities are in the same set and a superscript u if they are in different sets. It is also evident that to leading N order

$$K^{-1\,\mathrm{cc}} = K^{\mathrm{cc}\,-1}, \qquad K^{-1\,\mathrm{ssm}} = K^{\mathrm{ssm}\,-1}, \tag{3.8}$$

where $K^{\mathrm{cc}\,-1}$ is the inverse of the K^{cc} matrix and $K^{\mathrm{ssm}\,-1}$ is the inverse of the K^{ssm} matrix.

The leading N orders of the $M_{\alpha\beta}$ matrices defined in eq. (3.1) with no partial wavevector matches between the sets of α and β are found to be

$$M^{\mathrm{ssm}}_{\alpha\beta},\ M^{\mathrm{cc}}_{\alpha\beta},\ M^{\mathrm{cs}}_{\alpha\beta} \sim N^{1-|\beta|}, \qquad M^{\mathrm{sc}}_{\alpha\beta} \sim N^{-|\beta|}. \tag{3.9}$$

Furthermore, it is found that

$$M^{\mathrm{cc}}_{\alpha\beta} = N^{\mathrm{cc}}_{\alpha\hat{\beta}} * K^{\mathrm{cc}\,-1}_{\hat{\beta}\beta}(1 + \mathcal{O}(N^{-1})) \tag{3.10}$$

and

$$M^{\mathrm{ssm}}_{\alpha\beta} = N^{\mathrm{ssm}}_{\alpha\hat{\beta}} * K^{\mathrm{ssm}\,-1}_{\hat{\beta}\beta}(1 + \mathcal{O}(N^{-1}))\,. \tag{3.11}$$

Thus the single particle modes do not contribute to the hydrodynamic matrix for the collective modes and only matched single particle modes contribute to $M^{\mathrm{ssm}}_{\alpha\beta}$. Note that eq. (3.9) establishes that

$$\langle Q^{\mathrm{s}}_{\alpha}(z)\, Q^{\mathrm{s}*}_{\beta} \rangle^{\mathrm{m}} = (zI - M^{\mathrm{ssm}}(z))^{-1}_{\alpha\hat{\beta}} * \langle Q^{\mathrm{s}}_{\hat{\beta}} Q^{\mathrm{s}*}_{\beta} \rangle^{\mathrm{m}} + \mathcal{O}(N^{-1})\,, \tag{3.12}$$

where $|\hat{\beta}| = |\beta|$ by the orthogonality of the Q set. Similarly,

$$\langle Q^{\mathrm{c}}_{\alpha}(z)\, Q^{\mathrm{c}*}_{\beta} \rangle = (zI - M^{\mathrm{cc}}(z))^{-1}_{\alpha\hat{\beta}} * \langle Q^{\mathrm{c}}_{\hat{\beta}} Q^{\mathrm{c}*}_{\beta} \rangle + \mathcal{O}(N^{-1})\,, \tag{3.13}$$

which implies single particle densities play no role in determining the dynamics of correlations of purely collective densities in the thermodynamic limit. Thus the set $\bar{Q}$ is sufficiently large to describe the behavior of $\langle Q^{c}(z)\, Q^{c*}\rangle$, as was assumed in ref. [1]. Since eq. (3.12) implies that the purely collective type of sets α and β do not influence the dynamics of a correlation function like $\langle Q^{s}_{\alpha}(z)\, Q^{s*}_{\beta}\rangle^{m}$, which involves tagged particles, it is not necessary to include the $N+1$ particle hydrodynamic densities in the set $A(\boldsymbol{k})$. Henceforth, we shall designate $A(\boldsymbol{k})$ to be composed only of the slowly varying single particle densities of the system.

We are interested in computing correlation functions of the form $\langle \hat{A}'(\boldsymbol{k}, z)\, \hat{A}'(\boldsymbol{k})^{*}\rangle$, where the components of $A' \equiv Q_{1}$ are linear single or $N+1$ particle densities. It follows from eqs. (2.12), (2.14) and the N orders of the various M matrices that

$$\begin{aligned}\langle \hat{A}'^{s}(\boldsymbol{k}, z)\, \hat{A}'^{s}(\boldsymbol{k})^{*}\rangle &= (zI - \tilde{M}^{ss}(\boldsymbol{k}, z))^{-1} \cdot \langle \hat{A}'^{s}(\boldsymbol{k})\, \hat{A}'^{s}(\boldsymbol{k})^{*}\rangle \\ &= (zI - M^{ssm}(\boldsymbol{k}, z))^{-1}_{11} \cdot \langle \hat{A}'^{s}(\boldsymbol{k})\, \hat{A}'^{s}(\boldsymbol{k})^{*}\rangle\end{aligned}$$

and

$$\begin{aligned}\langle \hat{A}'^{c}(\boldsymbol{k}, z)\, \hat{A}'^{c}(\boldsymbol{k})^{*}\rangle &= (zI - \tilde{M}^{cc}(\boldsymbol{k}, z))^{-1} \cdot \langle \hat{A}'^{c}(\boldsymbol{k})\, \hat{A}'^{c}(\boldsymbol{k})^{*}\rangle \\ &= (zI - M^{cc}(\boldsymbol{k}, z))^{-1}_{11} \cdot \langle \hat{A}'^{c}(\boldsymbol{k})\, \hat{A}'^{c}(\boldsymbol{k})^{*}\rangle\, .\end{aligned}$$

The cross correlations $\langle \hat{A}'^{c}(\boldsymbol{k}, z)\, \hat{A}'^{s}(\boldsymbol{k})^{*}\rangle$ are more complicated. We define the propagator $G(z)$ by

$$G(z) \equiv (zI - M(z))^{-1}\, , \tag{3.14}$$

where $M(z) \equiv N(z) * K^{-1}$ according to eq. (2.7). It is convenient at this stage to introduce the matrix $\hat{M}$, which is defined by

$$\hat{M}(z) \equiv N(z) \cdot D^{-1}\, , \tag{3.15}$$

where D is the diagonal in the wavevector part of K. The off-diagonal part of K is denoted O, and thus

$$K = (I + O \cdot D^{-1}) \cdot D\, , \qquad M(z) = \hat{M}(z) * (I + O \cdot D^{-1})^{-1}\, ,$$

and

$$\begin{aligned}G(z) &= (I + O \cdot D^{-1}) * (zI - \hat{M} + zO \cdot D^{-1})^{-1} \\ &= (I + O \cdot D^{-1}) * \hat{G}(z)\, ,\end{aligned} \tag{3.16}$$

where $\hat{G}(z)$ is defined by eq. (3.16). Since $O_{11}=0$ by construction, it follows immediately that $G_{11}(z)=\hat{G}_{11}(z)$. We also define the "bare" diagonal propagator

$$\hat{G}^{s(d)}_{\alpha}(z) \equiv (zI - \hat{M}^{ssm(d)}(z))^{-1} ,$$

where $\hat{M}^{ssm(d)}(z)$ is the diagonal in the wavevector part of $\hat{M}^{ssm}$. Since $\hat{M}^{ssm(d)}(z)$ is block diagonal in mode order,

$$\hat{G}^{s(d)}_{\alpha}(z) = (zI - \tilde{M}^{ssm(d)}(z))^{-1}_{\alpha\alpha} = (zI - \hat{M}^{ssm(d)}_{\alpha\alpha}(z))^{-1} , \tag{3.17}$$

where $\hat{M}^{ssm(d)}(z) = M^{ssm(d)}(z)$. If we expand $\hat{G}_{\alpha\beta}(z)$ around the diagonal term $\hat{G}^{(d)}(z)$ for $|\alpha|=|\beta|=1$ and set $X \equiv \hat{M}^{0} - zO\cdot D^{-1}$, where $\hat{M}^{0}$ is the part of $\hat{M}$ which is off-diagonal in wavevector, we obtain [1]

$$\hat{G}_{\alpha\beta} = \hat{G}^{d}_{\alpha}\cdot I_{\alpha\beta} + \sum_{i=2}^{\infty} \hat{G}^{d}_{\alpha}\cdot \Theta^{i}_{\alpha\gamma} * \hat{G}_{\gamma\beta} , \tag{3.18}$$

where $|\alpha|=|\beta|=|\gamma|=1$, and

$$\begin{aligned}
\Theta^{(2)}_{\alpha\gamma} &= \sum_{|\gamma_1|=2}^{\infty} X_{\alpha\gamma_1} * \hat{G}^{d}_{\gamma_1}\cdot X_{\gamma_1\gamma} ,\\
\Theta^{(3)}_{\alpha\gamma} &= \sum_{|\gamma_1|=2}^{\infty}\sum_{|\gamma_2|=2}^{\infty} X_{\alpha\gamma_1} * \hat{G}^{d}_{\gamma_1}\cdot X_{\gamma_1\gamma_2} * \hat{G}^{d}_{\gamma_2}\cdot X_{\gamma_2\gamma} ,\\
&\vdots\\
\Theta^{(n)}_{\alpha\gamma} &= \sum_{|\gamma_1|=2}^{\infty}\cdots\sum_{|\gamma_{n-1}|=2}^{\infty} \overbrace{X_{\alpha\gamma_1} * \hat{G}^{d}_{\gamma_1}\cdot X_{\gamma_1\gamma_2}\cdots * \hat{G}^{d}_{\gamma_{n-1}}\cdot X_{\gamma_{n-1}\gamma}}^{n\text{ factors of }X} ,\\
&\vdots
\end{aligned} \tag{3.19}$$

where each $|\gamma_i| \neq 1$. Since

$$\langle \hat{A}'(z)\,\hat{A}'^{*}\rangle = \hat{G}_{11}(z)\cdot\langle \hat{A}'\hat{A}'\rangle = (zI - \tilde{M}(z))^{-1}\cdot\langle \hat{A}'\hat{A}'\rangle , \tag{3.20}$$

from eqs. (2.14) and (3.18), it follows that

$$\tilde{M}^{ss}(a(\boldsymbol{k}); b(\boldsymbol{k}), z) = M^{ss}_{11}(a(\boldsymbol{k}); b(\boldsymbol{k}), z) + \sum_{i=2}^{\infty} \Theta^{ss(i)}_{11}(a(\boldsymbol{k}); b(\boldsymbol{k}), z) . \tag{3.21}$$

The $\Theta^{(i)}_{\alpha\gamma}$ terms defined in eq. (3.19) may be reexpressed in terms of the full, diagonal, propagators $G_{\alpha\alpha'}(z)$, in which the wavevectors in the set α are identical to those in α', by resumming subseries of $\hat{G}^{(d)}(z)$ to obtain [1]

$$\begin{aligned}
\Theta^{(2)}_{\alpha\gamma} &= \sum_{|\gamma_2|=2}^{\infty} X_{\alpha\gamma_1} * G_{\gamma_1\gamma_1'} \cdot X_{\gamma_1'\gamma}\,, \\
\Theta^{(3)}_{\alpha\gamma} &= \sum_{|\gamma_1|=2}^{\infty} \sum_{|\gamma_2|=2}^{\infty} X_{\alpha\gamma_1} * G_{\gamma_1\gamma_1'} \cdot X_{\gamma_1'\gamma_2} * G_{\gamma_2\gamma_2'} \cdot X_{\gamma_2'\gamma}\,, \\
&\vdots \\
\Theta^{(n)}_{\alpha\gamma} &= \sum_{|\gamma_1|=2}^{\infty} \cdots \sum_{|\gamma_{n-1}|=2}^{\infty} \overbrace{X_{\alpha\gamma_1} * G_{\gamma_1\gamma_1'} \cdot X_{\gamma_1'\gamma_2} \cdots * G_{\gamma_{n-1}\gamma_{n-1}'} \cdot X_{\gamma_{n-1}'\gamma}}^{n \text{ factors of } X}\,, \\
&\vdots
\end{aligned} \tag{3.22}$$

where each $|\gamma_i| \neq 1$ and none of the full diagonal propagators has the same wavevector arguments. The N ordering of the propagators and X factors is established in the same manner as that described above for the M matrix, and

$$G^{\mathrm{cs}}_{\alpha'\alpha},\, G^{\mathrm{cc}}_{\alpha'\alpha},\, G^{\mathrm{ssm}}_{\alpha'a} \sim \mathcal{O}(1)\,, \qquad G^{\mathrm{ssu}}_{\alpha'\alpha},\, G^{\mathrm{sc}}_{\alpha'\alpha} \sim \mathcal{O}(N^{-1})\,,$$

and

$$X^{\mathrm{ssm}} \sim X^{\mathrm{cc}} \sim X^{\mathrm{cs}}\,, \qquad X^{\mathrm{ssu}} \sim X^{\mathrm{sc}} \sim \frac{1}{N}\, X^{\mathrm{cc}}\,.$$

Therefore, all of the terms in $\Theta^{\mathrm{cc}}_{11}$ contain G^{cc} and X^{cc} alone and all of the terms in $\Theta^{\mathrm{ssm}}_{11}$ contain G^{ssm} and X^{ssm} in the thermodynamic limit.

In the appendix, it is shown that if a wavevector $\boldsymbol{q}_1$ from the set α is equated with a wavevector $\boldsymbol{q}_1'$ from the set β, then

$$M^{\mathrm{ssm}}_{\alpha\beta}(z)\, \delta^{\mathrm{cc}}_{q_1q_1'} = (M^{\mathrm{ssm}}_{\alpha-1\,\beta-1}(z) + \mathcal{O}(N^{1-|\beta|}) + M^{\mathrm{cc}}_{11}(\boldsymbol{q}_1, t) \cdot I^{\mathrm{ss}}_{\alpha-1\,\beta-1})\, \delta^{\mathrm{cc}}_{q_1q_1'}\,, \tag{3.23}$$

where

$$\begin{aligned}
I^{\mathrm{ss}}_{\alpha-1\,\beta-1} &\equiv \langle Q_{\alpha-1}(t)\, Q^*_n \rangle * \langle Q(t)\, Q^* \rangle^{-1}_{n\,\beta-1} \\
&= \delta_{|\alpha||\beta|} \Bigg(\sum_{\{(b_i(\boldsymbol{q}_i), b_j'(\boldsymbol{q}_j'))\}}^{x} \; \sum_{i=2}^{|\alpha|-1} \delta_{b_i,b_j'} \delta_{\boldsymbol{q}_i\boldsymbol{q}_j'} + \delta_{a_0a_0'} \delta_{q_0q_0'} \Bigg)\,,
\end{aligned} \tag{3.24}$$

where x is the number of unique ways of pairing indices of the collective densities in the sets α and β, and b_i and b_j' are the densities which compose the sets α and β, respectively, excluding $i=1$. In eq. (3.23), M_{11}^{cc} is defined to be

$$M_{11}^{cc}(\boldsymbol{q}_1, t) \equiv (2\langle \dot{B}(\boldsymbol{q}_1)\, B(\boldsymbol{q}_1)^* \rangle \delta(t) - \langle \phi_B(\boldsymbol{q}_1, t)\, \phi_B(\boldsymbol{q}_1)^* \rangle) \cdot \langle B(\boldsymbol{q}_1)\, B(\boldsymbol{q}_1)^* \rangle^{-1} ,$$

where $\phi_B(\boldsymbol{q}_1, t) \equiv \mathrm{e}^{(1-\mathscr{P})\mathrm{i}Lt}(1-\mathscr{P})\dot{B}(\boldsymbol{q}_1)$, and $\delta_{q_1 q_1'}^{cc}$ indicates that both $\boldsymbol{q}_1$ and $\boldsymbol{q}_1'$ are wavevector arguments of collective densities. In addition,

$$M_{\alpha\beta}^{ssm}(z)\, \delta_{q_0 q_0'}^{ss} = (M_{\alpha-1\,\beta-1}^{cc}(z) + \mathcal{O}(N^{1-|\beta|}) + M_{11}^{ss}(\boldsymbol{q}_0, t) \cdot I_{\alpha-1\,\beta-1}^{cc})\, \delta_{q_0 q_0'}^{ss} , \tag{3.25}$$

where $\boldsymbol{q}_0$ and $\boldsymbol{q}_0'$ are wavevector arguments of the single particle densities in α and β, respectively, $I_{\alpha-1\,\beta-1}^{cc}$ is defined as in eq. (3.24) except that the case $i=1$ is included in the sum over i, and

$$M_{11}^{ss}(\boldsymbol{q}_1, t) \equiv (2\langle \dot{A}(\boldsymbol{q}_0)\, A(\boldsymbol{q}_0)^* \rangle \delta(t) - \langle \phi_A(\boldsymbol{q}_0, t)\, \phi_A(\boldsymbol{q}_0)^* \rangle) \cdot \langle A(\boldsymbol{q}_0)\, A(\boldsymbol{q}_0)^* \rangle^{-1} , \tag{3.26}$$

with $\phi_A(\boldsymbol{q}_0, t) \equiv \mathrm{e}^{(1-\mathscr{P})\mathrm{i}Lt}(1-\mathscr{P})\dot{A}(\boldsymbol{q}_0)$. It should be emphasized that only the slowly varying single particle densities appear in A and influence the mode coupling dynamics, and hence the set A' can include rapidly varying densities. As we shall see, this flexibility provides a mechanism to find physical cutoffs in integrals over repeated spatial arguments (or sum over wavevectors).

Since

$$\langle Q_l^s Q_l^{s*} \rangle = D_l^s + \mathcal{O}(N^{|l|-2}) ,$$

and

$$\begin{aligned}\langle Q_l^s(z) Q_l^{s*} \rangle &= \mathscr{L} \prod_{i=1}^{|l|-1} \langle b_i(l_i, t)\, b_i(l_i)^* \rangle \langle a_0(l_0, t)\, a_0(l_0)^* \rangle + \mathcal{O}(N^{|l|-2}) \\ &= \mathscr{L}\Big(\prod_{i=1}^{|l|-1} \mathscr{L}^{-1}(zI - \tilde{M}^{cc}(l_i, z))_{b_i b}^{-1} \\ &\quad \cdot \langle b(l_i)\, b_i(l_i)^* \rangle \mathscr{L}^{-1}(zI - \tilde{M}^{ss}(l_0, z))_{a_0 a}^{-1} \cdot \langle a(l_0)\, a_0(l_0)^* \rangle \Big)\end{aligned} \tag{3.27}$$

by eq. (2.12), where l_i are the wavevectors of the set l and $\mathscr{L}$ denotes the

Laplace transform, it follows that

$$\langle Q_l^{\rm s}(z)\, Q_l^{\rm s*}\rangle = G_{ll'}^{\rm ss}(z)\cdot\langle Q_{l'}^{\rm s} Q_l^{\rm s*}\rangle + G_{ll'}^{\rm sc}(z)\cdot\langle Q_{l'}^{\rm c} Q_l^{\rm s*}\rangle + \mathcal{O}(N^{|l|-2})$$
$$= G_{ll'}^{\rm ss}(z)\cdot \prod_{i=1}^{|l|-1} \langle b(l_i)\, b_i(l_i)\rangle\langle a(l_0)\, a_0(l_0)^*\rangle(1+\mathcal{O}(N^{-1}))\,,$$

and therefore

$$G_{ll'}^{\rm ss}(z) = \mathscr{L}[\mathscr{L}^{-1}G_{11}^{\rm ss}(l_0, z)\,\mathscr{L}^{-1}G_{11}^{\rm cc}(l_1, z)\cdots\mathscr{L}^{-1}G_{11}^{\rm cc}(l_{|l|-1}, z)]\,. \qquad (3.28)$$

Since $G_{11}^{\rm ss}(z) = (zI - \tilde{M}^{\rm ss}(z))^{-1}$ and $G_{11}^{\rm cc}(z) = (zI - \tilde{M}^{\rm cc}(z))^{-1}$, by eqs. (3.12), (3.13) and (2.14) we may replace the full G_{11} propagators by correlation functions. For example, if $\langle AA\rangle$ and $\langle BB\rangle$ are diagonal matrices,

$$G_{22'}^{\rm ss}(a_1(-\boldsymbol{q}), b_1(\boldsymbol{q}); a_2(-\boldsymbol{q}), b_2(\boldsymbol{q}), z)$$
$$= \mathscr{L}(\mathscr{L}^{-1}[zI - \tilde{M}^{\rm cc}(\boldsymbol{q}, z)]^{-1}_{(b_1;b_2)}\mathscr{L}^{-1}[zI - \tilde{M}^{\rm ss}(-\boldsymbol{q}, z)]^{-1}_{(a_1;a_2)})\,,$$
$$= \mathscr{L}\left[\frac{\langle a_1(-\boldsymbol{q}, t)\, a_2(-\boldsymbol{q})^*\rangle}{\langle a_2(-\boldsymbol{q})\, a_2(-\boldsymbol{q})^*\rangle}\,\frac{\langle b_1(\boldsymbol{q}, t)\, b_2(\boldsymbol{q})^*\rangle}{\langle b_2(\boldsymbol{q})\, b_2(\boldsymbol{q})^*\rangle}\right],$$

where a_1 and a_2 are single particle densities from the set A, and b_1 and b_2 are collective densities from the set B. Since the $G_{ll'}^{\rm ss}(z)$ can be written in terms of a product of full G_{11} propagators as in eq. (3.28), which in turn can be written in terms of linear density correlation functions, we have established a system of self-consistent integral equations which relate an arbitrary single particle density correlation function to N particle density correlation functions and tagged particle density correlations of the slowly varying single particle densities. Equations of this sort have been used in the study of critical dynamics of supercooled liquids [5].

4. The diffusion constant

We shall apply the mode coupling formalism for tagged particle correlation functions to investigate the properties of the diffusion constant for a large, massive Brownian particle of mass M and radius R immersed in a fluid of N point particles of mass m. We shall concentrate on the limit in which $\epsilon \to 0$ and $(\xi/R) \ll 1$, where $\epsilon \equiv (m/M)^{1/2}$ and ξ is the correlation length of correlation functions involving N particle fluid densities only. Following the work of Mazur and Oppenheim [6] on Brownian motion, we define the reduced momentum

p_0^*, where

$$p_0^* = \epsilon p_0 ,$$

and rewrite the Liouvillian for the tagged particle system as

$$iL = iL_0 + \epsilon iL_1 = iL_0 + \epsilon\left(\frac{p_0^*}{m}\cdot\nabla r_0 - \nabla r_0 \sum_{i=1}^{N} \phi(|r_{i0}|)\cdot\nabla p_0^*\right), \tag{4.1}$$

and

$$iL_0 \equiv \sum_{i=1}^{N} \frac{p_i}{m}\cdot\nabla r_i - \sum_{i=1}^{N}\left(\nabla r_i\phi(|r_{i0}|) + \tfrac{1}{2}\sum_{j\neq i}^{N}\nabla r_i u(|r_{ij}|)\right)\cdot\nabla p_i , \tag{4.2}$$

where $u(|r_{ij}|)$ is the short range potential between the fluid particles i and j and $\phi(|r_i - r_0|) \equiv \phi(|r_{i0}|)$ is the short range potential between fluid particle i and the tagged particle 0, which is the Brownian particle.

The set $A(k)$ must include all of the linear Brownian particle densities which are slow because their time derivatives contain factors of k and/or ϵ. In ref. [6], an appropriate projection operator which removes all of these quantities has been introduced. However, to order ϵ it is sufficient to define $A(k)$ to be composed of the Brownian particle number and momentum densities

$$A(k) = \begin{pmatrix} \hat{N}_1(k) \\ P_1(k) \equiv p_0\, e^{ik\cdot r_0} \end{pmatrix}. \tag{4.3}$$

There are an infinite number of slow single particle densities of the system, however, since the density of any analytic function of the Brownian particle is a slow variable. It can be shown that these additional single particle slowly varying densities do not effect the subsequent analysis to leading order in ϵ, although they do contribute to the diffusion constant at order ϵ. For simplicity, we will not include the non-linear momentum densities in the set $A(k)$ and will restrict our attention only to the leading order terms in ϵ.

The generalized diffusion coefficient for the Brownian particle is defined to be

$$D(k, z) \equiv \frac{1}{3M^2}\langle P_1(k, z)\cdot P_1(-k)\rangle . \tag{4.4}$$

To evaluate this correlation function in the mode coupling formalism, it is convenient to define the single particle density of the force exerted by the fluid on the Brownian particle,

$$F_1(k) \equiv \sum_{i=1}^{N} \nabla r_i \phi(|r_{0i}|)\, e^{ik\cdot r_0}\,, \tag{4.5}$$

and define $A'(k)$ to be

$$A'(k) = \begin{pmatrix} \hat{N}_1(k) \\ P_1(k) \\ F_1(k) \end{pmatrix}. \tag{4.6}$$

Using the Mori hierarchy [7], the diffusion constant is given by

$$D = \lim_{k,z\to 0} \frac{\langle P_1 \cdot P_1\rangle^2}{3M^2\langle F_1 \cdot F_1\rangle} \langle \dot{F}_1(k, z) \cdot \dot{F}_1(k)^*\rangle \cdot \langle F_1 \cdot F_1\rangle^{-1}\,, \tag{4.7}$$

where

$$\langle \dot{F}_1(k, z) \cdot \dot{F}_1(k)^*\rangle = \int_0^\infty d\tau\, \langle (e^{i(1-\tilde{\mathscr{P}})L\tau}(1-\tilde{\mathscr{P}})\dot{F}_1(k)) \cdot \dot{F}_1(k)^*\rangle\, e^{-z\tau} \tag{4.8}$$

and

$$\tilde{\mathscr{P}}B(k) \equiv \langle B(k)\, A'(k)^*\rangle \cdot \langle A'(k)\, A'(k)^*\rangle^{-1} \cdot A'(k)\,. \tag{4.9}$$

The advantage of applying the mode coupling formalism to the generalized Langevin equation of the correlation function of $F_1(k)$ is that all the slowly varying behavior of the correlation function due to the linear variables has been projected out of the transport coefficient (eq. (4.8)) so that the correlation function exists as epsilon approaches zero. If we derived a generalized Langevin equation for $P_1(k)$ instead of $F_1(k)$, we would discover that the memory function $\gamma(k, z)$, which appears in the generalized Langevin equation for $P_1(k)$,

$$\begin{aligned}\gamma(k, z) &\equiv \frac{\langle \dot{P}_1(k, z) \cdot \dot{P}_1(k)^*\rangle}{MK_BT} \\ &= \frac{1}{MK_BT} \int_0^\infty d\tau\, \langle (e^{i(1-\mathscr{P}_A)L\tau}(1-\mathscr{P}_A)\dot{P}_1(k)) \cdot \dot{P}_1(k)^*\rangle\, e^{-z\tau}\,,\end{aligned} \tag{4.10}$$

where $\mathscr{P}_A B(k) \equiv \langle B(k)\, A(k)^*\rangle \cdot \langle A(k)\, A(k)^*\rangle \cdot A(k)$, is proportional to ϵ^2. To evaluate D to leading order in ϵ from this starting point would be unnecessarily difficult since all terms in eq. (4.10) of order ϵ^2 must be identified and retained, which proves to be difficult. Therefore, it is much simpler to apply the mode coupling formalism to the autocorrelation function of the force exerted on the Brownian particle by the fluid starting from the expression for D given in eq. (4.7). The calculations below will be carried out to lowest order in ϵ, i.e. ϵ^0.

We define the column vector $B(\boldsymbol{k})$ to be the densities of hydrodynamic variables, which we assume to be the only slowly varying $N+1$ particle densities of the system,

$$B(\boldsymbol{k}) = \begin{pmatrix} \sigma(\boldsymbol{k}) \\ -\sigma(\boldsymbol{k}) \\ T(\boldsymbol{k}) \\ \eta_1(\boldsymbol{k}) \\ \eta_2(\boldsymbol{k}) \end{pmatrix}, \tag{4.11}$$

where the hydrodynamic densities can be written as a linearly independent combination of the densities $N(\boldsymbol{k})$, $E(\boldsymbol{k})$ and $\boldsymbol{P}(\boldsymbol{k})$ as

$$\begin{aligned} \pm\sigma(\boldsymbol{k}, t) &= \frac{\chi_n}{c_0}\,\hat{N}(\boldsymbol{k}, t) + \frac{\chi_e}{c_0}\,\hat{E}(\boldsymbol{k}, t) \pm \boldsymbol{P}(\boldsymbol{k}, t)\cdot\hat{\boldsymbol{k}}\,, \\ T(\boldsymbol{k}, t) &= \hat{E}(\boldsymbol{k}, t) - \frac{h}{\rho}\,\hat{N}(\boldsymbol{k}, t)\,, \\ \eta_j(\boldsymbol{k}, t) &= \boldsymbol{P}(\boldsymbol{k}, t)\cdot\hat{\boldsymbol{k}}_{\perp j}\,, \end{aligned} \tag{4.12}$$

where $j = 1, 2$, c_0 is the zero frequency adiabatic sound speed, h is the enthalpy density, e is the energy density, ρ is the average number density, $\hat{\boldsymbol{k}}$ is the unit vector along $\boldsymbol{k}$, $\hat{\boldsymbol{k}}_{\perp j}$ are two unit vectors perpendicular to each other and to $\hat{\boldsymbol{k}}$, and χ_n and χ_e are $(\partial p/\partial n)_e$ and $(\partial p/\partial e)_n$, respectively, where p is the pressure of the system. These modes diagonalize both $M_{11}(\boldsymbol{k}, z)$ and $\tilde{M}(\boldsymbol{k}, z)$ to order k^2. With the definitions in (4.11), $\tilde{M}(\boldsymbol{k}, z)$ to order $k^{5/2}$ and leading N order is

$$\begin{aligned} \tilde{M}^{\rm cc}(\sigma(\boldsymbol{k}); \sigma(\boldsymbol{k}), z) &= \mathrm{i}c_0 k - \frac{\Gamma(k, z)\,k^2}{m\rho}\,, \\ \tilde{M}^{\rm cc}(-\sigma(\boldsymbol{k}); -\sigma(\boldsymbol{k}), z) &= -\mathrm{i}c_0 \boldsymbol{k} - \frac{\Gamma(k, z)\,k^2}{m\rho}\,, \\ \tilde{M}^{\rm cc}(T(\boldsymbol{k}); T(\boldsymbol{k}), z) &= -\frac{\Gamma_T(k, z)\,k^2}{m\rho}\,, \\ \tilde{M}^{\rm cc}(\eta_j(\boldsymbol{k}); \eta_j(\boldsymbol{k}), z) &= \frac{\eta(k, z)\,k^2}{m\rho}\,, \end{aligned} \tag{4.13}$$

where $j=1, 2$, $\Gamma(k, z)$, $\Gamma_T(k, z)$ and $\eta(k, z)$ are the sound attenuation rate, thermal diffusivity, and shear relaxation rate coefficients, respectively, for the simple fluid in the absence of the Brownian particle.

From eq. (3.21), we have

$$\tilde{M}(\boldsymbol{F}_1(\boldsymbol{k}), \boldsymbol{F}_1(\boldsymbol{k}), z) = M_{11}^{\mathrm{ss}}(\boldsymbol{F}_1(\boldsymbol{k}), \boldsymbol{F}_1(\boldsymbol{k}), z) + \sum_{i=2}^{\infty} \Theta^{(i)}(\boldsymbol{F}_1(\boldsymbol{k}), \boldsymbol{F}_1(\boldsymbol{k}), z) ,$$

so that

$$\begin{aligned}\tilde{\boldsymbol{\nu}}(\boldsymbol{k}, z) &\equiv \int_0^{\infty} \mathrm{d}\tau \; \mathrm{e}^{-z\tau} \langle (\mathrm{e}^{\mathrm{i}(1-\tilde{\mathscr{P}})L\tau}(1-\tilde{\mathscr{P}})\dot{\boldsymbol{F}}_1(\boldsymbol{k}))\dot{\boldsymbol{F}}_1(\boldsymbol{k})^* \rangle \cdot \langle \boldsymbol{F}_1(\boldsymbol{k})\,\boldsymbol{F}_1(\boldsymbol{k})^* \rangle^{-1} \\ &= \int_0^{\infty} \mathrm{d}\tau \, \mathrm{e}^{-z\tau} \langle (\mathrm{e}^{\mathrm{i}(1-\mathscr{P})L\tau}(1-\mathscr{P})\dot{\boldsymbol{F}}_1(\boldsymbol{k}))\dot{\boldsymbol{F}}_1(\boldsymbol{k})^* \rangle \cdot \langle \boldsymbol{F}_1(\boldsymbol{k})\,\boldsymbol{F}_1(\boldsymbol{k})^* \rangle^{-1} \\ &\quad + \sum_{i=2}^{\infty} \Theta^{(i)}(\boldsymbol{F}_1(\boldsymbol{k}), \boldsymbol{F}_1(\boldsymbol{k}), z) \equiv \boldsymbol{\nu}(\boldsymbol{k}, z) + \sum_{i=2}^{\infty} \Theta_{\mathrm{FF}}^{(i)}(\boldsymbol{k}, z) . \end{aligned} \tag{4.14}$$

Here and below we omit the superscripts ssm, but must keep in mind that all the quantities which appear in Θ are of the ssm type. We expect that $\boldsymbol{\nu}(\boldsymbol{k}, z)$ is an analytic function of k and z since

$$\mathrm{e}^{\mathrm{i}(1-\mathscr{P})L\tau}(1-\mathscr{P})\dot{\boldsymbol{F}}_1(\boldsymbol{k})$$

has all slowly varying behavior removed from it by the full projection operator $\mathscr{P}$, whereas

$$\mathrm{e}^{\mathrm{i}(1-\tilde{\mathscr{P}})L\tau}(1-\tilde{\mathscr{P}})\dot{\boldsymbol{F}}_1(\boldsymbol{k})$$

has projections onto Q_i for $i \geq 2$ and therefore still retains slow characteristics and non-analytic k and z (and hence R) dependences. Keyes and Oppenheim [2] showed that $\boldsymbol{\nu}(\boldsymbol{k}, z)$ can be ignored compared to $\Theta_{\mathrm{FF}}^{(i)}$ provided $K_{\mathrm{C}} R \gg 1$. Since $R \sim 10^{-3}$ cm for a macroscopic particle and $K_{\mathrm{c}} \sim 10^{7}$ cm, $K_{\mathrm{c}} R \gg 1$ and hence $\boldsymbol{\nu}(\boldsymbol{k}, z)$ can be ignored in eq. (4.14). Combining (4.7) and (4.14), we have

$$D = \lim_{k,z,\epsilon \to 0} \frac{\langle \boldsymbol{P}_1(\boldsymbol{k}) \cdot \boldsymbol{P}_1(\boldsymbol{k}) \rangle^2}{3M^2 \langle \boldsymbol{F}_1(\boldsymbol{k}) \cdot \boldsymbol{F}_1(\boldsymbol{k})^* \rangle} \operatorname{Tr} \sum_{i=2}^{\infty} \Theta_{\mathrm{FF}}^{(i)}(\boldsymbol{k}, z) , \tag{4.15}$$

where Tr indicates the trace operator.

The first few terms of $\Sigma_{i=2}^{\infty} \Theta_{\mathrm{FF}}^{(i)}(\boldsymbol{k}, z)$ look like

$$\sum_{i=2}^{\infty} \Theta_{\mathrm{FF}}^{(i)}(\boldsymbol{k}, z) = \sum_{m,j=1}^{2} \sum_{l,i=1}^{5} \sum_{\boldsymbol{q}} \hat{M}_{12}(\boldsymbol{F}_1(\boldsymbol{k}); b_i(\boldsymbol{q})\, a_j(\boldsymbol{k}-\boldsymbol{q}))$$
$$\cdot\, G_{22}(b_i(\boldsymbol{q}), a_j(\boldsymbol{k}-\boldsymbol{q}); b_l(\boldsymbol{q})\, a_m(\boldsymbol{k}-\boldsymbol{q}))$$
$$\cdot\, \hat{M}_{21}(b_l(\boldsymbol{q}), a_m(\boldsymbol{k}-\boldsymbol{q}); \boldsymbol{F}_1(\boldsymbol{k}))$$
$$+ \hat{M}_{12} * G_{22} \cdot X_{22} * G_{22} \cdot \hat{M}_{21} + \hat{M}_{13} * G_{33} \cdot \hat{M}_{31} + \cdots ,$$

where the a_j are from the set A and the b_j are from the set B. We shall always order the tagged particle on the far right of the correlation function in order to avoid overcounting a particular product of densities since $b_i(\boldsymbol{q})\, a_j(-\boldsymbol{q})$ and $a_j(\boldsymbol{q})\, b_i(-\boldsymbol{q})$ give the same average in a correlation function. Since we are interested only in the leading power of $1/R$ and the limit where k, z and ϵ approach zero, only a few terms of $\hat{M}_{12}$ and $\hat{M}_{21}$ actually contribute. These are

$$\hat{M}_{12}^{\mathrm{E}}(\boldsymbol{F}_1; \pm\sigma(\boldsymbol{q})\, N_1(-\boldsymbol{q})) = \hat{M}_{12}^{\mathrm{E}}(\boldsymbol{F}_1; \pm\hat{\boldsymbol{q}} \cdot \boldsymbol{P}(\boldsymbol{q})\, N_1(-\boldsymbol{q}))$$
$$= \mp \frac{\langle (\mathrm{i}L_0 \nabla \boldsymbol{r}_0\, \Sigma_{j=1}^{N}\, \phi(|\boldsymbol{r}_{j0}|))\, \Sigma_{i=1}^{N}\, \hat{\boldsymbol{q}} \cdot \boldsymbol{p}_i\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i0}} \rangle}{\langle N \rangle m K_{\mathrm{B}} T}$$
$$+ \mathcal{O}(\epsilon) ,$$

$$\hat{M}_{21}^{\mathrm{E}}(\pm\sigma(\boldsymbol{q})\, N_1(-\boldsymbol{q}); \boldsymbol{F}_1)$$
$$= \pm \frac{\langle (\mathrm{i}L_0 \nabla \boldsymbol{r}_0\, \Sigma_{j=1}^{N}\, \phi(|\boldsymbol{r}_{j0}|))\, \Sigma_{i=1}^{N}\, \hat{\boldsymbol{q}} \cdot \boldsymbol{p}_i\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i0}} \rangle}{\frac{1}{3}\langle \boldsymbol{F}_1 \cdot \boldsymbol{F}_1 \rangle} + \mathcal{O}(\epsilon)$$

and

$$\hat{M}_{12}^{\mathrm{E}}(\boldsymbol{F}_1; \eta_i(\boldsymbol{q})\, N_1(-\boldsymbol{q}))$$
$$= - \frac{\langle (\mathrm{i}L_0 \nabla \boldsymbol{r}_0\, \Sigma_{j=1}^{N}\, \phi(|\boldsymbol{r}_{j0}|))\, \Sigma_{i=1}^{N}\, \hat{\boldsymbol{q}}_{\perp i} \cdot \boldsymbol{p}_i\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i0}} \rangle}{\langle N \rangle m K_{\mathrm{B}} T} + \mathcal{O}(\epsilon) , \qquad (4.16)$$

$$\hat{M}_{21}^{\mathrm{E}}(\eta_i(\boldsymbol{q})\, N_1(-\boldsymbol{q}); \boldsymbol{F}_1)$$
$$= \frac{\langle (\mathrm{i}L_0 \nabla \boldsymbol{r}_0\, \Sigma_{j=1}^{N}\, \phi(|\boldsymbol{r}_{j0}|))\, \Sigma_{i=1}^{N}\, \hat{\boldsymbol{q}}_{\perp i} \cdot \boldsymbol{p}_i\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i0}} \rangle}{\frac{1}{3}\langle \boldsymbol{F}_1 \cdot \boldsymbol{F}_1 \rangle} + \mathcal{O}(\epsilon) . \qquad (4.17)$$

The propagator $G_{\mathrm{p}}(\boldsymbol{q}, z)$ is given by

$$G_{\mathrm{p}}(\boldsymbol{q}, z) = (\boldsymbol{I} - \hat{\boldsymbol{q}}\hat{\boldsymbol{q}}) G_{\mathrm{tp}}(\boldsymbol{q}, z) + \hat{\boldsymbol{q}}\hat{\boldsymbol{q}} G_{\ell\mathrm{p}}(\boldsymbol{q}, z) ,$$

where

$$G_{\ell\mathrm{p}}(\boldsymbol{q}, z) = \mathscr{L}(\mathscr{L}^{-1}(zI - \tilde{M}^{\mathrm{cc}}(\pm\sigma(\boldsymbol{q}), z))^{-1}\mathscr{L}^{-1}(zI - \tilde{M}^{\mathrm{ss}}(-\boldsymbol{q}, z))^{-1}_{N_1N_1})$$
$$= \frac{1}{z + Dq^2 \pm \mathrm{i}c_0 q + \Gamma q^2} + \mathscr{O}(q^{-3/2}) ,$$
$$G_{\mathrm{tp}}(\boldsymbol{q}, z) = \mathscr{L}(\mathscr{L}^{-1}(zI - \tilde{M}^{\mathrm{cc}}(\eta_i(\boldsymbol{q}), z))^{-1}\mathscr{L}^{-1}(zI - \tilde{M}^{\mathrm{ss}}(-\boldsymbol{q}, z))^{-1}_{N_1N_1})$$
$$= \frac{1}{z + Dq^2 + \eta q^2} + \mathscr{O}(q^{-3/2}) . \quad (4.18)$$

It should be noted that the transport coefficients which appear in (4.18) are the "dressed", experimentally observable coefficients rather than "bare" transport coefficients which are often encountered in other derivations of the Stokes–Einstein law from microscopic principles [2, 3]. For large Brownian particles in normal fluids, $D \ll \eta$, and hence the D appearing in the propagators G can be ignored.

Since

$$\langle \boldsymbol{F}_1 \boldsymbol{F}_1 \rangle = \boldsymbol{I}\langle F_{1x}^2 \rangle = K_{\mathrm{B}}T\left\langle \nabla_{r_{0x}}\nabla_{r_{0x}} \sum_{j=1}^{N} \phi(|\boldsymbol{r}_{j0}|)\right\rangle \boldsymbol{I} ,$$

we get

$$\langle F_{1x}^2 \rangle \approx \tfrac{4}{3}\pi K_{\mathrm{B}}T \int \mathrm{d}r\, r^2 \rho(r)\, \phi''(r) , \quad (4.19)$$

where $\rho(r)$ is the pair distribution function for Brownian-fluid particles, since

$$\nabla \boldsymbol{r}_0 \nabla \boldsymbol{r}_0 \phi(|\boldsymbol{r}_{10}|) \approx \left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}\, \phi(r)\right)\hat{\boldsymbol{r}}\hat{\boldsymbol{r}} \equiv \phi''(r)\, \hat{\boldsymbol{r}}\hat{\boldsymbol{r}} ,$$

for a short ranged and steep potential. The pair distribution function for the Brownian-fluid particle $\rho(r)$ is defined formally as

$$\rho(r) = \rho\, \mathrm{e}^{-\beta\omega(r)} ,$$

where $\omega(r)$ is the potential of the mean force between the Brownian particle and the fluid particle. Following Madden and Masters [4], we use the fact that $\phi''(r)$ is strongly peaked around the radius of the Brownian particle so that for an arbitrary continuous function $D(r)$,

$$\int \mathrm{d}r\, 4\pi r^2 \rho(r)\, \phi''(r)\, D(r) \approx D(R) \int \mathrm{d}r\, 4\pi r^2 \rho(r)\, \phi''(r) \equiv D(R)\, C , \quad (4.20)$$

and hence eq. (4.19) may be written as

$$\langle F_{1x}^2 \rangle \approx \tfrac{1}{3} K_B T C . \tag{4.21}$$

Applying the same approximation to the correlation function in the numerator of $\hat{M}_{12}^{E}$ and $\hat{M}_{21}^{E}$ gives

$$\begin{aligned} &\pm \left\langle \left(iL_0 \nabla r_0 \sum_{j=1}^{N} \phi(|r_{j0}|) \right) \sum_{i=1}^{N} p_i \, e^{iq\cdot r_{i0}} \right\rangle \\ &\quad = \mp i K_B T C (\hat{q}\hat{q} a(qR) + (I - \hat{q}\hat{q}) b(qR)) , \end{aligned} \tag{4.22}$$

where $a(x) \equiv j_0(x) - \frac{2}{3}\chi(x)$ and $b(x) \equiv \frac{1}{3}\chi(x)$ with

$$j_0(x) = \frac{\sin x}{x} \quad \text{and} \quad \chi(x) = \frac{3\sin x - 3x\cos x}{x^3} . \tag{4.23}$$

It should be noted that $j_0(x)$ is a spherical Bessel function and that $\chi(x)$ can be written as the sum of two spherical Bessel functions, $\chi(x) = j_0(x) + j_2(x)$.

Putting eqs. (4.21), (4.16), (4.17), and (4.22) together, we see that $\hat{M}_{12}^{E}$ and $\hat{M}_{21}^{E}$ are approximately

$$\begin{aligned} &\hat{M}_{12}^{E}(F_1; P(q)\, N_1(-q)) \approx \frac{-iC}{\langle N \rangle m} (\hat{q}\hat{q} a(qR) + (I - \hat{q}\hat{q}) b(qR)) , \\ &\hat{M}_{21}^{E}(P(q)\, N_1(-q); F_1) \approx 3 i K_B T (\hat{q}\hat{q} a(qR) + (I - \hat{q}\hat{q}) b(qR)) , \end{aligned} \tag{4.24}$$

so that the first term of $\Theta_{FF}^{(i)}$ is

$$\begin{aligned} \Theta_{FF}^{(2)} &= \frac{3K_B T C}{\rho m} \sum_{q} (\hat{q}\hat{q} a(qR) + (I - \hat{q}\hat{q}) b(qR)) \\ &\quad \cdot ((I - \hat{q}\hat{q}) G_{tp}(q, z) + \hat{q}\hat{q} G_{\ell p}(q, z)) \cdot (\hat{q}\hat{q} a(qR) + (I - \hat{q}\hat{q}) b(qR)) \\ &= \frac{3K_B T C}{\rho m} \left(\frac{1}{2\pi} \right)^3 \int dq \, (\hat{q}\hat{q} a(qR)^2 G_{\ell p}(q) + (I - \hat{q}\hat{q}) b(qR)^2 G_{tp}(q)) . \end{aligned} \tag{4.25}$$

When the integrals are evaluated, the terms containing the longitudinal propagator $G_{\ell p}(q)$ are of $\mathcal{O}(c_0 R^{-2})$ while the integral over the transverse component gives the contribution

$$D^{(0)} = \frac{K_B T}{5\pi\eta R} , \tag{4.26}$$

where $D^{(n)}$ is the contribution to D from $\Theta_{\mathrm{FF}}^{(n+2)}$. If the higher order (dissipative) parts of the $\hat{M}_{12}$ and $\hat{M}_{21}$ vertices are used in $\Theta_{\mathrm{FF}}^{(2)}$, the integrand has at least one additional factor of q in the numerator, which yields terms of order $(1/R)^2$. Furthermore, the correction terms to the approximation for the propagators in eq. (4.18) which are of order $q^{-3/2}$ give terms of order $(1/R)^{3/2}$ and higher.

Analysis of the $\hat{M}_{13}$ and $\hat{M}_{31}$ vertices reveals that they are functions of qR and q_1R, which implies that the contribution of D^0 from $\hat{M}_{13} * G_{33} * \hat{M}_{31}$ is of order $(1/R)^2$:

$$\int_0^\infty \frac{\mathrm{d}\boldsymbol{q}\,\mathrm{d}\boldsymbol{q}_1}{q^2 q_1^2}\, f(q_1R)\, g(qR) \sim \mathcal{O}(R^{-2}) .$$

In general, the contribution from the term $\hat{M}_{1n} * G_{nn} \cdot \hat{M}_{n1}$ is of order $(1/R)^{n-1}$, and so to leading order in powers of $(1/R)$,

$$D^{(0)} = \frac{K_{\mathrm{B}}T}{5\pi\eta R} + \mathcal{O}(R^{-3/2}) .$$

At first glance, it appears that each vertex is a function of q_iR rather than q_i so that each additional integration introduces at least another factor of $(1/R)$. If this were true then we would have $D = D^{(0)}$ to order $(1/R)$ and the Stokes–Einstein law would not be recovered. We shall expand the intermediate vertices X_{nm} that appear in $\Theta_{\mathrm{FF}}^{(i)}$ for $i \geq 3$ in powers of R by exploiting the difference between correlation lengths for the Brownian-fluid particle pair distribution function and the fluid–fluid pair distribution function. Using this difference, it will be established that the tagged particle correlation functions involving only short range fluid–fluid functions give terms proportional to $R^3\chi(qR, q_1R, \ldots)$ plus correction terms of order $R^2\xi\chi$. It is then fairly easy to establish that an infinite number of terms involving only bilinear modes contribute to D to leading order in $1/R$.

To illustrate the expansion of correlation functions of the densities, we shall examine

$$\begin{aligned}
&\langle N(\boldsymbol{q})\, N_1(-\boldsymbol{q})\, N(\boldsymbol{q}_1)^*\, N_1(-\boldsymbol{q}_1)^* \rangle \\
&= \sum_{i,j=1}^{N} \langle \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i0}}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{j0}} \rangle \\
&= \langle N\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{10}} \rangle + \langle N(N-1)\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{10}}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{20}} \rangle \\
&= \frac{\rho}{V} \int \mathrm{d}\boldsymbol{r}_0\, \mathrm{d}\boldsymbol{r}_1\, g_{10}\, \mathrm{e}^{\mathrm{i}(\boldsymbol{q}-\boldsymbol{q}_1)\cdot\boldsymbol{r}_{10}} + \frac{\rho^2}{V} \int \mathrm{d}\boldsymbol{r}_0\, \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, g_{012}\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{10}}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{20}} ,
\end{aligned} \tag{4.27}$$

where $\boldsymbol{q}$ and $\boldsymbol{q}_1$ are non-zero and $\boldsymbol{q} \neq \boldsymbol{q}_1$, $g_{10} \equiv \rho(r_{10})/\rho$ is the Brownian-fluid radial distribution function and g_{012} is the Brownian-fluid triplet radial distribution function. For simplicity, we shall model g_{10} by

$$g_{10} = \begin{cases} 0, & \text{if } r_{10} \leq R\,, \\ \mathcal{O}(1), & \text{if } R < r_{10} \leq R + \xi\,, \\ 1, & \text{if } r_{10} > R + \xi\,. \end{cases} \tag{4.28}$$

where ξ is a short correlation length which corresponds approximately to the fluid–fluid correlation length; that is, $g_{12} = 1$ for $r_{12} > \xi$, where g_{12} is the fluid–fluid radial distribution function. Furthermore, we define the short ranged function ω_{012} by

$$g_{012} \equiv g_{01} g_{02} g_{12}\, \mathrm{e}^{-\omega_{012}}\,, \tag{4.29}$$

where $\omega_{012} = 0$ if either r_{01} or $r_{02} \leq R$, r_{01} or $r_{02} > R + \xi$, or $r_{12} > \xi$. If we define the cluster functions $f_{01} \equiv g_{01} - 1$, $f_{02} \equiv g_{02} - 1$, $f_{12} \equiv g_{12} - 1$ and $f_{012} \equiv \mathrm{e}^{-\omega_{012}} - 1$, we see that the first term in eq. (4.27) is given by

$$-\rho\left(\int_0^R r^2\, \mathrm{d}r \int \mathrm{d}\hat{\boldsymbol{r}}\, \mathrm{e}^{\mathrm{i}(\boldsymbol{q}-\boldsymbol{q}_1)\cdot \boldsymbol{r}} + \int_R^{R+\xi} r^2\, \mathrm{d}r \int \mathrm{d}\hat{\boldsymbol{r}}\, (g_{10} - 1)\, \mathrm{e}^{\mathrm{i}(\boldsymbol{q}-\boldsymbol{q}_1)\cdot \boldsymbol{r}} \right)$$
$$= -\rho\, \frac{4\pi R^3}{3}\, \chi(|\boldsymbol{q} - \boldsymbol{q}_1|R) + \mathcal{O}(R^2 \xi) \equiv h(|\boldsymbol{q} - \boldsymbol{q}_1|R)\,,$$

where the correction term comes from the region $r \in [R, R + \xi]$. If we expand g_{012} in terms of cluster functions, we get

$$g_{012} = (1 + f_{012})(1 + f_{01})(1 + f_{02})(1 + f_{12})$$
$$= (1 + f_{012})(1 + f_{01} + f_{02} + f_{12} + f_{01} f_{02} + f_{01} f_{12} + f_{02} f_{12} + f_{01} f_{02} f_{12})\,.$$

We first examine the contribution of terms independent of f_{012} in the second integral on the right hand side of (4.27). Since $\boldsymbol{q} \neq \boldsymbol{q}_1$ and both $\boldsymbol{q}$ and $\boldsymbol{q}_1$ are non-zero, the term $(1 + f_{01} + f_{02} + f_{12})$ from g_{012} gives no contribution to the integral in eq. (4.27). However, all products of two distribution functions give significant contributions:

$$\frac{\rho^2}{V} \int \mathrm{d}\boldsymbol{r}_0\, \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot \boldsymbol{r}_{10}}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot \boldsymbol{r}_{20}} (f_{01} f_{02} + f_{01} f_{12} + f_{02} f_{12})$$
$$= h(qR)\, h(q_1 R) + h(|\boldsymbol{q} - \boldsymbol{q}_1|R)\rho \int \mathrm{d}\boldsymbol{r}_{12}\, f_{12} (\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot \boldsymbol{r}_{12}} + \mathrm{e}^{\mathrm{i}\boldsymbol{q}_1\cdot \boldsymbol{r}_{12}})$$
$$= h(qR)\, h(q_1 R) + 2h(|\boldsymbol{q} - \boldsymbol{q}_1|R)\rho \int \mathrm{d}\boldsymbol{r}_{12}\, f_{12} (1 + \mathcal{O}(q\xi))\,.$$

Now $f_{01}f_{02}f_{12} = f_{01}^2 f_{12} + f_{01}f_{12}(f_{02} - f_{01})$, so

$$\int \mathrm{d}\boldsymbol{r}_0\, \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\; \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{10}}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{20}} f_{01}f_{02}f_{12} = I_1 + I_2\,,$$

where

$$I_1 = \int \mathrm{d}\boldsymbol{r}_0\, \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\; \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{10}}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{20}} f_{01}^2 f_{12}$$
$$= -h(|\boldsymbol{q} - \boldsymbol{q}_1|R)\rho \int \mathrm{d}\boldsymbol{r}_{12}\, f_{12} + \mathcal{O}(R^2\xi)\,,$$

$$I_2 = \int \mathrm{d}\boldsymbol{r}_0\, \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\; \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{10}}\, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{20}} f_{01}f_{12}(f_{02} - f_{01})\,.$$

Now $f_{12}(f_{02} - f_{01})$ is non-zero for $r_{01} \leqslant R - 2\xi$ only if $r_{02} \geqslant R$ and $r_{12} \leqslant \xi$. However these conditions can never be met since

$$r_{02} = (r_{01}^2 + r_{12}^2 + 2\boldsymbol{r}_{12}\cdot\boldsymbol{r}_{01})^{1/2}$$
$$\leqslant (R^2 - 4\xi R + 4\xi^2 + \xi^2 + 2(R - 2\xi)\xi)^{1/2} = R - \xi < R\,.$$

Thus, I_2 is non-zero only if $r_{10} \in [R - 2\xi, R + \xi]$, which implies that I_2 is ξ dependent and of order $R^2\xi$ at best. Similarly, the terms containing f_{012} exist only in the limits where both r_{01} and r_{02} are in the region $[R, R + \xi]$, and are therefore also ξ dependent and of lower order in R. Thus

$$\langle N(\boldsymbol{q})\, N_1(-\boldsymbol{q})\, N(\boldsymbol{q}_1)^*\, N_1(-\boldsymbol{q}_1)^*\rangle$$
$$= -\rho\, \frac{4\pi R^3}{3}\, \chi(|\boldsymbol{q} - \boldsymbol{q}_1|R)\, \frac{\langle \hat{N}\hat{N}\rangle}{\langle N\rangle} + \rho^2\left(\frac{4\pi R^3}{3}\right)^2 \chi(qR)\, \chi(q_1 R)$$
$$+ \mathcal{O}(\xi R^2)\,,$$

and since

$$\langle N(\boldsymbol{q})\, N_1(-\boldsymbol{q})\rangle = -\rho\, \frac{4\pi R^3}{3}\, \chi(qR) + \mathcal{O}(R^2\xi)\,,$$

we conclude that

$$\langle(\widehat{N(\boldsymbol{q})\, N_1}(-\boldsymbol{q}))(\widehat{N(\boldsymbol{q}_1)^*\, N_1}(-\boldsymbol{q}_1)^*)\rangle$$
$$= -\rho\, \frac{4\pi R^3}{3}\, \chi(|\boldsymbol{q} - \boldsymbol{q}_1|R)\, \frac{\langle \hat{N}\hat{N}\rangle}{\langle N\rangle}\, (1 + \mathcal{O}(q\xi)) + \mathcal{O}(R^2\xi)\,. \qquad (4.30)$$

The same techniques can be applied to the vertex $X_{22}(\boldsymbol{P}(\boldsymbol{q})\,N_1(-\boldsymbol{q});\ \boldsymbol{P}(\boldsymbol{q}_1)\,N_1(-\boldsymbol{q}_1))$, which is given by

$$X_{22} = -\int_0^\infty \mathrm{d}\tau \sum_{i,j=1}^{N} \frac{\langle (\mathrm{e}^{\mathrm{i}(1-\mathcal{P})L_0\tau}(1-\mathcal{P})\mathrm{i}L_0(\boldsymbol{p}_i\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i0}}))(\mathrm{i}L_0\boldsymbol{p}_j\,\mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{j0}})\rangle}{m\langle N\rangle\,K_\mathrm{B}T}\,, \tag{4.31}$$

as k, z and ϵ approach zero. Note that the term in $X \equiv \hat{M}^o - zO\cdot D^{-1}$ which involves the off-diagonal part, O, of K gives no contribution as z approaches zero. Since the time dependent correlation function has no slowly decaying behavior, it decays to zero for $\tau > \tau_\mathrm{m}$, where τ_m is a microscopic timescale. Thus we expect $(\boldsymbol{r}_{i0}(t) - \boldsymbol{r}_{i0})$ to be of the order of a few angstroms and hence

$$\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{r}_{i0}(t)-\boldsymbol{r}_{i0})} = 1 + \mathcal{O}(q\xi) \approx 1\,.$$

Since

$$\begin{aligned}\mathrm{i}L_0(\boldsymbol{p}_j\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{j0}}) &= (\mathrm{i}L_0^0 + \sum_{i=1}^{N} \boldsymbol{F}_{i0}\cdot\nabla\boldsymbol{p}_i)(\boldsymbol{p}_j\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{j0}}) \\ &= (\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{\sigma}_j + \boldsymbol{F}_{j0})\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{j0}}\,,\end{aligned}$$

where $\boldsymbol{F}_{j0}$ is the force exerted by the fluid on the Brownian particle,

$$\boldsymbol{\sigma}_j \equiv \frac{\boldsymbol{p}_j\boldsymbol{p}_j}{m} + \tfrac{1}{2}\sum_{l\neq j}^{N} \boldsymbol{r}_{jl}\boldsymbol{F}_{jl}(1 + \mathcal{O}(q\xi))$$

and

$$\mathrm{i}L_0^0 \equiv \sum_{i=1}^{N} \frac{\boldsymbol{p}_i}{m}\cdot\nabla\boldsymbol{r}_i - \tfrac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} \nabla\boldsymbol{r}_i u(|\boldsymbol{r}_{ij}|)\cdot\nabla\boldsymbol{p}_i\,,$$

X_{22} is given approximately by

$$X_{22} = -\int_0^\infty \mathrm{d}\tau \sum_{i,j=1}^{N} \frac{\langle (\mathrm{e}^{\mathrm{i}(1-\mathcal{P})L_0^0\tau}(1-\mathcal{P})\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{\sigma}_i)(\boldsymbol{\sigma}_j\cdot -\mathrm{i}\boldsymbol{q}_1)\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i0}}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{j0}})\rangle}{m\langle N\rangle\,K_\mathrm{B}T} + \mathcal{O}(R^0)\,. \tag{4.32}$$

The terms in eq. (4.32) involving the Brownian particle force can be ignored to leading order in $(1/R)$ since they give functions of $|\boldsymbol{q}-\boldsymbol{q}_1|R$, and therefore give contributions to D of order $(1/R)^4$. By applying the approximation techniques used to obtain eq. (4.30), it can be shown that

$$\begin{aligned}\langle (\mathrm{e}^{\mathrm{i}L_0^0\tau}\boldsymbol{\sigma}_i)\boldsymbol{\sigma}_j\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i0}}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{j0}}\rangle &= \left\langle\!\!\left\langle \sum_{n=0}^{\infty}\frac{\tau^n}{n!}\,((\mathrm{i}L_0^0)^n\boldsymbol{\sigma}_i)\boldsymbol{\sigma}_j\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i0}}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{j0}}\right\rangle\!\!\right\rangle \\ &= -\rho\,\frac{4\pi R^3}{3\langle N\rangle}\,\chi(|\boldsymbol{q}-\boldsymbol{q}_1|R)\left\langle\!\!\left\langle \sum_{n=0}^{\infty}\frac{\tau^n}{n!}\,(\mathrm{i}L_0^0)^n\boldsymbol{\sigma}_i\right\rangle\boldsymbol{\sigma}_j\right\rangle \\ &\quad + \sum_{n=0}^{\infty}\frac{\tau^n}{\langle N\rangle n!}\,\langle(\mathrm{i}L_0^0)^n\boldsymbol{\sigma}_i\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{i0}}\rangle\langle\boldsymbol{\sigma}_j\,\mathrm{e}^{-\mathrm{i}\boldsymbol{q}_1\cdot\boldsymbol{r}_{j0}}\rangle)\rangle\,. \end{aligned}\tag{4.33}$$

Note that the propagator in X_{22} contains $(1-\mathcal{P})$. Since $\mathcal{P}$ projects onto $Q_0\equiv 1$, $(1-\mathcal{P})$ subtracts off the second term on the right hand side of eq. (4.33), which implies that X_{22} is proportional to $R^3\chi(|\boldsymbol{q}-\boldsymbol{q}_1|R)$. The projections onto the other variables Q_i for $i\geq 1$ either vanish as ϵ and k approach zero, give terms which involve the force of the Brownian particle or give extra factors of $\boldsymbol{q}$ or $\boldsymbol{q}_1$, all of which can be neglected to leading powers of $1/R$. Thus we may finally conclude that

$$X_{22}=\rho\,\frac{4\pi R^3}{3mK_\mathrm{B}T\langle N\rangle^2}\,\chi(|\boldsymbol{q}-\boldsymbol{q}_1|R)\int_0^\infty \mathrm{d}t\,\hat{\boldsymbol{q}}\cdot\langle\boldsymbol{\sigma}(t)\,\boldsymbol{\sigma}\rangle\cdot\hat{\boldsymbol{q}}_1\,,\tag{4.34}$$

where $\boldsymbol{\sigma}$ is the stress tensor for the fluid in the absence of the tagged particle, and the time dependence of $\boldsymbol{\sigma}(t)$ is determined only by $\mathrm{i}L_0^0$, which is the Liouvillian for the N particle fluid system in the absence of the Brownian particle. It should be noted that eq. (4.34) is the approximation used by Madden and Masters [4], and was motivated by their work. We have merely justified their approximation in a systematic fashion.

As in the case for $\hat{M}_{12} * G_{22}\cdot\hat{M}_{21}$, the leading order term of

$$\hat{M}_{12} * G_{22}\cdot X_{22} * G_{22}\cdot\hat{M}_{21}\tag{4.35}$$

in powers of $1/R$ comes from the transverse propagators terms; the terms containing the longitudinal propagator $G_{\ell\mathrm{p}}\hat{\boldsymbol{q}}\hat{\boldsymbol{q}}$ are of $\mathcal{O}(R^{-2})$ at best. Since the Green–Kubo expression for the generalized transverse viscosity $\eta(\boldsymbol{k},z)$ of a simple fluid is given by

$$\eta(\boldsymbol{k},z)=\frac{1}{VK_\mathrm{B}T}\int_0^\infty \mathrm{d}\tau\,\langle\boldsymbol{\sigma}_{xz}(\boldsymbol{k},\tau)\,\boldsymbol{\sigma}_{xz}(\boldsymbol{k})^*\rangle\,\mathrm{e}^{-z\tau}\,,$$

where $\hat{\boldsymbol{k}}$ is parallel to $\hat{z}$, we may write

$$(\boldsymbol{I}-\hat{\boldsymbol{q}}\hat{\boldsymbol{q}})\cdot X_{22}\cdot(\boldsymbol{I}-\hat{\boldsymbol{q}}_1\hat{\boldsymbol{q}}_1)=\frac{4\pi R^3}{3m\langle N\rangle}\,\chi(|\boldsymbol{q}-\boldsymbol{q}_1|R)$$
$$\times\,\eta(\hat{\boldsymbol{q}}_1\hat{\boldsymbol{q}}+(\hat{\boldsymbol{q}}_1\cdot\hat{\boldsymbol{q}})(\boldsymbol{I}-2\hat{\boldsymbol{q}}\hat{\boldsymbol{q}}-2\hat{\boldsymbol{q}}_1\hat{\boldsymbol{q}}_1)+2(\hat{\boldsymbol{q}}_1\cdot\hat{\boldsymbol{q}})^2\hat{\boldsymbol{q}}\hat{\boldsymbol{q}}_1)\,, \tag{4.36}$$

where $\eta\equiv\lim_{k,z\to 0}\eta(\boldsymbol{k},z)$. When (4.36) is placed in (4.35) and the trace is taken, it is found that

$$D^{(1)}=\frac{K_\mathrm{B}T}{3\eta}\left(\frac{1}{2\pi}\right)^6\int\frac{\mathrm{d}\boldsymbol{q}\,\mathrm{d}\boldsymbol{q}_1}{q^2q_1^2}\,\chi(qR)\,\chi(q_1R)$$
$$\times\,\tfrac{2}{3}qq_1 4\pi R^3(\hat{\boldsymbol{q}}_1\cdot\hat{\boldsymbol{q}})^3\chi(|\boldsymbol{q}-\boldsymbol{q}_1|R)\,.$$

Since

$$\int\mathrm{d}\hat{\boldsymbol{q}}\;qq_1\,\frac{R^2}{3}\,(\hat{\boldsymbol{q}}_1\cdot\hat{\boldsymbol{q}})^3\chi(|\boldsymbol{q}-\boldsymbol{q}_1|R)=4\pi H(qR,q_1R)\,,$$

where

$$H(qR,q_1R)\equiv\tfrac{1}{2}(j_0(qR+q_1R)+j_0(qR-q_1R))$$
$$-\,j_0(qR)\,j_0(q_1R)-2j_2(qR)\,j_2(q_1R)\,,$$

if follows that

$$D^{(1)}=\frac{2K_\mathrm{B}T}{3\eta}\left(\frac{1}{2\pi}\right)^6(4\pi)^2\int\mathrm{d}\hat{\boldsymbol{q}}\int_0^\infty\mathrm{d}q\,\mathrm{d}q_1\,\chi(q_1R)\,\chi(qR)\,H(qR,q_1R)\,R$$
$$=\frac{2K_\mathrm{B}T}{3\eta R}\left(\frac{1}{2\pi}\right)^6(4\pi)^3\int_0^\infty\mathrm{d}x\,\mathrm{d}x_1\,\chi(x_1)\,\chi(x)\,H(x,x_1)\,, \tag{4.37}$$

where $x\equiv qR$ and $x_1\equiv q_1R$.

The contributions to $D^{(1)}$ from trilinear and higher order densities are of order R^{-2} and higher. For example, one of the trilinear mode terms in $\Theta_{\mathrm{FF}}^{(3)}$ is $\hat{M}_{13}*G_{33}\cdot X_{32}*G_{22}\cdot\hat{M}_{21}$. If the X_{32} vertex is reduced according to eq. (3.23), it is of $\mathcal{O}(\epsilon)$ or does not involve tagged particle densities and is therefore independent of R. The completely off-diagonal vertex X_{32} can be expanded in powers of R and is of order R^3 (as is X_{22}), and therefore contributes to order

$$\int\frac{\mathrm{d}\boldsymbol{q}_1\,\mathrm{d}\boldsymbol{q}_2\,\mathrm{d}\boldsymbol{q}_3}{(q_1^2+q_2^2)q_3^2}\,\boldsymbol{q}_2R^3f(q_1R,q_2R,q_3R)\sim\mathcal{O}(R^{-3})\,,$$

and can therefore be ignored to leading order in $1/R$.

If we examine

$$\hat{M}_{12} * G_{22} \cdot X_{22} * G_{22} \cdot X_{22} * G_{22} \cdot \hat{M}_{21} , \tag{4.38}$$

it is found that since

$$\begin{aligned} &\mathrm{Tr}((\boldsymbol{I} - \hat{\boldsymbol{q}}\hat{\boldsymbol{q}}) \cdot X_{22} \cdot (\boldsymbol{I} - \hat{\boldsymbol{q}}_1\hat{\boldsymbol{q}}_1) \cdot X_{22} \cdot (\boldsymbol{I} - \hat{\boldsymbol{q}}_2\hat{\boldsymbol{q}}_2)) \\ &\quad = 2\left(\frac{4\pi R^3 \eta}{3m\langle N\rangle}\right)^2 q q_1^2 q_2 (\hat{\boldsymbol{q}}_1 \cdot \hat{\boldsymbol{q}})^3 (\hat{\boldsymbol{q}}_2 \cdot \hat{\boldsymbol{q}}_1)^3 \chi(|\boldsymbol{q} - \boldsymbol{q}_1| R)\, \chi(|\boldsymbol{q}_1 - \boldsymbol{q}_2| R) , \end{aligned}$$

we have

$$\begin{aligned} D^{(2)} &= \frac{2K_\mathrm{B}T}{3\eta R} \left(\frac{1}{2\pi}\right)^9 (4\pi)^4 (4\pi) \\ &\quad \times \int_0^\infty \mathrm{d}x\, \mathrm{d}x_1\, \mathrm{d}x_2\, \chi(x_2)\, \chi(x)\, H(x, x_1)\, H(x_1, x_2) . \end{aligned} \tag{4.39}$$

It is straightforward to show that the higher order modes also do not contribute to $D^{(2)}$ to order R^{-1}. For example, the terms in $\Theta_{\mathrm{FF}}^{(4)}$ with X_{23} and X_{32} vertices give contributions either of $\mathcal{O}(\epsilon)$ or of order

$$\int \frac{\mathrm{d}\boldsymbol{q}_1\, \mathrm{d}\boldsymbol{q}_2\, \mathrm{d}\boldsymbol{q}_3\, \mathrm{d}\boldsymbol{q}_4}{q_1^2 (q_2^2 + q_3^2) q_4^2}\, q_2 q_4 R^6 f(q_1 R, q_2 R, q_3 R, q_4 R) \sim \mathcal{O}(R^{-2}) ,$$

and, in general, terms with X_{2n} and X_{n2} give contributions at order R^{7-3n} for $n \geq 3$.

These types of arguments can be repeated at arbitrary order and it is then clear that only the bilinear modes in $\Theta_{\mathrm{FF}}^{(i)}$ contribute to order R^{-1}, and

$$\begin{aligned} D^{(n)} &= \frac{2K_\mathrm{B}T}{3\eta R} \left(\frac{4\pi}{(2\pi)^3}\right) \frac{(4\pi)^{2n}}{(2\pi)^{3n}} \int_0^\infty \mathrm{d}x\, \mathrm{d}x_1 \cdots \mathrm{d}x_{n-1}\, \chi(x_{n-1})\, \chi(x) \\ &\quad \times H(x, x_1) \cdots H(x_{n-2}, x_{n-1}) . \end{aligned} \tag{4.40}$$

To obtain eq. (4.40), we have assumed that the angular dependence of the vertices which contribute to $D^{(n)}$ are of the form

$$\begin{aligned} &2\left(\frac{4\pi R^3 \eta}{3m\langle N\rangle}\right)^n q q_1^2 q_2^2 \cdots q_{n-1}^2 q_n (\hat{\boldsymbol{q}}_1 \cdot \hat{\boldsymbol{q}})^3 (\hat{\boldsymbol{q}}_2 \cdot \hat{\boldsymbol{q}}_1)^3 \cdots (\hat{\boldsymbol{q}}_n \cdot \hat{\boldsymbol{q}}_{n-1})^3 \\ &\quad \times \chi(|\boldsymbol{q} - \boldsymbol{q}_1| R) \cdots \chi(|\boldsymbol{q}_{n-1} - \boldsymbol{q}_n| R) . \end{aligned} \tag{4.41}$$

We have verified eq. (4.41) up to order $n=3$ through tedious calculation, which strongly suggests that the form of the angular dependence of the vertices is correct for all n. However, we have not found a general argument to support this claim. We should emphasize that this assumption is also implicit in the work of Madden and Masters [4].

The integrals in eq. (4.40) can be done at all orders in n since

$$\int_0^\infty \mathrm{d}x_1\ \chi(x_1)\ H(x_1, x) = \int_0^\infty \mathrm{d}x_1\ j_2(x_1)\ H(x, x_1) = \left(\frac{3\pi}{10}\right) j_2(x)\ ,$$

and hence

$$D^{(n)} = \frac{2K_\mathrm{B}T}{3\eta R}\ \frac{1}{(2\pi^2)} \left(\frac{3}{5}\right)^n \int_0^\infty \mathrm{d}x\ \chi(x)\ j_2(x)$$

$$= \frac{K_\mathrm{B}T}{30\pi\eta R} \left(\frac{3}{5}\right)^n . \tag{4.42}$$

We can resum all the terms for $n \geq 1$ to get

$$D = D^{(0)} + \sum_{n=1}^{\infty} D^{(n)} = \frac{K_\mathrm{B}T}{5\pi\eta R} + \frac{K_\mathrm{B}T}{30\pi\eta R} \sum_{n=1}^{\infty} \left(\frac{3}{5}\right)^n = \frac{K_\mathrm{B}T}{4\pi\eta R}\ , \tag{4.43}$$

which is the Stokes–Einstein law in the "slip" limit. It should be noted that this is an alternative way of solving the integral obtained by Madden and Masters [4], whose results we have reproduced.

5. Summary and conclusions

In this paper, a systematic mode coupling theory for classical time dependent equilibrium tagged particle density correlation functions was developed using the inverse system size as a small parameter. From this formalism, self-consistent equations for tagged and $N+1$ particle correlation functions were obtained. The resulting expression is contained in eq. (3.21).

If we define $A(\boldsymbol{k}) \equiv \hat{N}_1(\boldsymbol{k})$,

$$B(\boldsymbol{k}) = \begin{pmatrix} \hat{N}(\boldsymbol{k}) \\ \hat{E}(\boldsymbol{k}) - \dfrac{\langle \hat{E}(\boldsymbol{k})\ \hat{N}(\boldsymbol{k})^* \rangle}{\langle \hat{N}(\boldsymbol{k})\ \hat{N}(\boldsymbol{k})^* \rangle}\ \hat{N}(\boldsymbol{k}) \\ \boldsymbol{P}(\boldsymbol{k}) \cdot \hat{\boldsymbol{k}} \\ \boldsymbol{P}(\boldsymbol{k}) \cdot \hat{\boldsymbol{k}}_{\perp i} \end{pmatrix}, \qquad \phi_{ab}(\boldsymbol{k}, z) = \frac{\langle a(\boldsymbol{k}, z)\ b(\boldsymbol{k})^* \rangle}{\langle b(\boldsymbol{k})\ b(\boldsymbol{k})^* \rangle}\ ,$$

and

$$\phi^{s}_{N}(\boldsymbol{k}, z) = \langle N_1(\boldsymbol{k}, z)\, N_1(\boldsymbol{k})^* \rangle ,$$

then the kernel $\tilde{\Gamma}(\boldsymbol{k}, z)$ of an arbitrary single particle density $C(\boldsymbol{k})$ can be written as

$$\begin{aligned}\tilde{\Gamma}(\boldsymbol{k}, z) &\equiv \int_0^\infty \mathrm{d}\tau\, \frac{\langle (\mathrm{e}^{\mathrm{i}(1-\tilde{\mathscr{P}})L\tau}(1-\tilde{\mathscr{P}})\mathrm{i}LC(\boldsymbol{k}))(\mathrm{i}LC(\boldsymbol{k}))^* \rangle}{\langle C(\boldsymbol{k})\, C(\boldsymbol{k})^* \rangle}\, \mathrm{e}^{-z\tau} \\ &= \int_0^\infty \mathrm{d}\tau\, \frac{\langle (\mathrm{e}^{\mathrm{i}(1-\mathscr{P})L\tau}(1-\mathscr{P})\mathrm{i}LC(\boldsymbol{k}))(\mathrm{i}LC(\boldsymbol{k}))^* \rangle}{\langle C(\boldsymbol{k})\, C(\boldsymbol{k})^* \rangle}\, \mathrm{e}^{-z\tau} \\ &\quad + \hat{M}^{\mathrm{ss}}_{12}(C(\boldsymbol{k}); b_i(\boldsymbol{k}-\boldsymbol{q})\, N_1(\boldsymbol{q})) \cdot \mathscr{L}[\phi_{b_i b_j}(\boldsymbol{k}-\boldsymbol{q}, t)\, \phi^{s}_{N}(\boldsymbol{q}, t)] \\ &\quad \cdot \hat{M}^{\mathrm{ss}}_{21}(b_j(\boldsymbol{k}-\boldsymbol{q})\, N_1(\boldsymbol{q}); C(\boldsymbol{k})) + \cdots ,\end{aligned} \tag{5.1}$$

where i and j are summed from 1 to 5, $\tilde{\mathscr{P}}$ projects onto

$$A'(\boldsymbol{k}) \equiv \begin{pmatrix} N_1(\boldsymbol{k}) \\ C(\boldsymbol{k}) \end{pmatrix},$$

and b_i and b_j are elements of the column vector B. The first term on the right hand side of eq. (5.1) contains the full projection operator and is therefore an analytic function of k and z. Equations such as (5.1) have been presented by several researchers in their investigations of the glass transition [5]. Furthermore, we expect the formalism developed here will be essential in the description of the properties of a tagged particle in the flow of inelastic granular materials in which clustering is especially pronounced [8].

This paper also suggests a way to avoid using an unphysical mode coupling cutoff factor K_c in the sums over intermediate wavevectors. These cutoffs are required whenever the vertices in the theory are long ranged spatial functions in order to make the integrals over wavevectors finite. This is unnecessary if all the vertices are short ranged functions. The exact designation of the linear density set A' is arbitrary in the formalism and thereby allows short ranged vertices to be obtained. For example if one is looking for a mode coupling expression for the autocorrelation function of a single particle density it may be useful to actually work with the time derivative of that density if the vertices containing the time derivative of the density are short ranged and the vertices containing the density itself are not. The connection between the mode coupling expressions between the single particle density and its time derivative is established through the Mori hierarchy [7]. Such an approach was used here to evaluate the autocorrelation function of a tagged particle momentum density by actually focussing on the equation of motion for the force exerted by the tagged particle on the surrounding fluid.

The mode coupling formalism was applied to the derivation of the Stokes–Einstein law. Using systematic approximations, the law was recovered from bilinear contributions to the mode coupling equation for the autocorrelation function of the tagged particle momentum density. We should emphasize that it has been shown that all other modes do not contribute to leading order in powers of $1/R$. Thus the Stokes–Einstein law is an exact result to order $1/R$ from the mode coupling series. Generalization of this law to include z dependence and higher orders of $1/R$ is non-trivial since other multilinear orders aside from the bilinear modes may contribute.

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Appendix

In this appendix, justifications for the factorization property of $M^{\rm ssm}_{\alpha\beta}(t)$ will be given. Many of the details necessary to prove this property rigorously will be omitted here since they have been presented in ref. [1] for a similar problem. We shall investigate the factorization properties of $M^{\rm ssm}_{\alpha\beta}(t)$ when a wavevector from the set α is equated with a wavevector from β. We shall denote the equation of a wavevector $\boldsymbol{q}_0$ from α with wavevector $\boldsymbol{q}_0'$ from β by $\delta^{\rm ss}_{\boldsymbol{q}_0\boldsymbol{q}_0'}$ if both $\boldsymbol{q}_0$ and $\boldsymbol{q}_0'$ are the wavevector arguments of single particle densities and so forth.

The factorization property states that

$$M^{\rm ssm}_{\alpha\beta}(t)\,\delta^{\rm ss}_{\boldsymbol{q}_0\boldsymbol{q}_0'} = (M^{\rm cc}_{\alpha-1\,\beta-1}(t) + M^{\rm ss}_{11}(\boldsymbol{q}_0, t)\cdot I^{\rm cc}_{\alpha-1\,\beta-1} + \mathcal{O}(N^{1-|\beta|}))\delta^{\rm ss}_{\boldsymbol{q}_0\boldsymbol{q}_0'}\,, \tag{A.1}$$

where $M^{\rm ss}_{11}$ and $I^{\rm cc}_{\alpha-1\,\beta-1}$ are defined in eqs. (3.26) and (3.24), respectively. As in ref. [1], we shall look at the factorization property of $\mathscr{M}(t) \equiv \langle \dot{Q}(t)\, Q^* \rangle * \langle Q(t)\, Q^* \rangle^{-1}$, since

$$\mathscr{M}(t) = \int_0^\infty \mathrm{d}\tau\, M(\tau) + \mathscr{O}(\tau_\mathrm{m}/\tau_\mathrm{H}) ,$$

where τ_m is a microscopic timescale and τ_H is the much longer "hydrodynamic" timescale on which the slow variables of the system change.

We first note that in the proof of the factorization property in ref. [1], Q_1 appears in the higher order Q_n only through the subtractions necessary to make the components Q_i of Q mutually orthogonal in mode order. The terms proportional to Q_1 in the multilinear order modes are always contained in the correction terms $R_n(t)$ of the factorization of $Q_n(t)$ and therefore vanish in the thermodynamic limit. Thus the exact designation of the Q_1 column vector is irrelevant in the factorization of $M_{\alpha\beta}(t)$. For example,

$$\begin{aligned}
&\langle Q_2^\mathrm{s}(\boldsymbol{k}-\boldsymbol{q}, \boldsymbol{q}, t)\, Q_2^\mathrm{s}(\boldsymbol{k}-\boldsymbol{q}_1, \boldsymbol{q}_1)^* \rangle^\mathrm{m} \delta^\mathrm{ss}_{\boldsymbol{q}\boldsymbol{q}_1} \\
&\quad = (\langle Q_2^\mathrm{s}(\boldsymbol{k}-\boldsymbol{q}, \boldsymbol{q}, t)\, B(\boldsymbol{k}-\boldsymbol{q}_1)^*\, A(\boldsymbol{q}_1) \rangle + \mathscr{O}(1))\delta^\mathrm{ss}_{\boldsymbol{q}\boldsymbol{q}_1} \\
&\quad = (\langle B(\boldsymbol{k}-\boldsymbol{q}_1, t)\, A(\boldsymbol{q}_1)\, B(\boldsymbol{k}-\boldsymbol{q}_1)^*\, A(\boldsymbol{q}_1)^* \rangle \\
&\qquad + \langle R_2(\boldsymbol{k}-\boldsymbol{q}, \boldsymbol{q}, t)\, B(\boldsymbol{k}-\boldsymbol{q}_1)^*\, A(\boldsymbol{q}_1)^* \rangle)\delta^\mathrm{ss}_{\boldsymbol{q}\boldsymbol{q}_1} \\
&\quad = \Big(\langle B(\boldsymbol{k}-\boldsymbol{q}_1, t)\, B(\boldsymbol{k}-\boldsymbol{q}_1)^* \rangle \langle A(\boldsymbol{q}_1, t)\, A(\boldsymbol{q}_1)^* \rangle \\
&\qquad + \mathscr{O}(1) + \overbrace{\langle R_2(\boldsymbol{k}-\boldsymbol{q}, \boldsymbol{q}, t)\, B(\boldsymbol{k}-\boldsymbol{q}_1)^*\, A(\boldsymbol{q}_1)^* \rangle}^{\mathscr{O}(1)} \Big) \delta^\mathrm{ss}_{\boldsymbol{q}\boldsymbol{q}_1} ,
\end{aligned} \tag{A.2}$$

where

$$R_2(\boldsymbol{k}-\boldsymbol{q}, \boldsymbol{q}, t) \equiv -\langle B(\boldsymbol{k}-\boldsymbol{q})\, A(\boldsymbol{q})\, Q_1(\boldsymbol{k})^* \rangle \cdot \langle Q_1(\boldsymbol{k})\, Q_1(\boldsymbol{k})^* \rangle^{-1} \cdot Q_1(\boldsymbol{k}) .$$

As is evident from eq. (A.2), only the densities which appear in the sets B and A determine the leading N order term in the factorization of a multilinear correlation function.

The proof of the factorization property in eq. (A.2) follows immediately from ref. [1] once it is established that equating wavevectors of unlike type of densities (single–collective densities) gives terms which vanish in the thermodynamic limit whereas equating wavevectors of single–single or collective–collective densities give non-vanishing factorizations.

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