Memory effects in collective dynamics of Brownian suspensions

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We obtain macroscopic equations for average suspension velocity and particle current in a Brownian suspension valid on long time scales for which the memory effects are important. The coefficients in these equations depend solely on local properties of the medium. This formalism allows one to obtain well-defined theoretical expressions for transport coefficients, free of the integrals diverging with the size of the system. As an example, the expression for long-time collective diffusion coefficient is derived and the memory contribution to this coefficient is estimated. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1767994]

I. INTRODUCTION

Suspensions of interacting Brownian particles display a rich diversity of dynamical behavior which is the subject of ongoing theoretical studies and experiments. However, the analysis of Brownian suspensions is hindered by complicated nature of interparticle interactions which include direct forces (such as Coulomb or van der Waals) as well as indirect interactions mediated by the solvent. These so-called hydrodynamic interactions are truly complex: They are long ranged, nonlinear in nature, and cannot be expressed as a sum of two-body terms. Instead, they are characterized by either the friction matrix (which gives the forces and torques acting on the particles in terms of their velocities) or its inverse, mobility matrix, which relates velocities to the forces.

For a typical colloidal suspension, the time scales probed by dynamic light scattering and sedimentation experiments are much longer than both the particle velocity relaxation time ($\tau_v = a^2 \rho_p / \eta$) and the viscous relaxation time ($\tau_\eta = a^2 \rho_f / \eta$). Here ρ_p and ρ_f are the particle and fluid density, respectively, a is the particle radius, and η is the viscosity of the fluid. In this time regime, the main role in the suspension dynamics is played by the Brownian motion. A characteristic time scale of this process is a structural relaxation time, $\tau_R = a^2/D_o$, i.e., the time required for a particle to diffuse over its radius (D_o is the single-particle diffusion coefficient).

In general, transport coefficients have different values in the short-time regime (i.e., for times t short with respect to τ_R but still long with respect to both τ_v and τ_η) in which particles have hardly moved and for long times ($t \gg \tau_R$) when the relaxation of the distribution of particle positions becomes important. This relaxation gives rise to the memory effects described by an appropriate memory function. Then, the difference between short- and long-time transport coefficients can be expressed in terms of the small wave number, $\mathbf{k} \rightarrow 0$, limit of the memory function.[1,2] However, this limit is often cumbersome to carry out and, in particular, it is not equal to the $k=0$ value of the memory function. This type of discontinuity at $k=0$ is a common feature of calculations of transport coefficients in suspensions[3–8] inseparably connected with the presence of long-range hydrodynamic inter-

actions. In fact zero wave number value of the memory function picks up a contribution from the motion of a system as a whole. This contribution depends on shape of the container and is given by integrals which diverge with the size of the system. To remove it, the equations should be supplemented by the condition that the system as a whole is at rest, i.e., the container walls are kept immobile (zero net flux condition). For incompressible fluid, this condition is equivalent to

$$\int_V \mathbf{v}(\mathbf{r}) d\mathbf{r} = 0. \tag{1.1}$$

Here $\mathbf{v}(\mathbf{r})$ is equal to the fluid velocity if $\mathbf{r}$ is inside the fluid and coincides with the rigid body motion wherever $\mathbf{r}$ lies inside the particle. The proof of the above relation is given in Appendix A.

Notably, a similar problem occurs when calculating the flow field in a suspension with periodic boundary conditions.[9,10] Here the solution of Stokes equations contains terms which diverge with the size of the system. To get rid of them, one either supplements the equations with the rigid wall boundary condition at the outer boundary of the system[9] or counterbalances the forces acting on particles with a force density exerted on the fluid, so that the total force acting on the suspension vanishes.[10] It can be shown that both procedures lead to the zero net flux condition (1.1).

It is not always easy to take the condition (1.1) into account while calculating transport coefficients. For a sedimentation coefficient such a procedure has been successfully carried out by Noziéres,[11] Felderhof,[12] and Noetinger.[5] They have obtained macroscopic equations for average suspension velocity and sedimentation velocity with the coefficients depending on local properties of the suspension only. The shape and size of the system enter the equations solely through the boundary conditions. As it has been pointed out[11,13] the situation here is reminiscent of that encountered in the theory of dielectrics, which are described in terms of polarization $\mathbf{P}$ and electric field $\mathbf{E}$. Even though the fields, which are obtained by solving Maxwell's equations, are strongly dependent on geometry of the system, the coefficients in the constitutive equations (such as dielectric constant) are local properties of the medium.

Our goal is to apply similar considerations to the analysis of memory effects in dynamics of colloidal suspensions. We show that also in this time regime, when the relaxation of the distribution of particle positions must be taken into account, the suspension can be described by macroscopic equations with local coefficients. This time, however, coefficients attain frequency dependent terms. In particular, we obtain a well-defined expression for long-time collective diffusion coefficient, which is free of any discontinuities at $k=0$ and estimate its value numerically.

The paper is organized as follows: In Sec. II, the memory formalism is applied to the dynamics governed by Smoluchowski equation. In particular, memory function for collective diffusion of Brownian particles is introduced. In the following section basic characteristics of hydrodynamic interactions in a suspension are given. The presence of hydrodynamic interactions is crucial for existence of nonzero memory effect in collective diffusion: It may be proved[14] that the memory function vanishes for suspensions so dilute that either hydrodynamic interactions can be totally neglected or the two-body approximation for mobility matrix used. In Sec. IV we analyze the particle current and convective flow induced in the system by external disturbances both in short-time and long-time regime. We find that the response kernels are long ranged and diverge with the size of the system. To circumvent that problem a special regularization scheme, similar in spirit to that presented by Felderhof in Ref. 12, is devised. For short-time response kernels, the regularization scheme is outlined in Secs. V and VI. Next, in Sec. VIII the regularization scheme is constructed for kernels describing time-dependent response of the system. This leads to macroscopic equations for average velocity fields with local frequency-dependent coefficients derived in Sec. X. Next, in Sec. XI the problem of long-time diffusion is revisited and the expression for collective diffusion memory function in terms of regularized response kernels is derived. Finally, the numerical results for the memory contribution to long-time collective diffusion coefficient are presented in Sec. XII.

II. MEMORY EFFECTS

The system under consideration consists of N identical spherical particles of radius a immersed in an incompressible fluid of shear viscosity η. The particle Reynolds number is assumed to be small so that the inertial effects are negligible and the fluid can be described by Stokes equations. As it was mentioned in the Introduction, the time scales of interest are much longer than both the particle velocity relaxation time τ_v and the viscous relaxation time τ_η. On these time scales the fluid motion is governed by stationary Stokes equations whereas the evolution of the particle distribution function in the configuration space, $P(\mathbf{X},t)$, is described by the generalized Smoluchowski equation[15]

$$\frac{\partial}{\partial t}P(\mathbf{X},t)=\mathcal{D}(\mathbf{X})P(\mathbf{X},t),$$

$$\mathcal{D}(\mathbf{X})\equiv\sum_{i,j=1}^{N}\frac{\partial}{\partial\mathbf{R}_i}\cdot\mathbf{D}_{ij}(\mathbf{X})\cdot\left[\frac{\partial}{\partial\mathbf{R}_j}+\beta\mathbf{F}_i\right], \tag{2.1}$$

where $\mathbf{X}=(\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N)$, $\mathbf{R}_i$ being the position of ith particle and $\mathbf{F}_i$—the force acting on it. Next, $\beta=1/k_BT$ and $\mathbf{D}(\mathbf{X})$ is the diffusion matrix, which by the generalized Einstein relation

$$\mathbf{D}_{ij}=k_BT\boldsymbol{\mu}_{ij}^{tt} \tag{2.2}$$

is connected with the translational mobility matrix $\boldsymbol{\mu}^{tt}$. The latter is obtained by solving the hydrodynamic problem of finding the velocities of the particles, $\mathbf{U}_i, i=1,\ldots,N$, in terms of the forces acting on them (in the absence of torques)

$$\mathbf{U}_i=\sum_j\boldsymbol{\mu}_{ij}^{tt}\mathbf{F}_j. \tag{2.3}$$

In general, due to hydrodynamic interactions, the mobility matrix depends on configuration $\mathbf{X}$ and is nondiagonal in particle indices (the exact definition of $\boldsymbol{\mu}$ will be given in Sec. III).

The basic correlation function probing the collective dynamics of the suspension is the intermediate scattering function

$$F(\mathbf{k},t)=\lim_\infty\frac{1}{N}\langle c(\mathbf{k},0)c(-\mathbf{k},t)\rangle, \tag{2.4}$$

which is the autocorrelation function of microscopic density fluctuations

$$c(\mathbf{k},t)=C(\mathbf{k},t)-\langle C(\mathbf{k},t)\rangle, \tag{2.5}$$

with

$$C(\mathbf{k},t)=\sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i(t)}. \tag{2.6}$$

In the above $\mathbf{k}$ is the wave vector, $\mathbf{R}_i(t)$—the position of ith particle at time t, and $c(\mathbf{k})\equiv c(\mathbf{k},0)$. Brackets $\langle\cdots\rangle$ stand for the average over the equilibrium distribution

$$P_{eq}(\mathbf{X})=e^{-\beta\phi(\mathbf{X})}/\mathcal{Q}, \tag{2.7}$$

where $\mathcal{Q}$ is the normalization constant and $\phi(\mathbf{X})$—potential of interparticle interactions. Next, $\mathcal{L}$ is the adjoint Smoluchowski operator obeying

$$\mathcal{D}P_{eq}(\mathbf{X})\ldots=P_{eq}(\mathbf{X})\mathcal{L}\ldots\ .$$

Finally, $\lim_\infty$ stands for the thermodynamic limit in which the size of the sample goes to infinity while densities of extensive parameters are kept constant.

For convenience, we will adopt the following bra-ket notation

$$\langle A|=\int d\mathbf{X}P_{eq}(\mathbf{X})A(\mathbf{X}) \tag{2.8}$$

and

$$|B\rangle=B^*(\mathbf{X}), \tag{2.9}$$

where star denotes complex conjugation. Thus the equilibrium distribution P_{eq} is always placed at the left-hand side of an expression. In the above notation, the expression (2.4) for intermediate scattering function can be rewritten as

$$F(\mathbf{k},t) = \lim_{\infty} \frac{1}{N}\langle c(\mathbf{k})|e^{\mathcal{L}t}|c(\mathbf{k})\rangle. \tag{2.10}$$

The $t=0$ value of $F(\mathbf{k},t)$ defines the static structure factor $S(\mathbf{k})$

$$S(\mathbf{k}) = \lim_{\infty} \frac{1}{N}\langle c(\mathbf{k})|c(\mathbf{k})\rangle. \tag{2.11}$$

The time derivative of intermediate scattering function can be written as[1]

$$\frac{\partial}{\partial t}F(\mathbf{k},t) = -\Omega(\mathbf{k})F(\mathbf{k},t) + \Omega(\mathbf{k})$$

$$\times \int_0^t d\tau M(\mathbf{k},\tau)F(\mathbf{k},t-\tau), \tag{2.12}$$

with the first cumulant $\Omega(\mathbf{k})$ defined by

$$\Omega(\mathbf{k}) = -\left.\frac{\partial \log F(\mathbf{k},t)}{\partial t}\right|_{t=0} \tag{2.13}$$

and the memory function $M(\mathbf{k},t)$. In the limit $t\to0$ only an instantaneous response described by the function $\Omega(\mathbf{k})$ governs the evolution of $F(\mathbf{k},t)$. For small wave numbers the decay rate of intermediate scattering function in this time regime is characterized by the short-time collective diffusion coefficient

$$D_c^s = \lim_{\mathbf{k}\to0} \frac{\Omega(\mathbf{k})}{k^2}. \tag{2.14}$$

For long times, $t\gg\tau_R$, the effects of the relaxation of the distribution of particle positions must be taken into account. The corresponding long-time diffusion coefficient D_c^l reads

$$D_c^l = \lim_{\mathbf{k}\to0} \frac{\Omega(\mathbf{k})}{k^2}\left[1 - \int_0^\infty M(\mathbf{k},\tau)d\tau\right]. \tag{2.15}$$

The collective diffusion coefficient can be also assessed in a different way. Namely, as it was first pointed out by Einstein,[16] D_c may be obtained by studying the current induced in the system by an external force applied to the particles. The corresponding relation reads

$$D_c = \frac{k_B T}{S(0)}K, \tag{2.16}$$

where the sedimentation coefficient K is given by the ratio of sedimentation velocity to the acceleration of external field. As the time scales involved in sedimentation experiments are usually considerably longer than the structural relaxation time the diffusion coefficient obtained in that way can be identified with D_c^l.

We return to the memory function equation (2.12). In frames of Zwanzig–Mori projection operator formalism[17,18] the first cumulant can be shown to be

$$\Omega(\mathbf{k}) = -\frac{1}{NS(\mathbf{k})}\langle c(\mathbf{k})|\mathcal{L}|c(\mathbf{k})\rangle, \tag{2.17}$$

whereas the memory function (in the Laplace domain) reads

$$M(\mathbf{k},z) = \frac{1}{S(\mathbf{k})\Omega(\mathbf{k})}\langle c(\mathbf{k})|\mathcal{L}Q\frac{1}{z-\hat{\mathcal{L}}}Q\mathcal{L}|c(\mathbf{k})\rangle. \tag{2.18}$$

Here the Laplace transform is defined as

$$M(\mathbf{k},z) = \int_0^\infty M(\mathbf{k},t)e^{-zt}dz,$$

and Q is the projection operator,

$$Q = 1 - \frac{|c(\mathbf{k})\rangle\langle c(\mathbf{k})|}{S(\mathbf{k})}, \tag{2.19}$$

onto the subspace of dynamic variables orthogonal to $c(\mathbf{k})$ and $\hat{\mathcal{L}}$ is the orthogonal part of the operator $\mathcal{L}$,

$$\hat{\mathcal{L}} = Q\mathcal{L}Q. \tag{2.20}$$

However, evaluation of diffusion coefficients with the use of Eqs. (2.14) and (2.15) is nontrivial because of the long-wavelength, $\mathbf{k}\to0$, limit involved. Namely, due to the presence of hydrodynamic interactions in the system, the diffusion matrix $\mathbf{D}_{ij}$ has nonzero nondiagonal ($i\neq j$) elements, which decay with interparticle distance R_{ij} as $R_{ij}^{-\gamma}$ with $\gamma=1,2,3$. Such long-ranged interactions can cause discontinuity in memory function at $k=0$,[1] so that in general it is not possible to identify $\lim_{\mathbf{k}\to0}M(\mathbf{k})$ with $M(\mathbf{k}=0)$ which would be desirable for practical reasons. As it was mentioned in the Introduction, the discontinuity can be removed if one ensures that the zero net flux condition (1.1) is fulfilled. However, it is hard to take this condition into account while using the memory function formalism. One of the ways of dealing with this problem is to use an alternative way of obtaining transport coefficients: by investigating the linear response of the system to external disturbances. It turns out then that it is possible to incorporate the zero net flux condition (1.1) directly into the equations.

However, before applying the linear response theory, let us review the basic facts about hydrodynamic interactions as they are playing a crucial role in determining the dynamics of the system.

III. HYDRODYNAMIC INTERACTIONS

The dynamics of colloidal suspension has many-body character due to the presence of hydrodynamic interactions. As mentioned at the beginning of Sec. II the flow in our system is governed by the stationary Stokes equations. In this case the relation between the forces and torques acting on the particles and their velocities is linear. In the absence of external flow, this relation defines the friction matrix $\boldsymbol{\zeta}$

$$\begin{pmatrix} \mathcal{F} \\ \mathcal{T} \end{pmatrix} = \zeta\begin{pmatrix} \mathbf{U} \\ \boldsymbol{\Omega} \end{pmatrix}, \tag{3.1}$$

with

$$\zeta = \begin{pmatrix} \zeta^{tt} & \zeta^{tr} \\ \zeta^{rt} & \zeta^{rr} \end{pmatrix}.$$

Here $\tilde{\mathcal{F}} = (\mathcal{F},\mathcal{T})$ is the 6N-dimensional vector comprising the forces and torques acting on the each of N particles:

$(\mathcal{F},\mathcal{T})=(\mathbf{F}_1,\mathbf{F}_2,\ldots,\mathbf{F}_N,\mathbf{T}_1,\ldots,\mathbf{T}_N)$ whereas $\tilde{\mathcal{U}}=(\mathcal{U},\mathbf{\Omega})$ is the vector built from the translational and rotational velocities of the particles $\tilde{\mathcal{U}}=(\mathbf{U}_1,\ldots,\mathbf{U}_N,\mathbf{\Omega}_1,\ldots,\mathbf{\Omega}_N)$. The matrices ζ^{pq} ($p,q=t$ or r) are the $3N\times3N$ Cartesian tensors, and the superscripts t and r correspond to the translational and the rotational components, respectively.

As it was shown by Mazur and Bedeaux[19] if the particles are impenetrable to the flow and the stick boundary conditions at their surfaces are assumed, then validity of Stokes equations may be formally extended inside the particles:

$$\eta\nabla^2\mathbf{v}-\nabla p+\mathbf{f}_o(\mathbf{r})+\mathbf{f}(\mathbf{r})=0,$$

$$\nabla\cdot\mathbf{v}=0,$$

$$\mathbf{v}(\mathbf{r})=\mathbf{u}_i(\mathbf{r})=\mathbf{U}_i+\mathbf{\Omega}_i\times(\mathbf{r}-\mathbf{R}_i)\quad\text{for }|\mathbf{r}-\mathbf{R}_i|\leq a,$$

$$p(\mathbf{r})=0\quad\text{for }|\mathbf{r}-\mathbf{R}_i|\leq a. \tag{3.2}$$

Here $\mathbf{f}_o(\mathbf{r})$ is an external force density applied to the fluid, such as gravity. Next, $\mathbf{f}(\mathbf{r})$ is an induced force density localized on the particle surfaces.[19,20]

The total force and torque with which particles act on a fluid are then given by

$$\mathbf{F}_i=\int\mathbf{f}(\mathbf{r})\,\theta_i(\mathbf{r})\,d\mathbf{r},$$

$$\mathbf{T}_i=\int(\mathbf{r}-\mathbf{R}_i)\times\mathbf{f}(r)\,\theta_i(\mathbf{r})\,d\mathbf{r}, \tag{3.3}$$

where

$$\theta_i(\mathbf{r})=\theta(a-|\mathbf{r}-\mathbf{R}_i|) \tag{3.4}$$

is the characteristic function of the particle i.

The solution of hydrodynamic equations (3.2) can be written as

$$\mathbf{v}(\mathbf{r})=\mathbf{v}_o(\mathbf{r})+\int\mathbf{G}(\mathbf{r},\mathbf{r}')\cdot\mathbf{f}(\mathbf{r}')\,d\mathbf{r}', \tag{3.5}$$

where $\mathbf{v}_o(\mathbf{r})$ is the flow in absence of the particles and $\mathbf{G}(\mathbf{r},\mathbf{r}')$ is the Green tensor. For an unbounded fluid $\mathbf{G}(\mathbf{r},\mathbf{r}')$ is given by the Oseen tensor $\mathbf{G}_o$

$$\mathbf{G}(\mathbf{r},\mathbf{r}')=\mathbf{G}_o(\mathbf{r}-\mathbf{r}'),$$

$$\mathbf{G}_o(\mathbf{r})\equiv\frac{1}{8\pi\eta}\frac{\mathbf{1}+\hat{\mathbf{r}}\hat{\mathbf{r}}}{r},\quad\hat{\mathbf{r}}=\frac{\mathbf{r}}{r}. \tag{3.6}$$

From now on we follow the formalism and notation devised by Felderhof, Cichocki, and their co-workers.[21–24] From linearity of Stokes equations one infers that the force density can be expressed as

$$\mathbf{f}(\mathbf{r})=\int\mathcal{Z}(\mathbf{r},\mathbf{r}')\cdot[\mathbf{v}(\mathbf{r}')-\mathbf{v}_o(\mathbf{r}')]\,d\mathbf{r}', \tag{3.7}$$

with the friction kernel $\mathcal{Z}(\mathbf{r},\mathbf{r}')$. This kernel can be assessed by the following procedure. Let us consider some point on the surface of ith sphere $\mathbf{r}\in S_i$. Expression (3.5) for the flow velocity $\mathbf{v}(\mathbf{r})$, which in this case must be equal to $\mathbf{u}_i(\mathbf{r})$, can be written as a sum of the following terms:

$$\mathbf{v}(\mathbf{r})=\mathbf{u}_i(\mathbf{r})=\mathbf{v}_o(\mathbf{r})+\int\mathbf{G}(\mathbf{r},\mathbf{r}')\cdot\mathbf{f}_i(\mathbf{r}')\,d\mathbf{r}'$$

$$+\sum_{j\neq i}\int\mathbf{G}(\mathbf{r},\mathbf{r}')\cdot\mathbf{f}_j(\mathbf{r}')\,d\mathbf{r}'$$

$$\mathbf{r}\in S_i,\quad i=1,\ldots,N, \tag{3.8}$$

where the contributions to $\mathbf{u}_i(\mathbf{r})$ from the force density on the particle i:$[\mathbf{f}_i(\mathbf{r})=\mathbf{f}(\mathbf{r})\,\theta_i(\mathbf{r})]$ and on the particles $j\neq i$ have been singled out. The first of these terms can be written using the one-particle friction operator $\mathbf{Z}_o(i)$ [defined by Eq. (3.7) for a single sphere] as

$$[\mathbf{Z}_o^{-1}(i)\mathbf{f}_i](\mathbf{r})\equiv\int\mathbf{G}(\mathbf{r},\mathbf{r}')\cdot\mathbf{f}_i(\mathbf{r}')\,d\mathbf{r}'\quad\mathbf{r}\in S_i, \tag{3.9}$$

whereas the second one is used to define the Green operator $\mathbf{G}(ij)$[25]

$$[\mathbf{G}(ij)\mathbf{f}_j](\mathbf{r})\equiv\int\mathbf{G}(\mathbf{r},\mathbf{r}')\cdot\mathbf{f}_j(\mathbf{r}')\,d\mathbf{r}'\quad i\neq j\quad\mathbf{r}\in S_i. \tag{3.10}$$

Equation (3.8) can be rewritten in a compact way as

$$\mathbf{u}_i-\mathbf{v}_o=\sum_j\;(\mathcal{Z}_o^{-1}+\mathcal{G})_{ij}\mathbf{f}_j, \tag{3.11}$$

where

$$\mathcal{Z}_{oij}=\mathbf{Z}_o(i)\,\delta_{ij}\quad\mathcal{G}_{ij}=\mathbf{G}(ij)(1-\delta_{ij}) \tag{3.12}$$

are the $N\times N$ operator matrices in the particle indices. Here and below we use the script letters ($\mathcal{Z}_o,\mathcal{G},\mathcal{F},\ldots$) for objects acting in the particle index space. Subsequently, we further simplify the notation by omitting the sum over particle indices. Under this notation, Eq. (3.11) becomes simply

$$\mathbf{u}-\mathbf{v}_o=(\mathcal{Z}_o^{-1}+\mathcal{G})\mathbf{f}, \tag{3.13}$$

with

$$\mathbf{u}=(\mathbf{u}_1,\ldots,\mathbf{u}_N), \tag{3.14}$$

$$\mathbf{f}=(\mathbf{f}_1,\ldots,\mathbf{f}_N). \tag{3.15}$$

Comparing Eq. (3.13) with Eq. (3.7) yields the following expression for the friction kernel

$$\mathcal{Z}=\frac{1}{\mathcal{Z}_o^{-1}+\mathcal{G}}. \tag{3.16}$$

The forces and the torques acting on the particles are obtained from the force density $\mathbf{f}$ by Eq. (3.3), which can be written in the operator language as

$$\tilde{\mathcal{F}}=\mathcal{P}\mathbf{f}, \tag{3.17}$$

where the tensor projection operator $\mathcal{P}=(\mathcal{P}^t,\mathcal{P}^r)$ is given by

$$\mathcal{P}_i^t(\mathbf{r})=\theta_i(\mathbf{r})\mathbf{1},\quad i=1,\ldots,N$$

$$\mathcal{P}_i^r(\mathbf{r})=\theta_i(\mathbf{r})\epsilon_{\alpha\beta\gamma}(\mathbf{r}-\mathbf{R}_i)_\gamma. \tag{3.18}$$

With the use of $\mathcal{P}$ the relation between the friction matrix ζ and the friction kernel $\mathcal{Z}$ can be written as

$$\zeta=\mathcal{P}\mathcal{Z}\mathcal{P}. \tag{3.19}$$

For example $\boldsymbol{\zeta}_{12}^{tt}$ is given by

$$\boldsymbol{\zeta}_{12}^{tt} = \int \int d\mathbf{r} d\mathbf{r}' \, \theta_1(\mathbf{r}) \boldsymbol{\mathcal{Z}}(\mathbf{r},\mathbf{r}') \theta_2(\mathbf{r}') = \boldsymbol{\mathcal{P}}^t \boldsymbol{\mathcal{Z}} \boldsymbol{\mathcal{P}}^t. \quad (3.20)$$

To solve the integral equation (3.13), the velocity field $[\mathbf{u}_i(\mathbf{r}) - \mathbf{v}_o(\mathbf{r})]_{\mathbf{r} \in S_i}$ and force densities $\mathbf{f}_i$ are expanded in terms of irreducible multipoles.[26] In this way the problem is reduced to an infinite system of linear algebraic equations for matrix elements, which are labeled by the particle number and by three multipole indices l, m, σ, where $l = 1, 2, \ldots$, while $m = -l, \ldots, +l$, and $\sigma = 0, 1, 2$.

In particular, the lowest force multipole $\mathbf{f}_{i; \, l=1, \sigma=0}$ is proportional to the total force $\mathbf{F}_i$ acting on ith particle whereas the multipole $\mathbf{f}_{i; \, l=1, \sigma=1}$ is proportional to the total torque $\mathbf{T}_i$. In the case of velocity field the multipoles $l = 1$; $\sigma = 0, 1$ correspond to particle translational and rotational velocities, respectively. Hence in the multipole formalism the operator $\boldsymbol{\mathcal{P}}$ is a projector on subspace $l = 1$; $\sigma = (0, 1)$.

An explicit form of the operators $\boldsymbol{\mathcal{Z}}_o$ and $\boldsymbol{\mathcal{G}}$ in multipole notation can be found, e.g., in Ref. 25. Here we only mention that the matrix element $\mathbf{G}(l, \sigma; l', \sigma'; \mathbf{R}_{ji})$ describing an influence of the force multipole (l', σ') on ith sphere on the velocity multipole (l, σ) on the jth sphere for the case of infinite space decays with an interparticle distance as $R_{ji}^{-(l+l'+\sigma+\sigma'-1)}$. Hence the interactions between low multipoles are of infinite range as they contain terms $R_{ji}^{-\gamma}$ with $\gamma = 1, 2, 3$.

Returning to the analysis of hydrodynamic operators, let us now find forces acting on particles in the presence of the ambient flow. From Eq. (3.7) one gets in this case

$$\tilde{\boldsymbol{\mathcal{F}}} = \boldsymbol{\zeta} \cdot \tilde{\boldsymbol{\mathcal{U}}} - \boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}} \mathbf{v}_o. \quad (3.21)$$

The above formalism can also be used to solve the mobility problem: finding velocities of the particles $\tilde{\boldsymbol{\mathcal{U}}}$ for given forces $\tilde{\boldsymbol{\mathcal{F}}}$ and flow $\mathbf{v}_o$. In this case, the relation (3.21) gives

$$\tilde{\boldsymbol{\mathcal{U}}} = \boldsymbol{\zeta}^{-1} \tilde{\boldsymbol{\mathcal{F}}} + \boldsymbol{\zeta}^{-1} \boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}} \mathbf{v}_o \equiv \boldsymbol{\mu} \tilde{\boldsymbol{\mathcal{F}}} + \boldsymbol{\mathcal{C}} \mathbf{v}_o, \quad (3.22)$$

which defines the mobility matrix $\boldsymbol{\mu}$,

$$\boldsymbol{\mu} = \boldsymbol{\zeta}^{-1}, \quad (3.23)$$

together with the convection kernel $\boldsymbol{\mathcal{C}}$,

$$\boldsymbol{\mathcal{C}} = \boldsymbol{\mu} \boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}}. \quad (3.24)$$

The mobility matrix $\boldsymbol{\mu}$ allows us to find translational and rotational velocities of particles in terms of forces and torques acting on them in the absence of an external flow

$$\begin{pmatrix} \mathbf{U} \\ \boldsymbol{\Omega} \end{pmatrix} = \boldsymbol{\mu} \begin{pmatrix} \boldsymbol{\mathcal{F}} \\ \boldsymbol{\mathcal{T}} \end{pmatrix},$$

$$\boldsymbol{\mu} = \begin{pmatrix} \boldsymbol{\mu}^{tt} & \boldsymbol{\mu}^{tr} \\ \boldsymbol{\mu}^{rt} & \boldsymbol{\mu}^{rr} \end{pmatrix}. \quad (3.25)$$

Finally, let us consider a problem of finding the force density $\mathbf{f}$ for given forces $\tilde{\boldsymbol{\mathcal{F}}} \neq 0$ and ambient flow $\mathbf{v}_o$. In this case, from Eqs. (3.21) and (3.7) we obtain

$$\mathbf{f} = \tilde{\boldsymbol{\mathcal{C}}} \tilde{\boldsymbol{\mathcal{F}}} - \hat{\boldsymbol{\mathcal{Z}}} \mathbf{v}_o, \quad (3.26)$$

where $\tilde{\boldsymbol{\mathcal{C}}}$ is the transpose of $\boldsymbol{\mathcal{C}}$ operator

$$\tilde{\boldsymbol{\mathcal{C}}} = \boldsymbol{\mathcal{Z}} \boldsymbol{\mathcal{P}} \boldsymbol{\mu}, \quad (3.27)$$

while the convective friction kernel $\hat{\boldsymbol{\mathcal{Z}}}$[27] is given by

$$\hat{\boldsymbol{\mathcal{Z}}} = \boldsymbol{\mathcal{Z}} - \boldsymbol{\mathcal{Z}} \boldsymbol{\mathcal{P}} \boldsymbol{\mu} \boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}}. \quad (3.28)$$

For further considerations, we need the scattering expansions of the above introduced kernels in terms of one-particle operators and the Green operator $\boldsymbol{\mathcal{G}}$, analogous to Eq. (3.16) for the friction kernel.

For example, for the convective friction kernel $\hat{\boldsymbol{\mathcal{Z}}}$ one gets the expression

$$\hat{\boldsymbol{\mathcal{Z}}} = \hat{\boldsymbol{\mathcal{Z}}}_o (1 + \boldsymbol{\mathcal{G}} \hat{\boldsymbol{\mathcal{Z}}}_o)^{-1} = \sum_{k=0}^{\infty} \hat{\boldsymbol{\mathcal{Z}}}_o (-\boldsymbol{\mathcal{G}} \hat{\boldsymbol{\mathcal{Z}}}_o)^k, \quad (3.29)$$

whereas the mobility operator can be written as

$$\boldsymbol{\mu} = \boldsymbol{\mu}_o + \boldsymbol{\mu}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}}_o \frac{1}{1 + \boldsymbol{\mathcal{G}} \hat{\boldsymbol{\mathcal{Z}}}_o} \boldsymbol{\mathcal{G}} \boldsymbol{\mathcal{Z}}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mu}_o$$

$$= \boldsymbol{\mu}_o + \sum_{k=0}^{\infty} \boldsymbol{\mu}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}}_o (-\boldsymbol{\mathcal{G}} \hat{\boldsymbol{\mathcal{Z}}}_o)^k \boldsymbol{\mathcal{G}} \boldsymbol{\mathcal{Z}}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mu}_o, \quad (3.30)$$

where

$$\boldsymbol{\mu}_o = \frac{1}{\boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}}_o \boldsymbol{\mathcal{P}}} \quad (3.31)$$

is the one-particle mobility matrix whereas $\hat{\boldsymbol{\mathcal{Z}}}_o$ is one-particle convective friction matrix, given by a relation analogous to Eq. (3.28)

$$\hat{\boldsymbol{\mathcal{Z}}}_o = \boldsymbol{\mathcal{Z}}_o - \boldsymbol{\mathcal{Z}}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mu}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}}_o. \quad (3.32)$$

The matrix $\hat{\boldsymbol{\mathcal{Z}}}_o$ differs from $\boldsymbol{\mathcal{Z}}_o$ only in $l = 1$ subspace. Moreover, since

$$\boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}}_o \boldsymbol{\mu}_o = \boldsymbol{\mathcal{P}}, \quad (3.33)$$

one concludes that $\hat{\boldsymbol{\mathcal{Z}}}_o \boldsymbol{\mathcal{P}} = \boldsymbol{\mathcal{P}} \hat{\boldsymbol{\mathcal{Z}}}_o = 0$.

Finally, formulas for the kernels $\boldsymbol{\mathcal{C}}$ and $\tilde{\boldsymbol{\mathcal{C}}}$ introduced above read[20]

$$\tilde{\boldsymbol{\mathcal{C}}} = \boldsymbol{\mathcal{Z}}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mu}_o - \hat{\boldsymbol{\mathcal{Z}}} \boldsymbol{\mathcal{G}} \boldsymbol{\mathcal{Z}}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mu}_o = \sum_{k=0}^{\infty} (-\hat{\boldsymbol{\mathcal{Z}}}_o \boldsymbol{\mathcal{G}})^k \boldsymbol{\mathcal{Z}}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mu}_o, \quad (3.34)$$

$$\boldsymbol{\mathcal{C}} = \boldsymbol{\mu}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}}_o - \boldsymbol{\mu}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}}_o \boldsymbol{\mathcal{G}} \hat{\boldsymbol{\mathcal{Z}}} = \sum_{k=0}^{\infty} \boldsymbol{\mu}_o \boldsymbol{\mathcal{P}} \boldsymbol{\mathcal{Z}}_o (-\boldsymbol{\mathcal{G}} \hat{\boldsymbol{\mathcal{Z}}}_o)^k. \quad (3.35)$$

From now on we are going to denote translational part of mobility matrix $\boldsymbol{\mu}^{tt}$ simply by $\boldsymbol{\mu}$, as only $\boldsymbol{\mu}^{tt}$ appears in subsequent considerations. Analogous convention is to be adopted when writing other hydrodynamic operators like $\boldsymbol{\mathcal{C}}$ and $\tilde{\boldsymbol{\mathcal{C}}}$. Here we would also be concerned only with their translational parts, but we are not going to denote them by $\tilde{\boldsymbol{\mathcal{C}}}^t$ and $\boldsymbol{\mathcal{C}}^t$ in order to keep the notation simple.

IV. LINEAR RESPONSE FOR SMOLUCHOWSKI DYNAMICS

In this section we apply the linear response theory to generalized Smoluchowski equation. Our aim here is to evaluate the mean force density and particle current induced by external disturbances: imposed flow field $\mathbf{v}_o(\mathbf{r})$ and external forces $\boldsymbol{\mathcal{E}} = (\mathbf{E}_1, \ldots, \mathbf{E}_N)$.

To begin with, let us notice that in the presence of the flow $\mathbf{v}_o(\mathbf{r})$ and external forces $\boldsymbol{\mathcal{E}}$ the Smoluchowski operator $\boldsymbol{\mathcal{D}}(\mathbf{X}, t)$ (2.1) acquires additional terms and reads[28]

$$\boldsymbol{\mathcal{D}}(\mathbf{X}, t) \equiv \sum_{i,j=1}^{N} \frac{\partial}{\partial \mathbf{R}_i} \cdot \mathbf{D}_{ij}(\mathbf{X}) \cdot \left[\frac{\partial}{\partial \mathbf{R}_j} + \beta (\mathbf{F}_i + \mathbf{E}_i) \right]$$
$$+ \frac{\partial}{\partial \mathbf{R}_i} \cdot \boldsymbol{\mathcal{C}}_i(\mathbf{X}) \cdot \mathbf{v}_o. \tag{4.1}$$

Next, let us find the mean particle current and force density. The former is given by the following ensemble average

$$\langle \mathbf{j}(\mathbf{r}, \mathbf{X}) \rangle_t \equiv \left\langle \sum_{i=1}^{N} \dot{\mathbf{R}}_i \delta(\mathbf{r} - \mathbf{R}_i) \right\rangle$$
$$= \left\langle \sum_{i=1}^{N} \mathcal{L} \mathbf{R}_i \delta(\mathbf{r} - \mathbf{R}_i) \right\rangle_t, \tag{4.2}$$

where the symbol $\langle \ \rangle_t$ denotes the average over $P(\mathbf{X}, t)$. Inserting the explicit form of adjoint Smoluchowski operator yields

$$\langle \mathbf{j}(\mathbf{r}, \mathbf{X}) \rangle_t = \left\langle \sum_{i=1}^{N} \left\{ \left(\beta^{-1} \frac{\partial}{\partial \mathbf{X}} + \boldsymbol{\mathcal{F}} + \boldsymbol{\mathcal{E}} \right) \cdot \boldsymbol{\mu}(\mathbf{X}) \right.\right.$$
$$\left.\left. + \boldsymbol{\mathcal{C}}(\mathbf{X}) \mathbf{v}_o \right\}_i \delta(\mathbf{r} - \mathbf{R}_i) \right\rangle_t, \tag{4.3}$$

where $\{ \ \}_i$ stands for ith component (in particle indexes) of the operator in brackets. For example

$$\{ \boldsymbol{\mathcal{E}} \cdot \boldsymbol{\mu}(\mathbf{X}) \}_i = \sum_j \mathbf{E}_j \cdot \boldsymbol{\mu}_{ji} = \sum_j \boldsymbol{\mu}_{ij} \cdot \mathbf{E}_j, \tag{4.4}$$

where the symmetry of mobility matrix has been used in the last equality.

By considerations similar to the above one can also find the mean force density. As it has been shown in Ref. 28 it is given by the formula

$$\langle \mathbf{f}(\mathbf{r}, \mathbf{X}) \rangle_t = \left\langle \left(\beta^{-1} \frac{\partial}{\partial \mathbf{X}} + \boldsymbol{\mathcal{F}} + \boldsymbol{\mathcal{E}} \right) \cdot \boldsymbol{\mathcal{C}}(\mathbf{X}) - \hat{\boldsymbol{\mathcal{Z}}}(\mathbf{X}) \mathbf{v}_o \right\rangle_t. \tag{4.5}$$

In deriving the linear response formulas for the system of Brownian particles the approach due to Felderhof and Jones[29,30] is adopted. It is assumed that particles were at equilibrium in the infinite past so that the probability distribution $P(\mathbf{X}, t \to -\infty)$ is equal to $P_{eq}(\mathbf{X})$ given by Eq. (2.7).

Subsequently the fields $\boldsymbol{\mathcal{E}}$ and $\mathbf{v}_o$ are turned on and the distribution changes to

$$P(\mathbf{X}, t) = P_{eq}(\mathbf{X}) + \delta P(\mathbf{X}, t), \tag{4.6}$$

with $\delta P(\mathbf{X}, t)$ obeying (to the linear order in $\boldsymbol{\mathcal{E}}$ and $\mathbf{v}_o$)

$$\frac{\partial \delta P(\mathbf{X}, t)}{\partial t} - \boldsymbol{\mathcal{D}} \delta P = -\frac{\partial}{\partial \mathbf{X}} \cdot \{ [\boldsymbol{\mu} \boldsymbol{\mathcal{E}}(t) + \boldsymbol{\mathcal{C}} \mathbf{v}_o(t)] P_{eq} \}. \tag{4.7}$$

The solution with initial condition $\delta P = 0$ for $t = -\infty$ is given by

$$\delta P(\mathbf{X}, t) = -P_{eq} \int_{-\infty}^{t} dt' \, e^{\mathcal{L}(t-t')} \left(\frac{\partial}{\partial \mathbf{X}} + \beta \boldsymbol{\mathcal{F}} \right)$$
$$\cdot [\boldsymbol{\mu} \boldsymbol{\mathcal{E}}(t') + \boldsymbol{\mathcal{C}} \mathbf{v}_o(t')]. \tag{4.8}$$

This allows us to rewrite the expressions for $\langle \mathbf{f}(\mathbf{r}, \mathbf{X}) \rangle_t$ and $\langle \mathbf{j}(\mathbf{r}, \mathbf{X}) \rangle_t$ as

$$\langle \mathbf{j}(\mathbf{r}) \rangle_t = \int d\mathbf{r}' [\mathbf{Y}_{jE}(\mathbf{r}, \mathbf{r}') \mathbf{E}(\mathbf{r}', t) + \mathbf{Y}_{jv}(\mathbf{r}, \mathbf{r}') \mathbf{v}_o(\mathbf{r}', t)]$$
$$+ \int d\mathbf{r}' \int_{-\infty}^{t} dt' [\mathbf{X}_{jE}(\mathbf{r}, \mathbf{r}', t-t') \mathbf{E}(\mathbf{r}', t')$$
$$+ \mathbf{X}_{jv}(\mathbf{r}, \mathbf{r}', t-t') \mathbf{v}_o(\mathbf{r}', t')] \equiv \langle \mathbf{j} \rangle_t^{inst} + \langle \mathbf{j} \rangle_t^{ret}, \tag{4.9}$$

$$\langle \mathbf{f}(\mathbf{r}) \rangle_t = \int d\mathbf{r}' [\mathbf{Y}_{fE}(\mathbf{r}, \mathbf{r}') \mathbf{E}(\mathbf{r}', t) + \mathbf{Y}_{fv}(\mathbf{r}, \mathbf{r}') \mathbf{v}_o(\mathbf{r}', t)]$$
$$+ \int d\mathbf{r}' \int_{-\infty}^{t} dt' [\mathbf{X}_{fE}(\mathbf{r}, \mathbf{r}', t-t') \mathbf{E}(\mathbf{r}', t')$$
$$+ \mathbf{X}_{fv}(\mathbf{r}, \mathbf{r}', t-t') \mathbf{v}_o(\mathbf{r}', t')] \equiv \langle \mathbf{f} \rangle_t^{inst} + \langle \mathbf{f} \rangle_t^{ret}, \tag{4.10}$$

where an auxiliary force field $\mathbf{E}(\mathbf{r}, t)$ was introduced, such that

$$\mathbf{E}_i(t) = \int \delta(\mathbf{r} - \mathbf{R}_i) \mathbf{E}(\mathbf{r}, t) d\mathbf{r} \tag{4.11}$$

and we have singled out instantaneous and retarded part of system's response [corresponding to averaging over P_{eq} and δP in Eq. (4.6), respectively]. The former appears immediately after $\mathbf{E}$ or $\mathbf{v}_o$ is turned on and follows the change of the external perturbation, while the latter describes memory effects due to the change of the distribution function induced by external forces.

Instantaneous response kernels introduced above read[29]

$$\mathbf{Y}_{jE}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i,j=1}^{N} \delta(\mathbf{r} - \mathbf{R}_i) \boldsymbol{\mu}_{ij} \delta(\mathbf{r}' - \mathbf{R}_j) \right\rangle, \tag{4.12a}$$

$$\mathbf{Y}_{jv}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{R}_i) \boldsymbol{\mathcal{C}}_i(\mathbf{r}') \right\rangle, \tag{4.12b}$$

$$\mathbf{Y}_{fE}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{j=1}^{N} \tilde{\boldsymbol{\mathcal{C}}}(\mathbf{r})_j \delta(\mathbf{r}' - \mathbf{R}_j) \right\rangle, \tag{4.12c}$$

$$\mathbf{Y}_{fv}(\mathbf{r}, \mathbf{r}') = \langle -\hat{\boldsymbol{\mathcal{Z}}}(\mathbf{r}, \mathbf{r}') \rangle, \tag{4.12d}$$

whereas time-dependent response kernels $\mathbf{X}$ are given by

$$\mathbf{X}_{jE}(\mathbf{r},\mathbf{r}',t)=-\beta^{-1}\left\langle \sum_{i,j=1}^{N}\delta(\mathbf{r}-\mathbf{R}_i)[\boldsymbol{\mu}\cdot\overleftarrow{\tilde{\nabla}}]_i e^{\mathcal{L}t}\right.$$

$$\left.\times[(\vec{\nabla}+\beta\mathcal{F})\cdot\boldsymbol{\mu}]_j\delta(\mathbf{r}'-\mathbf{R}_j)\right\rangle, \qquad (4.13\text{a})$$

$$\mathbf{X}_{jv}(\mathbf{r},\mathbf{r}',t)=-\beta^{-1}\left\langle \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{R}_i)[\boldsymbol{\mu}\cdot\overleftarrow{\tilde{\nabla}}]_i e^{\mathcal{L}t}\right.$$

$$\left.\times(\vec{\nabla}+\beta\mathcal{F})\cdot\mathbf{C}(\mathbf{r}')\right\rangle, \qquad (4.13\text{b})$$

$$\mathbf{X}_{fE}(\mathbf{r},\mathbf{r}',t)=-\beta^{-1}\left\langle \tilde{\mathbf{C}}(\mathbf{r})\cdot\overleftarrow{\tilde{\nabla}}e^{\mathcal{L}t}\right.$$

$$\left.\times\sum_{j=1}^{N}[(\vec{\nabla}+\beta\mathcal{F})\cdot\boldsymbol{\mu}]_j\delta(\mathbf{r}'-\mathbf{R}_j)\right\rangle,$$

$$(4.13\text{c})$$

$$\mathbf{X}_{fv}(\mathbf{r},\mathbf{r}',t)=-\beta^{-1}\langle\tilde{\mathbf{C}}(\mathbf{r})\cdot\overleftarrow{\tilde{\nabla}}e^{\mathcal{L}t}(\vec{\nabla}+\beta\mathcal{F})\cdot\mathbf{C}(\mathbf{r}')\rangle,$$

$$(4.13\text{d})$$

where the symbols $\overleftarrow{\tilde{\nabla}}$ and $\vec{\nabla}$ denote the operator $\partial/\partial\mathbf{X}$ acting to the left and to the right, respectively.

In the next sections we study the internal structure of the response kernels in a detailed way. Particular attention will be paid to identification and subsequent removal of long-range terms in the kernels, which make the relations (4.9) and (4.10) nonlocal.

V. CLUSTER STRUCTURE

The kernels $\mathbf{Y}$ and $\mathbf{X}$ defined in Eqs. (4.12) and (4.13) contain integrals of the form

$$I=\int A(\mathbf{X},\mathbf{r},\mathbf{r}')P_{eq}(\mathbf{X})d\mathbf{X}, \qquad (5.1)$$

where A stands for an operator such as $\Sigma_{i,j=1}^{N}\delta(\mathbf{r}-R_i)\boldsymbol{\mu}_{ij}\delta(\mathbf{r}'-R_j)$ or $\hat{\mathcal{Z}}(\mathbf{r},\mathbf{r}')$. To analyze the structure of these expressions let us rewrite $A(\mathbf{X},\mathbf{r},\mathbf{r}')$ in form of multiple scattering series[20]—i.e., as a sum of terms, each containing the product of one particle operators and Green operators [cf. Eqs. (3.29), (3.30), (3.34) and (3.35)]. For example Eq. (3.29) gives for the convective friction kernel,

$$\hat{\mathcal{Z}}(1..N)_{ij}=\hat{\mathbf{Z}}_o(i)\delta_{ij}-\hat{\mathbf{Z}}_o(i)\mathbf{G}(ij)\hat{\mathbf{Z}}_o(j)(1-\delta_{ij})$$

$$+\sum_{k}\hat{\mathbf{Z}}_o(i)\mathbf{G}(ik)\hat{\mathbf{Z}}_o(k)\mathbf{G}(kj)\hat{\mathbf{Z}}_o(j)+\cdots,$$

$$(5.2)$$

with the condition that no label should be repeated in succession. Successive terms in the series (5.2) have clear physical interpretation—they correspond to increasing number of subsequent reflections of the velocity field by intermediate spheres propagating the interaction.

The next step is to group the terms in the scattering series according to the particles involved. In this way A can be represented as

$$A(1,2,\ldots,N)=\sum_{i}a(i)+\sum_{i<j}a(i,j)$$

$$+\sum_{i<j<k}a(i,j,k)+\cdots, \qquad (5.3)$$

where $a(i_1,\ldots,i_s)$ comprises all the terms in the scattering series of A which involve each and every particle $\{i_1,i_2,..,i_s\}$.

Hence the integral I takes the form,

$$I=\sum_{s=1}^{N}\frac{1}{s!}\int a(1,2,\ldots,s)n(1,2,\ldots,s)d1d2\cdots ds,$$

$$(5.4)$$

where the s particle partial distribution function is given by

$$n(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s)=\left\langle \sum_{i_1,i_2,\ldots,i_s}'\delta(\mathbf{r}_1-\mathbf{R}_{i_1})\right.$$

$$\left.\times\delta(\mathbf{r}_2-\mathbf{R}_{i_2})\cdots\delta(\mathbf{r}_s-\mathbf{R}_{i_s})\right\rangle, \qquad (5.5)$$

which in a shorthand notation will be denoted as $\langle 1, 2, \ldots s\rangle$. The sum Σ' in the above expression is supplied with the condition that all the particle indices i_k, $k=1,\ldots,s$ are different each from the other. The partial distribution function can be decomposed according to the cluster structure[31]

$$n(1)=h(1),$$

$$n(1,2)=n(1)n(2)+h(1,2),$$

$$n(1,2,3)=n(1)n(2)n(3)+n(1)h(2,3)+n(2)h(1,3)$$

$$+n(3)h(1,2)+h(1,2,3),\ldots, \qquad (5.6)$$

where the s particle correlation function $h(1,2,\ldots,s)$ goes to zero as one drags any subset of particles $\subset\{1,2,\ldots,s\}$ away from the rest.

With the above decompositions one can write the integral I in Eq. (5.1) as the sum of terms of the general form

$$T_s(\Lambda,c)=\int\Lambda(i_1,i_2,\ldots,i_s)c(i_1,i_2,\ldots,i_s)d1d2\cdots ds,$$

$$(5.7)$$

where $c(i_1,i_2,\ldots,i_s)$ is a product of a number of correlation functions involving particles $\{i_1,\ldots,i_s\}$ whereas $\Lambda(i_1,i_2,\ldots,i_s)$ is one of the scattering sequences making up $a(i_1,i_2,\ldots,i_s)$.

VI. REDUCTION OF INSTANTANEOUS RESPONSE KERNELS

This section is devoted to detailed analysis of the kernels $\mathbf{Y}$ which describe the instantaneous response of the system to external disturbances. In particular, we prove that the response kernels are long-ranged and therefore the response is dependent on shape and size of the system. Next, it is demonstrated how to describe the system's response using short-ranged kernels by rewriting equations in terms of mean suspension velocity $\langle\mathbf{v}(\mathbf{r})\rangle$ rather than the imposed flow field $\mathbf{v}_o(\mathbf{r})$.

A. Internal structure of the terms

To begin with, we introduce a number of formal definitions which will help us to analyze the internal structure of terms $T_s(\Lambda,c)$ as given by Eq. (5.7). First of all, an operator $\mathbf{G}(i_k,i_{k+1})$ will be called **a connection line** of a term $T_s(\Lambda,c)$ if the latter can be written as

$$
T_s(\Lambda,c) = \int \Lambda_1(i_1,\ldots,i_k)c_1(i_1,\ldots,i_k)
$$
$$
\times \mathbf{G}(i_k,i_{k+1})\Lambda_2(i_{k+1},\ldots,i_s)c_2(i_{k+1},\ldots,i_s)
$$
$$
\times d1d2\cdots ds, \tag{6.1}
$$

i.e., after the removal of $\mathbf{G}(i_k,i_{k+1})$ the term $T_s(\Lambda,c)$ becomes a product of two independent integrals. The term $T_s(\Lambda,c)$ with one or more connection lines will be called reducible and the one without any connection lines— **irreducible**. Next, a connection line which appears first in a scattering sequence (starting from the left) will be called **an articulation line**. In an analogous way we define reducibility for the scattering sequence $\Lambda(i_1,i_2,\ldots,i_s)$ only. Let us, namely, call $\mathbf{G}(i_k,i_{k+1})$ **a nodal line** of a scattering sequence $\Lambda(i_1,i_2,\ldots,i_s)$ if the latter can be written in the form

$$
\Lambda(i_1,i_2,\ldots,i_s)
$$
$$
= \Lambda_1(i_1,i_2,\ldots,i_k)\mathbf{G}(i_k,i_{k+1})\Lambda_2(i_{k+1},\ldots,i_s). \tag{6.2}
$$

Next, scattering sequences with one or more nodal lines will be called **S-reducible**.

Nodal lines divide the particles in a given scattering sequence on the set of **nodal blocks** C_i: C_1 denotes the set of particles to the left of the first nodal line, C_2—the particles between the first and second nodal line, and so on. Note that the definition of the nodal line assures that $C_i \cap C_j = \emptyset$ if only $i \neq j$. The nodal structure of sequence $\Lambda(i_1,i_2,\ldots,i_s)$ will be written in the form $C_1|C_2|\cdots|C_k$.

B. Block distribution function

Consider all irreducible terms $T_s(\Lambda,c)$ which share the same scattering sequence and differ only in correlation function. Note that a task of summing all such terms boils down to finding the sum of their correlation functions. However, the irreducibility of the term requires that whenever there is is a nodal line in the scattering sequence, the particles to the left of it cannot be totally uncorrelated from particles to the right. Therefore the sum of the correlation functions that we are looking for is given by

$$
h(C_1|C_2|\cdots|C_k) = \langle C_1(1-P_{unc})C_2(1-P_{unc})\cdots
$$
$$
(1-P_{unc})C_k\rangle. \tag{6.3}
$$

Here $C_1|C_2|\cdots|C_k$ describes the nodal structure of Λ, whereas the operator P_{unc} is the "uncorrelating operator" introduced by Michels[32]

$$
P_{unc} = \rangle\,\langle, \tag{6.4}
$$

which has the property of statistically uncorrelating the variables at its left from those at its right, i.e.,

$$
\langle AP_{unc}B\rangle = \langle A\rangle\langle B\rangle. \tag{6.5}
$$

and so, for example, two-particle correlation function can be written as

$$
\langle 1(1-P_{unc})2\rangle = \langle 12\rangle - \langle 1\rangle\langle 2\rangle
$$
$$
= n(1,2) - n(1)n(2) = h(1,2). \tag{6.6}
$$

The function $h(C_1|C_2|\cdots|C_k)$ defined in Eq. (6.3) is called the block distribution function.[33] For example

$$
h(1|23|45) = \langle 1(1-P_{unc})23(1-P_{unc})45\rangle
$$
$$
= \langle 12345\rangle - \langle 1\rangle\langle 2345\rangle - \langle 123\rangle\langle 45\rangle
$$
$$
+ \langle 1\rangle\langle 23\rangle\langle 45\rangle
$$
$$
= n(1,2,3,4,5) - n(1)n(2,3,4,5)
$$
$$
- n(1,2,3)n(4,5) + n(1)n(2,3)n(4,5), \tag{6.7}
$$

which vanishes whenever the particle $\{1\}$ or the group $\{4,5\}$ is dragged away from the rest of the particles.

Note that if there are no nodal lines in the scattering structure of a given s-particle term, then h becomes the full s-particle partial distribution function $n(1,2,\ldots,s)$.

C. Long-range character of the kernels

The kernels $\mathbf{Y}(\mathbf{r},\mathbf{r}')$ in Eq. (4.12) are of a very long range since the reducible terms in their expansions behave asymptotically as $|\mathbf{r}-\mathbf{r}'|^{-k}$ with $k \leq 3$. To prove it, note that in every reducible term there is at least one connection line: let it be $\mathbf{G}(ij)$ joining particles i and j. One of the following holds.

(1) The connection line $\mathbf{G}(ij)$ joins two $\hat{\mathbf{Z}}_o$ operators: $\hat{\mathbf{Z}}_o(i)$ and $\hat{\mathbf{Z}}_o(j)$. But, since $\hat{\boldsymbol{\mathcal{Z}}}_o\mathcal{P} = \mathcal{P}\hat{\boldsymbol{\mathcal{Z}}}_o = 0$, in the multipole formalism all the components of $\hat{\mathbf{Z}}_o(l=1,m,\sigma;l'=1,m',\sigma')$, except for $\hat{\mathbf{Z}}_o(l=1,m,\sigma=2;l'=1,m',\sigma'=2)$, vanish. This, together with the fact that $\mathbf{G}(l,m,\sigma;l',m',\sigma';\mathbf{R})$ decays as $R^{-(l+l'+\sigma+\sigma'-1)}$, leads to the conclusion that the leading term in the connection line behaves as R_{ji}^{-3} (for $l=l'=2$ and $\sigma=\sigma'=0$).

(2) The connection line joins the $\mathbf{Z}_o$ operator with $\hat{\mathbf{Z}}_o$. In this case the leading term behaves as R_{ji}^{-2} (for $l=1;l'=2$ and $\sigma=0;\sigma'=0$). Here the prime variables refer to the $\hat{\mathbf{Z}}_o$ operator.

(3) The connection line joins two $\mathbf{Z}_o$ operators. Then the leading term behaves as R_{ji}^{-1} (for $l=l'=1$ and $\sigma=\sigma'=0$). However this is the case only for the terms representing $\mathbf{Y}_{jE}$ (as only this kernel has more than one $\mathbf{Z}_o$ operator in its scattering sequence). As there are exactly two $\mathbf{Z}_o$ operators in $\mathbf{Y}_{jE}$, one at the beginning and one at the end of the scattering sequence [cf. Eqs. (4.12a) and (3.30)] the only scattering structure that allows for R_{ji}^{-1} connector is a two-particle term of the form

$$
S_o = \boldsymbol{\mu}_o(1)\mathcal{P}(1)\mathbf{Z}_o(1)\mathbf{G}(12)\mathbf{Z}_o(2)\mathcal{P}(2)\boldsymbol{\mu}_o(2). \tag{6.8}
$$

It should be stressed that long-range elements are absent in irreducible terms. Namely, consider a long-range bond linking particles i and j in an irreducible term K. As the term is irreducible, one of the following holds:

J. Chem. Phys., Vol. 121, No. 7, 15 August 2004

Collective dynamics of Brownian suspensions   3337

(1) Particles i and j are connected by a correlation function. In this case the long-range connector between i and j causes no trouble, as the correlation function decays rapidly as i is dragged away from j.

(2) Particles i and j are connected by some other bond (**G** operator) or a path of bonds coming through other particles. But then K contains more than two bonds and therefore its scattering sequence is different from S_o [Eq. (6.8)]. This in turn implies that each of the two bonds between i and j decays at least as R^{-2}. Together they decay as R^{-4} or faster, which assures convergence.

D. Reduction of long-range kernels

In the following we concentrate on the analysis of the terms making up the kernel $\mathbf{Y}_{jE}$. Due to Eq. (4.12a) this kernel is expressed in terms of the mobility tensor $\boldsymbol{\mu}$, the scattering structure of which is given by Eq. (3.30). First, let us consider reducible terms. Each of them can be written in the form of the product:

$$T_{jE}(\mathbf{r},\mathbf{r}') = \int I_{jE}(\mathbf{r},\mathbf{r}'')\mathbf{G}(\mathbf{r}'',\mathbf{r}''')R_{jE}(\mathbf{r}''',\mathbf{r}')d\mathbf{r}'\,d\mathbf{r}''', \tag{6.9}$$

where T_{jE} stands for the term under consideration, I_{jE} is its part to the left of the articulation line and R_{jE} is the part to the right of it. The definition of articulation line implies that I_{jE} is irreducible.

The terms making up I_{jE} have the following scattering structure:

$$\Lambda(I_{jE}) = \boldsymbol{\mu}_o\mathcal{P}\mathbf{Z}_o(-\mathbf{G}\hat{\mathbf{Z}}_o)^n, \quad n=0,1,\ldots, \tag{6.10}$$

where n is the number of **G** operators in the term. Similarly, the structure of R_{jE} terms reads

$$\Lambda(R_{jE}) = (-\hat{\mathbf{Z}}_o\mathbf{G})^n\mathbf{Z}_o\mathcal{P}\boldsymbol{\mu}_o. \tag{6.11}$$

Note that the scattering structure of R_{jE} given by Eq. (6.11) is the same as the scattering structure of the terms of the kernel $\mathbf{Y}_{fE}$ [cf. Eqs. (4.12c) and (3.34)]. Therefore in the thermodynamic limit the sum of all R_{jE} terms equals $\mathbf{Y}_{fE}$.

Similarly, the scattering structure of I_{jE} is the same as that of the kernel $\mathbf{Y}_{jv}$ [cf. Eqs. (4.12b) and (3.35)]. Thus in the limit $N\to\infty$ the sum of all I_{jE} equals the sum of all **irreducible** terms making up $\mathbf{Y}_{jv}$, which we are going to denote by $\mathbf{Y}_{jv}^{irr}$. Hence in the thermodynamic limit

$$\int \mathbf{Y}_{jE}(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}')d\mathbf{r}'$$

$$= \int \mathbf{Y}_{jE}^{irr}(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}')d\mathbf{r}'$$

$$+ \int \mathbf{Y}_{jv}^{irr}(\mathbf{r},\mathbf{r}'')\mathbf{G}(\mathbf{r}'',\mathbf{r}''')\mathbf{Y}_{fE}(\mathbf{r}''',\mathbf{r}')\mathbf{E}(\mathbf{r}')d\mathbf{r}'\,d\mathbf{r}''\,d\mathbf{r}'''. \tag{6.12}$$

A similar reduction can be performed on the kernel $\mathbf{Y}_{jv}$. Writing down the decompositions analogous to Eq. (6.9) we obtain the terms I_{jv} and R_{jv} with the following scattering structures:

$$\Lambda(I_{jv}) = \boldsymbol{\mu}_o\mathcal{P}\mathbf{Z}_o(-\mathbf{G}\hat{\mathbf{Z}}_o)^n = \Lambda(I_{jE}),$$

$$\Lambda(R_{jv}) = -(-\hat{\mathbf{Z}}_o\mathbf{G})^n\hat{\mathbf{Z}}_o. \tag{6.13}$$

In the limit of a macroscopic system the sum of all R_{jv} terms is equal to $\mathbf{Y}_{fv}$. Therefore in this limit the following holds:

$$\int \mathbf{Y}_{jv}(\mathbf{r},\mathbf{r}')\mathbf{v}_o(\mathbf{r}')$$

$$= \int \mathbf{Y}_{jv}^{irr}(\mathbf{r},\mathbf{r}')\mathbf{v}_o(\mathbf{r}')d\mathbf{r}'$$

$$+ \int \mathbf{Y}_{jv}^{irr}(\mathbf{r},\mathbf{r}'')\mathbf{G}(\mathbf{r}'',\mathbf{r}''')\mathbf{Y}_{fv}(\mathbf{r}''',\mathbf{r}')\mathbf{v}_o(\mathbf{r}')d\mathbf{r}''d\mathbf{r}'. \tag{6.14}$$

Adding Eq. (6.12) to the above equation gives

$$\langle\mathbf{j}(\mathbf{r})\rangle_t^{inst} = \int [\mathbf{Y}_{jE}(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}')+\mathbf{Y}_{jv}(\mathbf{r},\mathbf{r}')\mathbf{v}_o(\mathbf{r}')]d\mathbf{r}'$$

$$= \int [\mathbf{Y}_{jE}^{irr}(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}')+\mathbf{Y}_{jv}^{irr}(\mathbf{r},\mathbf{r}')\mathbf{v}_o(\mathbf{r}')]d\mathbf{r}'$$

$$+ \int d\mathbf{r}''d\mathbf{r}'''\mathbf{Y}_{jv}^{irr}(\mathbf{r},\mathbf{r}'')\mathbf{G}(\mathbf{r}'',\mathbf{r}''')$$

$$\times\left(\int d\mathbf{r}'\mathbf{Y}_{fE}(\mathbf{r}''',\mathbf{r}')\mathbf{E}(\mathbf{r}')\right.$$

$$\left.+\mathbf{Y}_{fv}(\mathbf{r}''',\mathbf{r}')\mathbf{v}_o(\mathbf{r}')\right). \tag{6.15}$$

However, the expression in brackets is just the instantaneous force density $\langle\mathbf{f}(\mathbf{r})\rangle_t^{inst}$ [see Eq. (4.10)]. Hence, introducing an instantaneous suspension velocity as

$$\langle\mathbf{v}(\mathbf{r})\rangle_t^{inst} = \mathbf{v}_o(\mathbf{r})+\int d\mathbf{r}'\mathbf{G}(\mathbf{r},\mathbf{r}')\langle\mathbf{f}(\mathbf{r}')\rangle_t^{inst}, \tag{6.16}$$

we can rewrite Eq. (6.15) in the compact notation in the form,

$$\langle\mathbf{j}\rangle_t^{inst} = \mathbf{Y}_{jE}^{irr}\mathbf{E}+\mathbf{Y}_{jv}^{irr}\langle\mathbf{v}\rangle_t^{inst}. \tag{6.17}$$

Note that the kernels in the above equation are short ranged, as all their terms are irreducible and therefore devoid of solitary **G** connectors.

In an exactly analogous manner one may carry out the reduction of instantaneous kernels in Eq. (4.10) for force density and arrive at the expression

$$\langle\mathbf{f}\rangle_t^{inst} = \mathbf{Y}_{fE}^{irr}\mathbf{E}+\mathbf{Y}_{fv}^{irr}\langle\mathbf{v}\rangle_t^{inst}. \tag{6.18}$$

VII. EFFECTIVE EQUATIONS FOR SHORT-TIME DYNAMICS

We have expressed the instantaneous particle current $\langle\mathbf{j}\rangle_t^{inst}$ in terms of the short-range kernels $\mathbf{Y}^{irr}$ acting on the external field $\mathbf{E}$ and mean suspension velocity $\langle\mathbf{v}\rangle_t^{inst}$. Because of their short range, the kernels $\mathbf{Y}^{irr}$ are independent of the shape and size of the sample provided that it is macroscopic. In this case, however, one can equally well assume that the sample is infinite. It would not affect the kernels

$\mathbf{Y}^{irr}(\mathbf{r},\mathbf{r}')$ but greatly facilitate the calculations as the hydrodynamic Green function for an infinite system (3.6) can now be used.

To obtain the transport coefficients, let us transform the equations into $\mathbf{k}$ space and analyze their long-wavelength limit. The Fourier transform of Eq. (6.17) for the homogeneous system reads

$$\langle\mathbf{j}(\mathbf{k})\rangle_t^{inst}=\mathbf{Y}_{jE}^{irr}(\mathbf{k})\mathbf{E}(\mathbf{k})+\mathbf{Y}_{jv}^{irr}(\mathbf{k})\langle\mathbf{v}(\mathbf{k})\rangle_t^{inst}. \tag{7.1}$$

In the limit $(\mathbf{k}\rightarrow0)$ the tensor $\mathbf{Y}_{jv}^{irr}$ takes a particularly simple form. Namely, Eqs. (4.12b) and (3.35) yield

$$\mathbf{Y}_{jv}^{irr}(\mathbf{k}=0)=\int\left\langle\sum_{i=1}^{N}\delta(\mathbf{R}_i)[\boldsymbol{\mu}_o\boldsymbol{\mathcal{P}}\boldsymbol{\mathcal{Z}}_o\right.$$
$$\left.-\boldsymbol{\mu}_o\boldsymbol{\mathcal{P}}\boldsymbol{\mathcal{Z}}_o\boldsymbol{\mathcal{G}}(1+\hat{\boldsymbol{\mathcal{Z}}}_o\boldsymbol{\mathcal{G}})^{-1}\hat{\boldsymbol{\mathcal{Z}}}_o]_i(\mathbf{r}')\right\rangle^{irr}d\mathbf{r}'. \tag{7.2}$$

However, since both $\boldsymbol{\mathcal{Z}}_o(i;\mathbf{r}')$ and $\hat{\boldsymbol{\mathcal{Z}}}_o(i;\mathbf{r}')$ vanish for $\mathbf{r}'$ outside of the particle i, the above expression is equivalent to

$$\mathbf{Y}_{jv}^{irr}(\mathbf{k}=0)=\left\langle\sum_{i=1}^{N}\delta(\mathbf{R}_i)[\boldsymbol{\mu}_o\boldsymbol{\mathcal{P}}\boldsymbol{\mathcal{Z}}_o\boldsymbol{\mathcal{P}}^t\right.$$
$$\left.-\boldsymbol{\mu}_o\boldsymbol{\mathcal{P}}\boldsymbol{\mathcal{Z}}_o\boldsymbol{\mathcal{G}}(1+\hat{\boldsymbol{\mathcal{Z}}}_o\boldsymbol{\mathcal{G}})^{-1}\hat{\boldsymbol{\mathcal{Z}}}_o\boldsymbol{\mathcal{P}}^t]_i\right\rangle^{irr}. \tag{7.3}$$

Using the fact that $\hat{\boldsymbol{\mathcal{Z}}}_o\boldsymbol{\mathcal{P}}^t=0$ one gets finally

$$\mathbf{Y}_{jv}^{irr}(\mathbf{k}=0)=\left\langle\sum_{i=1}^{N}\delta(\mathbf{R}_i)\boldsymbol{\mu}_o(i)\boldsymbol{\mathcal{P}}(i)\mathbf{Z}_o(i)\boldsymbol{\mathcal{P}}^t(i)\right\rangle^{irr}$$
$$=\left\langle\sum_{i=1}^{N}\delta(\mathbf{R}_i)\right\rangle\mathbf{1}=n\mathbf{1}. \tag{7.4}$$

The next nonvanishing term in the expansion of $\mathbf{Y}_{jv}(\mathbf{k})$ in $\mathbf{k}$ is the second-order one,

$$\mathbf{Y}_{jv}^{irr}(\mathbf{k})=n\mathbf{1}+k^2\mathbf{y}_{jv}+\cdots, \tag{7.5}$$

with the tensor $\mathbf{y}_{jv}$ of the form

$$\mathbf{y}_{jv}=y_{jv}^l\hat{\mathbf{k}}\hat{\mathbf{k}}+y_{jv}^t(1-\hat{\mathbf{k}}\hat{\mathbf{k}}), \tag{7.6}$$

where y_{jv}^l and y_{jv}^t are scalars. Because of the incompressibility constraint,

$$\mathbf{k}\cdot\langle\mathbf{v}(\mathbf{k})\rangle^{inst}=0, \tag{7.7}$$

the first term in Eq. (7.6) does not contribute to Eq. (7.1). Hence in the small $\mathbf{k}$ limit this equation can be rewritten as

$$\langle\mathbf{j}(\mathbf{k})\rangle_t^{inst}-n\langle\mathbf{v}(\mathbf{k})\rangle_t^{inst}=y_{jE}\mathbf{E}(\mathbf{k})+k^2y_{jv}^t\langle\mathbf{v}(\mathbf{k})\rangle_t^{inst}, \tag{7.8}$$

with y_{jE} given by

$$\mathbf{Y}_{jE}^{irr}(\mathbf{k}=0)=y_{jE}\mathbf{1}. \tag{7.9}$$

Let us now turn to the equation for the suspension velocity. The Fourier transform of the hydrodynamic Green function for an infinite space reads

$$\mathbf{G}(\mathbf{k})=\frac{1}{\eta k^2}(1-\hat{\mathbf{k}}\hat{\mathbf{k}}), \tag{7.10}$$

so that the velocity field in this case may be written as

$$k^2\langle\mathbf{v}(\mathbf{k})\rangle_t^{inst}=\frac{1}{\eta}(1-\hat{\mathbf{k}}\hat{\mathbf{k}})[\langle\mathbf{f}(\mathbf{k})\rangle_t^{inst}+\mathbf{f}_o(\mathbf{k})]. \tag{7.11}$$

Inserting the instantaneous force density $\langle\mathbf{f}\rangle_t^{inst}$ as given by Eq. (6.18) yields

$$k^2\langle\mathbf{v}(\mathbf{k})\rangle_t^{inst}=\frac{1}{\eta}(1-\hat{\mathbf{k}}\hat{\mathbf{k}})[\mathbf{f}_o(\mathbf{k})+\mathbf{Y}_{fE}^{irr}(\mathbf{k})\mathbf{E}(\mathbf{k})+\mathbf{Y}_{fv}^{irr}(\mathbf{k})$$
$$\times\langle\mathbf{v}(\mathbf{k})\rangle_t^{inst}]. \tag{7.12}$$

Next we investigate the lowest order $[O(1)]$ term in the expansion of the operators $\mathbf{Y}_{fE}^{irr}(\mathbf{k})$ and $\mathbf{Y}_{fv}^{irr}(\mathbf{k})$ in wave number. Since $\mathbf{Y}_{fE}^{irr}$ is adjoint to $\mathbf{Y}_{jv}^{irr}$,

$$\mathbf{Y}_{fE}^{irr}(\mathbf{k}=0)=\mathbf{Y}_{jv}^{irr}(\mathbf{k}=0)=n\mathbf{1}. \tag{7.13}$$

To find $\mathbf{k}=0$ value of $\mathbf{Y}_{fv}^{irr}(\mathbf{k})$ we recall the scattering structure of this operator. From Eqs. (4.12d) and (3.29) it follows that

$$\mathbf{Y}_{fv}^{irr}(\mathbf{k}=0)=-\int\langle\hat{\boldsymbol{\mathcal{Z}}}_o(1+\boldsymbol{\mathcal{G}}\hat{\boldsymbol{\mathcal{Z}}}_o)^{-1}(\mathbf{r}=0,\mathbf{r}')\rangle^{irr}d\mathbf{r}'. \tag{7.14}$$

Here the scattering sequence ends with $\hat{\boldsymbol{\mathcal{Z}}}_o$ operator, hence the same reasoning as that following the Eq. (7.2) leads to the conclusion that

$$\mathbf{Y}_{fv}^{irr}(\mathbf{k}=0)=0. \tag{7.15}$$

Therefore the small $\mathbf{k}$ expansions of operators $\mathbf{Y}_{fE}$ and $\mathbf{Y}_{fv}$ read

$$\mathbf{Y}_{fE}^{irr}(\mathbf{k})=n\mathbf{1}+k^2\mathbf{y}_{fE}+\cdots,$$
$$\mathbf{Y}_{fv}^{irr}(\mathbf{k})=-k^2\mathbf{y}_{fv}+\cdots. \tag{7.16}$$

The tensors $\mathbf{y}_{fv}$ and $\mathbf{y}_{fE}$ can be decomposed, similarly to $\mathbf{y}_{jv}$, in longitudinal and transverse part. Finally, using the fact that $(1-\hat{\mathbf{k}}\hat{\mathbf{k}})\mathbf{v}(\mathbf{k})=\mathbf{v}(\mathbf{k})$, due to the incompressibility condition, Eq. (7.12) can be rewritten as

$$k^2(\eta+y_{fv}^t)\langle\mathbf{v}(\mathbf{k})\rangle_t^{inst}=(1-\hat{\mathbf{k}}\hat{\mathbf{k}})[\mathbf{f}_o(\mathbf{k})+n\mathbf{E}(\mathbf{k})$$
$$+k^2y_{fE}^t\mathbf{E}(\mathbf{k})]. \tag{7.17}$$

Because of the symmetry between the operators $\mathbf{Y}_{jv}$ and $\mathbf{Y}_{fE}$ the coefficient y_{fE}^t is equal to y_{jv}^t introduced earlier. This is the manifestation of the Onsager symmetry guessed by Nozières.[11]

An interesting aspect of Eqs. (7.8) and (7.17) is the natural appearance of the particle current relative to the suspension flow

$$\mathbf{J}_d^{inst}=\langle\mathbf{j}(\mathbf{k})\rangle_t^{inst}-n\langle\mathbf{v}(\mathbf{k})\rangle_t^{inst} \tag{7.18}$$

and the total external force (per unit volume) exerted on the suspension

$$\mathbf{F}_{tot}=\mathbf{f}_o+n\mathbf{E}. \tag{7.19}$$

Returning to the real space, the system of Eqs. (7.8) and (7.17) can be cast into the form

$$\mathbf{J}_d^{inst} = y_{jE}\mathbf{E} - y_{jv}^t\nabla^2\langle\mathbf{v}\rangle_t^{inst}, \tag{7.20a}$$

$$-(\eta+y_{fv}^t)\nabla^2\langle\mathbf{v}\rangle_t^{inst} = \mathbf{F}_{\text{tot}} - \text{grad}\,p - y_{fE}^t(\nabla^2\mathbf{E}^{inst}$$

$$- \text{grad div }\mathbf{E}^{inst}), \tag{7.20b}$$

where use has been made of the fact that longitudinal part of the force $\mathbf{F}_{\text{tot}}$ is compensated by a pressure gradient

$$-i\mathbf{k}p(\mathbf{k}) = \hat{\mathbf{k}}\hat{\mathbf{k}}\cdot\mathbf{F}_{\text{tot}}(\mathbf{k}). \tag{7.21}$$

Equation (7.20b) can be further rewritten using Eq. (7.20a) to express $\mathbf{E}$ in terms of $\mathbf{J}_d$. Keeping the lowest terms in wave vector, we get

$$\mathbf{J}_d^{inst} = y_{jE}\mathbf{E} - y_{jv}^t\nabla^2\langle\mathbf{v}\rangle_t^{inst}, \tag{7.22a}$$

$$-(\eta+y_{fv}^t)\nabla^2\langle\mathbf{v}\rangle_t^{inst}$$

$$= \mathbf{F}_{\text{tot}} - \text{grad}\,p - \frac{y_{fE}^t}{y_{jE}}(\nabla^2\mathbf{J}_d^{inst} - \text{grad div }\mathbf{J}_d^{inst}). \tag{7.22b}$$

The dynamics described by the above set of equations is relatively complex. First of all, there are direct effects: The diffusion current is induced by an external force $\mathbf{E}$ applied to the particles whereas the suspension velocity field is induced by the overall external force acting on the particles and the fluid, $\mathbf{F}_{\text{tot}}$. The effective viscosity of the suspension is modified by the presence of the particles and reads

$$\eta^{\text{eff}} = \eta + y_{fv}^t. \tag{7.23}$$

However, there are also cross effects linking the suspension velocity with the diffusion current. These are given by the terms $y_{jv}^t\nabla^2\langle\mathbf{v}^{inst}\rangle$ and $(y_{fE}^t/y_{jE})\nabla^2\mathbf{J}_d^{inst}$ and describe the processes in which inhomogeneities in suspension velocity field drive the diffusion current and vice versa. The above equations were first derived by Nozières[11] in a rather phenomenological way. The throughout derivation was given by Felderhof[12,34] and Noetinger.[5] Felderhof used a technique called renormalized cluster expansion[35] to derive Eqs. (6.17) and (6.18) and proved that all response kernels in these equations are short ranged. The reduction presented in this paper can be seen as a simplified version of this technique. On the other hand, Noetinger worked from the very start in the Fourier space. He performed only partial reduction of the kernels and therefore was left with a number of cumbersome $\mathbf{k}\to0$ limits to calculate. Nevertheless he obtained the same equations as Felderhof and here, although written in a slightly different language (as he used the hydrodynamic formalism of Mazur, van Saarlos, and Beenakker[7,36,37]).

VIII. REDUCTION OF RETARDED RESPONSE KERNELS

Our next task is to perform the reduction of the retarded response kernels $\mathbf{X}$ given by Eq. (4.13). The general form of these kernels is

$$\mathbf{X} = \langle Ae^{\mathcal{L}t}B\rangle,$$

with two operators A and B on both sides of the evolution operator $e^{\mathcal{L}t}$. It is precisely the presence of this operator in

the kernels that makes the reduction complicated. Therefore, let us focus on the evolution operator first. To begin with, the adjoint Smoluchowski operator

$$\mathcal{L} = [\beta^{-1}\vec{\nabla} + \mathcal{F}]\cdot\boldsymbol{\mu}\cdot\vec{\nabla} \tag{8.1}$$

is decomposed as

$$\mathcal{L}(1,2,\ldots,N) = \sum_{i=1}^N \mathcal{L}_o(i) + \delta\mathcal{L}(1,2,\ldots,N), \tag{8.2}$$

where $\mathcal{L}_o(i)$ is the one-particle operator

$$\mathcal{L}_o(i) = D_o\nabla_i^2, \tag{8.3}$$

with ∇_i^2 denoting the Laplacian with respect to $\mathbf{R}_i$. It is worth noting that $\mathcal{L}_o$ does not introduce any correlation between the particles. Now the evolution operator can be written as a series

$$e^{\mathcal{L}t} = S(t) + \int_0^t d\tau S(t-\tau)\delta\mathcal{L}S(\tau)$$

$$+ \int_0^t d\tau\int_0^\tau d\tau'S(t-\tau)\delta\mathcal{L}S(\tau-\tau')\delta\mathcal{L}S(\tau)+\cdots, \tag{8.4}$$

where

$$S(1,2,\ldots,N;t) = \prod_i^N S(i;t) \tag{8.5}$$

and

$$S(i;t) = e^{\mathcal{L}_o(i)t}. \tag{8.6}$$

Next, one performs the scattering expansion of the operators A, B, and $\delta\mathcal{L}$. Then, after inserting the expansions into $\langle Ae^{\mathcal{L}t}B\rangle$ one ends up with the representation of the retarded response kernel as a sum of terms of the following structure:

$$R_s(\Lambda,c) = \int d1\cdots ds \int_0^t d\tau\int_0^{\tau_1} d\tau_2\cdots$$

$$\int_0^{\tau_{n-1}} d\tau_n A'(t)S(t-\tau_1)\delta L'(\tau_1)S(\tau_1-\tau_2)$$

$$\times \delta L'(\tau_2)\cdots S(\tau_n)B'(\tau_n), \tag{8.7}$$

where A', B', and $\delta L'$ stand for some elements of the scattering expansions of A, B, and $\delta\mathcal{L}$, respectively, and s is the number of particles appearing in the given term. The time variables have been added to time-independent operators $\delta L'$, A', and B' just to indicate their positions relative to the evolution operators in the above integral.

The next task is to perform the reduction of $R_s(\Lambda,c)$ along similar lines to the approach presented in Sec. VI D— i.e., by identification of long-ranged connection lines. The definition of a connection line is analogous to that in instantaneous response terms: an operator $\mathbf{G}(i_k,i_{k+1})$ is called a connection line of a term $R_s(\Lambda,c)$ if the latter can be written as

$$R_s(\Lambda,c) = \int \Lambda_1(i_1,i_2,\ldots,i_k)c_1(i_1,i_2,\ldots,i_k)$$
$$\times \mathbf{G}(i_k,i_{k+1})\Lambda_2(i_{k+1},\ldots,i_s)$$
$$\times c_2(i_{k+1},\ldots,i_s)d1\,d2\cdots ds, \tag{8.8}$$

so that after the removal of $\mathbf{G}(i_k,i_{k+1})$ the term $R_s(\Lambda,c)$ becomes a product of two independent integrals. Integrals over time have been omitted in the above expression as they are irrelevant to our definition. The nodal line and nodal blocks for terms $R_s(\Lambda,c)$ are defined analogously to the instantaneous response case. However, because of the fact that retarded response terms consist of a number of individual operators A', $\delta L'(\tau_1), \delta L'(\tau_2),\ldots$ the nodal structure of $R_s(\Lambda,c)$ is usually very complicated and in general it is impossible to apply the concept of block distribution function here. To facilitate analysis of the nodal structure of retarded response kernels a special diagrammatic technique[38] has been developed. One of the important elements of this analysis is a concept of a proper term. To define it, let us consider a term R_s with a scattering structure $\Lambda(i_1,i_2,\ldots,i_s)$ and a nodal line $\mathbf{G}(i_k,i_{k+1})$ such that

$$\Lambda(i_1,i_2,\ldots,i_s) = \Lambda_1(i_1,i_2,\ldots,i_k)\mathbf{G}(i_k,i_{k+1})$$
$$\times \Lambda_2(i_{k+1},\ldots,i_s). \tag{8.9}$$

The term R_s will be called proper if all the operators in which the particles from $\{i_1,i_2,\ldots,i_k\}$ appear have larger or equal time coordinates than these in which $\{i_{k+1},\ldots,i_s\}$ appear. For example a term of the form

$$\int_0^t d\tau \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 h(i_1,i_2,i_5)A_1'(i_1,i_2;t)$$
$$\times \mathbf{G}(i_2,i_3)A_2'(i_3,i_4;t)S(t-\tau_1)\delta L'(i_3,i_4,i_5;\tau_1)$$
$$\times S(\tau_1-\tau_2)\delta L_1'(i_3,i_5;\tau_2)\mathbf{G}(i_5,i_6)\delta L_2'(i_6,i_7;\tau_2)$$
$$\times S(\tau_3)B'(i_6,i_7,i_8;\tau_3) \tag{8.10}$$

is proper whereas

$$\int_0^t d\tau \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 h(i_1,i_2,i_5)A_1'(i_1,i_2;t)\mathbf{G}(i_2,i_3)$$
$$\times A_2'(i_3,i_4;t)S(t-\tau_1)\delta L_1'(i_5,i_6;\tau_1)\mathbf{G}(i_6,i_7)$$
$$\times \delta L_2'(i_7,i_3;\tau_1)S(\tau_1-\tau_2)\delta L_3'(i_3,i_4,i_7;\tau_2)\mathbf{G}(i_7,i_8)$$
$$\times \delta L_4'(i_8,i_9;\tau_2)S(\tau_3)B'(i_8,i_9,i_{10};\tau_3) \tag{8.11}$$

is not proper. In other words, for proper terms the division of the particles by a nodal line is consistent with the ordering induced by time dimension. Note that the definition of a proper term concerns only the scattering structure in R_s, the correlation structure is irrelevant here.

"Properness" has a particularly simple interpretation if one presents the nodal structure of an operator in a graphical way. For example, the term given by Eq. (8.11) can be depicted schematically as in Fig. 1.

In graph theory such a structure is called **a tree**: a connected graph which do not contain any circuits (the lack of circuits stems directly from the definition of the nodal line). The nodal structure graph (NSG) of the proper terms is even
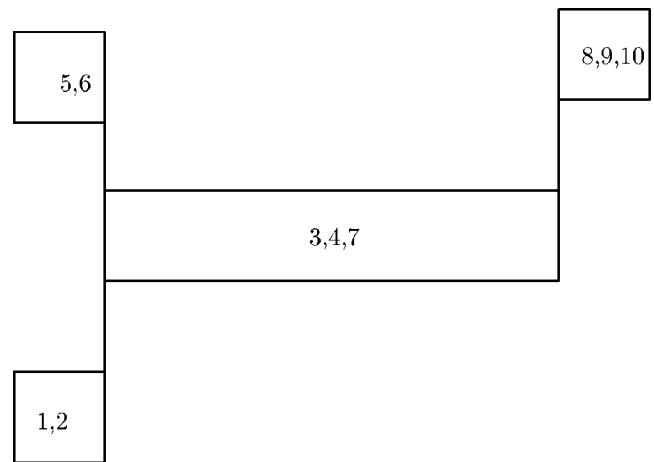

FIG. 1. Nodal structure of the term given by Eq. (8.11).

simpler. For example, the NSG of the term (8.10) is given in Fig. 2. It is **a simple chain**—a tree with two terminal vertices only. It can be proved[38] that all the proper terms share such a structure.

Thus in proper terms nodal lines divide the particles $i_1,\ldots,i_s$ into nodal blocks $C_1,C_2,\ldots$ which can be ordered according to the place in the chain. This means that the nodal structure can again be written in the form $C_1|C_2|\ldots|C_k$, where $C_1,C_2,\ldots,C_k$ come one after another in the time integral (8.7). For such a structure a block distribution function can again be defined by Eq. (6.3).

Unfortunately, these concepts cannot be applied in the case of improper terms. However, it may be shown[38] that in the thermodynamic limit the sum of all improper terms making up a given retarded response kernel vanishes. Therefore in the subsequent analysis we can safely consider proper terms only. Because of their chainlike form, it is relatively easy to sum the proper terms which share a similar nodal structure. For example, for the proper terms making up the kernel $\mathbf{X}_{jE}$ [Eq. (4.13a)] one gets the following:

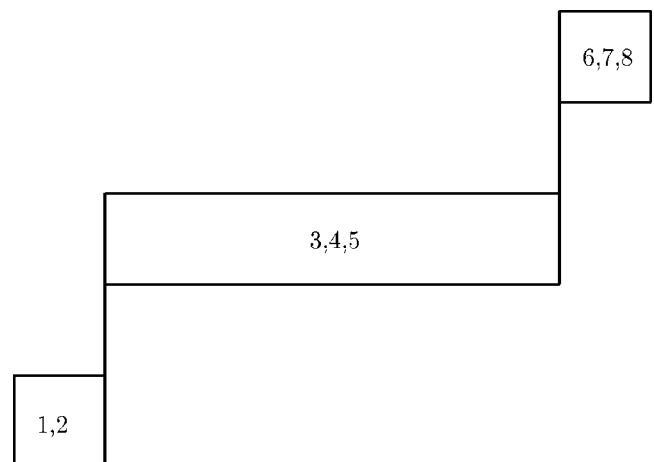(1) Terms with an articulation line in A block sum up in the limit of macroscopic system to

FIG. 2. Nodal structure graph of the term given by Eq. (8.10).

$$\mathbf{Y}_{jv}^{irr}\mathbf{G}\mathbf{X}_{fE}(t). \tag{8.12}$$

(2) Terms with an articulation line in δL block sum up to

$$\int_0^t d\tau \mathbf{X}_{jv}^{irr}(t-\tau)\mathbf{G}\mathbf{X}_{fE}(\tau). \tag{8.13}$$

(3) The sum of terms with an articulation line inside B block is equal to

$$\mathbf{X}_{jv}^{irr}(t)\mathbf{G}\mathbf{Y}_{fE}. \tag{8.14}$$

Using the above results the kernel $\mathbf{X}_{jE}$ may be written as

$$\mathbf{X}_{jE}(t)=\mathbf{X}_{jE}^{irr}(t)+\mathbf{Y}_{jv}^{irr}\mathbf{G}\mathbf{X}_{fE}(t)+\int_0^t d\tau \mathbf{X}_{jv}^{irr}(t-\tau)\mathbf{G}\mathbf{X}_{fE}(\tau)$$

$$+\mathbf{X}_{jv}^{irr}(t)\mathbf{G}\mathbf{Y}_{fE}. \tag{8.15}$$

In an analogous way it is possible to prove that

$$\mathbf{X}_{jv}(t)=\mathbf{X}_{jv}^{irr}(t)+\mathbf{Y}_{jv}^{irr}\mathbf{G}\mathbf{X}_{fv}(t)+\int_0^t d\tau \mathbf{X}_{jv}^{irr}(t-\tau)\mathbf{G}\mathbf{X}_{fv}(\tau)$$

$$+\mathbf{X}_{jv}^{irr}(t)\mathbf{G}\mathbf{Y}_{fv}. \tag{8.16}$$

After inserting these equations into Eq. (4.9) we get the following expression for the retarded part of the particle current

$$\langle\mathbf{j}\rangle_t^{ret}=\int_{-\infty}^t dt'[\mathbf{X}_{jE}^{irr}(t-t')\mathbf{E}(t')+\mathbf{X}_{jv}^{irr}(t-t')\mathbf{v}_o(t')]$$

$$+\mathbf{Y}_{jv}^{irr}\mathbf{G}\int_{-\infty}^t dt'[\mathbf{X}_{fE}(t-t')\mathbf{E}(t')$$

$$+\mathbf{X}_{fv}(t-t')\mathbf{v}_o(t')]+\int_{-\infty}^t dt'\int_0^{t-t'}d\tau$$

$$\times\mathbf{X}_{jv}^{irr}(t-t'-\tau)\mathbf{G}[\mathbf{X}_{fE}(\tau)\mathbf{E}(t')+\mathbf{X}_{fv}(\tau)\mathbf{v}_o(t')]$$

$$+\int_{-\infty}^t dt'\mathbf{X}_{jv}^{irr}(t-t')\mathbf{G}[\mathbf{Y}_{fE}\mathbf{E}(t')+\mathbf{Y}_{fv}\mathbf{v}_o(t')]. \tag{8.17}$$

The third term can be simplified by first changing the variables of integration to $(t',t''=t'+\tau)$, then changing the order of integration, and finally using the fact that [cf. Eq. (4.10)]

$$\int_{-\infty}^{t''} dt'[\mathbf{X}_{fE}(t''-t')\mathbf{E}(t')+\mathbf{X}_{fv}(t''-t')\mathbf{v}_o(t')]=\langle\mathbf{f}\rangle_{t''}^{ret}. \tag{8.18}$$

By this means the above-mentioned term can be cast into the form

$$\int_{-\infty}^t dt''\mathbf{X}_{jv}^{irr}(t-t'')\mathbf{G}\langle\mathbf{f}\rangle_{t''}^{ret}. \tag{8.19}$$

Equation (8.17) can be further simplified by noting that due to Eqs. (6.16) and (4.10),

$$\mathbf{G}[\mathbf{Y}_{fE}\mathbf{E}(t')+\mathbf{Y}_{fv}\mathbf{v}_o(t')]=\langle\mathbf{v}\rangle_{t'}^{inst}-\mathbf{v}_o. \tag{8.20}$$

Hence Eq. (8.17) takes the form

$$\langle\mathbf{j}\rangle_t^{ret}=\int_{-\infty}^t dt'[\mathbf{X}_{jE}^{irr}(t-t')\mathbf{E}(t')+\mathbf{X}_{jv}^{irr}(t-t')\langle\mathbf{v}\rangle_{t'}^{ins}]$$

$$+\mathbf{Y}_{jv}^{irr}\langle\mathbf{v}\rangle_{t'}^{ret}+\int_{-\infty}^t dt'\mathbf{X}_{jv}^{irr}(t-t')\langle\mathbf{v}\rangle_{t'}^{ret}$$

$$=\int_{-\infty}^t dt'[\mathbf{X}_{jE}^{irr}(t-t')\mathbf{E}(t')+\mathbf{X}_{jv}^{irr}(t-t')\langle\mathbf{v}\rangle_{t'}]$$

$$+\mathbf{Y}_{jv}^{irr}\langle\mathbf{v}\rangle_t^{ret}, \tag{8.21}$$

where the retarded part of the mean suspension velocity is given by

$$\langle\mathbf{v}\rangle_t^{ret}=\langle\mathbf{v}\rangle_t-\langle\mathbf{v}\rangle_t^{inst}=\mathbf{G}\langle\mathbf{f}\rangle_t^{ret}. \tag{8.22}$$

Finally, using expression (6.17) for $\langle\mathbf{j}\rangle_t^{inst}$ the total particle current can be written as

$$\langle\mathbf{j}\rangle_t=\mathbf{Y}_{jE}^{irr}\mathbf{E}(t)+\mathbf{Y}_{jv}^{irr}\langle\mathbf{v}\rangle_t+\int_{-\infty}^t dt'[\mathbf{X}_{jE}^{irr}(t-t')\mathbf{E}(t')$$

$$+\mathbf{X}_{jv}^{irr}(t-t')\langle\mathbf{v}\rangle_{t'}]. \tag{8.23}$$

Note that the above equation relates $\langle\mathbf{j}\rangle_t$ to the fields $\mathbf{E}$ and $\langle\mathbf{v}\rangle$ in terms of short-ranged, irreducible response kernels only.

IX. FORCE DENSITY

The same decomposition procedure can be performed on the kernels $\mathbf{X}_{fE}$ and $\mathbf{X}_{fv}$, Eq. (4.13). Proceeding analogously to the previous case, we obtain

$$\mathbf{X}_{fE}(t)=\mathbf{X}_{fE}^{irr}(t)+\mathbf{Y}_{fv}^{irr}\mathbf{G}\mathbf{X}_{fE}(t)$$

$$+\int_0^t d\tau\mathbf{X}_{fv}^{irr}(t-\tau)\mathbf{G}\mathbf{X}_{fE}(\tau)+\mathbf{X}_{fv}^{irr}(t)\mathbf{G}\mathbf{Y}_{fE},$$

$$\mathbf{X}_{fv}(t)=\mathbf{X}_{fv}^{irr}(t)+\mathbf{Y}_{fv}^{irr}\mathbf{G}\mathbf{X}_{fv}(t)$$

$$+\int_0^t d\tau\mathbf{X}_{fv}^{irr}(t-\tau)\mathbf{G}\mathbf{X}_{fv}(\tau)+\mathbf{X}_{fv}^{irr}(t)\mathbf{G}\mathbf{Y}_{fv}, \tag{9.1}$$

and for the force density

$$\langle\mathbf{f}\rangle_t=\mathbf{Y}_{fE}^{irr}\mathbf{E}(t)+\mathbf{Y}_{fv}^{irr}\langle\mathbf{v}\rangle_t+\int_{-\infty}^t dt'[\mathbf{X}_{fE}^{irr}(t-t')\mathbf{E}(t')$$

$$+\mathbf{X}_{fv}^{irr}(t-t')\langle\mathbf{v}\rangle_{t'}]. \tag{9.2}$$

The above result can be inserted into the Stokes equation to yield, after the Fourier transform,

$$k^2\langle\mathbf{v}(\mathbf{k})\rangle_t=\frac{1}{\eta}(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\Big[\mathbf{f}_o(\mathbf{k},t)+\mathbf{Y}_{fE}^{irr}\mathbf{E}(\mathbf{k},t)$$

$$+\mathbf{Y}_{fv}^{irr}\langle\mathbf{v}(\mathbf{k})\rangle_t+\int_{-\infty}^t dt'[\mathbf{X}_{fE}^{irr}(\mathbf{k},t-t')\mathbf{E}(t')$$

$$+\mathbf{X}_{fv}^{irr}(\mathbf{k},t-t')\langle\mathbf{v}(\mathbf{k})\rangle_{t'}]\Big]. \tag{9.3}$$

X. FULL EFFECTIVE EQUATIONS

In this section we obtain the effective equations governing the dynamics of Brownian suspensions on long-time scales when the memory effects are important. Our starting point are Eqs. (8.23) and (9.3) for the particle current and suspension velocity, respectively. The structure of the equations can be seen most clearly after the Fourier transform in time

$$
\mathbf{J}(\mathbf{k},\omega) = \mathbf{Y}_{jE}^{irr}(\mathbf{k})\mathbf{E}(\mathbf{k},\omega) + \mathbf{Y}_{jv}^{irr}(\mathbf{k})\mathbf{V}(\mathbf{k},\omega)
$$
$$
+ \mathbf{X}_{jE}^{irr}(\mathbf{k},\omega)\mathbf{E}(\mathbf{k},\omega) + \mathbf{X}_{jv}^{irr}(\mathbf{k},\omega)\mathbf{V}(\mathbf{k},\omega),
$$
$$
\tag{10.1}
$$

$$
k^2\mathbf{V}(\mathbf{k},\omega) = \frac{1}{\eta}(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})[\mathbf{f}_o(\mathbf{k},\omega) + \mathbf{Y}_{fE}^{irr}(\mathbf{k})\mathbf{E}(\mathbf{k},\omega)
$$
$$
+ \mathbf{Y}_{fv}^{irr}(\mathbf{k})\mathbf{V}(\mathbf{k},\omega) + \mathbf{X}_{fE}^{irr}(\mathbf{k},\omega)\mathbf{E}(\mathbf{k},\omega)
$$
$$
+ \mathbf{X}_{fv}^{irr}(\mathbf{k},\omega)\mathbf{V}(\mathbf{k},\omega)],
$$
$$
\tag{10.2}
$$

where

$$
\mathbf{V}(\mathbf{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\mathbf{v}(\mathbf{k})\rangle_t e^{i\omega t}dt,
\tag{10.3}
$$

and analogously for $\mathbf{J}(\mathbf{k},\omega)$. The kernels $\mathbf{X}=\langle Ae^{\mathcal{L}t}B\rangle$ are transformed as

$$
\mathbf{X}(\omega) = \int_0^{\infty}\langle Ae^{\mathcal{L}t}B\rangle e^{i\omega t}dt.
\tag{10.4}
$$

Using the expansion in $\mathbf{k}$ of the kernels $\mathbf{Y}(\mathbf{k})$ derived in Sec. VII together with analogous expansions for the kernels $\mathbf{X}(\mathbf{k})$

$$
\mathbf{X}_{jE}^{irr}(\mathbf{k},\omega) = x_{jE}(\omega)\mathbf{1}+\cdots,
\tag{10.5}
$$

$$
\mathbf{X}_{jv}^{irr}(\mathbf{k},\omega) = k^2\mathbf{x}_{jv}(\omega)+\cdots,
\tag{10.6}
$$

$$
\mathbf{X}_{fv}^{irr}(\mathbf{k},\omega) = -k^2\mathbf{x}_{fv}(\omega)+\cdots,
\tag{10.7}
$$

$$
\mathbf{X}_{fE}^{irr}(\mathbf{k},\omega) = k^2\mathbf{x}_{fE}(\omega)+\cdots,
\tag{10.8}
$$

one arrives at the following equations for the diffusion current and force density for small but finite $\mathbf{k}$:

$$
\mathbf{J}_d(\mathbf{k},\omega) = [y_{jE}+x_{jE}(\omega)]\mathbf{E}(\mathbf{k},\omega)
$$
$$
+ k^2(\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})[y_{jv}^t+x_{jv}^t(\omega)]\mathbf{V}(\mathbf{k},\omega),
\tag{10.9a}
$$

$$
k^2[\eta+y_{fv}^t+x_{fv}^t(\omega)]\mathbf{V}(\mathbf{k},\omega)
$$
$$
= (\mathbf{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\{\mathbf{f}_o(\mathbf{k},\omega) + n\mathbf{E}(\mathbf{k},\omega)
$$
$$
+ k^2[y_{fE}^t+x_{fE}^t(\omega)]\mathbf{E}(\mathbf{k},\omega)\},
\tag{10.9b}
$$

where x_{ab}^t denotes as before the transversal part of the operator $\mathbf{x}_{ab}$. Finally, we transform back into the spatial domain obtaining the set of equations in the form analogous to Eq. (7.22)

$$
\mathbf{J}_d(\omega) = [y_{jE}+x_{jE}(\omega)]\mathbf{E}(\omega) - [y_{jv}^t+x_{jv}^t(\omega)]\nabla^2\mathbf{V}(\mathbf{k},\omega),
\tag{10.10a}
$$

$$
-[\eta+y_{fv}^t+x_{fv}^t(\omega)]\nabla^2\mathbf{V}(\mathbf{k},\omega)
$$
$$
= \mathbf{F}_{\text{tot}}(\omega) - \text{grad}\, p(\omega) - \frac{y_{fE}^t+x_{fE}^t(\omega)}{y_{jE}+x_{jE}(\omega)}
$$
$$
\times[\nabla^2\mathbf{J}_d(\omega) - \text{grad div}\,\mathbf{J}_d(\omega)],
\tag{10.10b}
$$

where as before [cf. Eqs. (7.18) and (7.19)]

$$
\mathbf{J}_d(\omega) = \mathbf{J}(\omega) - n\mathbf{E}(\omega)
\tag{10.11}
$$

and

$$
\mathbf{F}_{\text{tot}}(\omega) = \mathbf{f}_o(\omega) + n\mathbf{E}(\omega).
\tag{10.12}
$$

As it can be seen, the inclusion of the retarded response terms in the effective equations adds new elements in comparison with the instantaneous response described by Eq. (7.22): the effective viscosity and the effective mobility coefficient attain the frequency-dependent terms x_{fv}^t and x_{jE}, respectively. Also the cross terms linking $\mathbf{J}_d$ with the Laplacian of $\mathbf{V}$ and the Laplacian of $\mathbf{V}$ with $\mathbf{E}$ gain the new, frequency-dependent contributions x_{jv}^t and x_{fE}^t, which are equal to each other due to the Onsager symmetry. The overall picture remains the same: We get Eq. (10.9b) for the velocity which must be solved first (for given boundary conditions). Then, once we have the velocity field, we calculate the particle current with respect to it with use of the Eq. (10.9a). Note that all the coefficients in the above equations are obtained from the short-range response kernels and therefore they are well-defined, local characteristics of the system.

XI. COLLECTIVE DIFFUSION COEFFICIENT

The expressions for short-range response kernels obtained in Secs. VI D and VIII are a good starting point for calculating transport coefficients of a Brownian suspension. Here we illustrate this procedure by deriving well-defined formulas for short- and long-time collective diffusion coefficient.

To this end, we recall an alternative way of obtaining diffusion coefficient mentioned in Sec. II: by analyzing the current induced in the system by an external force acting on particles. Formula (2.16) together with Eq. (4.9) imply that

$$
D_c^s = \lim_{\mathbf{k}\to 0}\frac{k_BT}{nS(0)}Y_{jE}(\mathbf{k})
\tag{11.1}
$$

and

$$
D_c^l = \lim_{\mathbf{k}\to 0}\frac{k_BT}{nS(0)}\frac{1}{3}\left[Y_{jE}(\mathbf{k}) + \int_0^{\infty}dt'X_{jE}(\mathbf{k},t')\right],
\tag{11.2}
$$

respectively. Further simplification is achieved by comparing the expression (10.1) for the particle current with the Fourier transform of Eq. (4.9) which—in the absence of the imposed flow $\mathbf{v}_o$—reads

$$
\mathbf{J}(\mathbf{k},\omega) = \mathbf{Y}_{jE}(\mathbf{k})\mathbf{E}(\mathbf{k},\omega) + \mathbf{X}_{jE}(\mathbf{k},\omega)\mathbf{E}(\mathbf{k},\omega).
\tag{11.3}
$$

Analyzing the small $\mathbf{k}$ behavior of both Eqs. (10.1) and (11.3) and using the zero net flux condition for the average suspension velocity, Eq. (1.1), one concludes that

$$\lim_{\mathbf{k}\to 0} Y_{jE}(\mathbf{k}) = y_{jE} \tag{11.4}$$

and

$$\lim_{\mathbf{k}\to 0} X_{jE}(\mathbf{k},t) = x_{jE}(t), \tag{11.5}$$

where Eqs. (7.9) and (10.5) have been used. Thus the collective diffusion coefficients can be identified with

$$D_c^s = \frac{k_B T}{n S(0)} y_{jE} \tag{11.6}$$

and

$$D_c^l = \frac{k_B T}{n S(0)} \left[y_{jE} + \int_0^\infty x_{jE}(t') dt' \right], \tag{11.7}$$

where no $\mathbf{k}\to 0$ limit is performed.

A similar formula can be obtained for the long-wavelength limit of the memory function. Namely, by comparing Eqs. (11.6) and (11.7) with relations (2.14) and (2.15) one concludes that

$$M(t) = \frac{\langle (\Sigma_{i,j,k}[\boldsymbol{\nabla}_i + \beta\mathbf{F}_{ji}]\cdot\boldsymbol{\mu}_{ik})\cdot(\Sigma_{l,m,p}[\boldsymbol{\nabla}_l + \beta\mathbf{F}_{ml}]\cdot\boldsymbol{\mu}_{lp}(t'))\rangle^{irr}}{\beta\langle \Sigma_{i,j=1}^N \mathrm{Tr}\,\boldsymbol{\mu}_{ij}\rangle^{irr}}. \tag{11.9}$$

It is instructive to calculate the memory function in the absence of hydrodynamic interactions, i.e., when the mobility matrix is of the form

$$\boldsymbol{\mu}_{ij} = \boldsymbol{\mu}_o \delta_{ij}. \tag{11.10}$$

In this limit $M(t)$ reads simply

$$\frac{1}{3N\mu_o} \left\langle \sum_{i,j=1} \mathbf{F}_{ij} \cdot \sum_{k,l=1} \mathbf{F}_{kl}(t) \right\rangle, \tag{11.11}$$

where the irreducibility requirement in the average is relaxed, since in the absence of hydrodynamic interactions the terms are devoid of all $\mathbf{G}$ connectors, not only the solitary ones. However, the sums in vertices of Eq. (11.11) vanish since the sum of all interparticle forces is equal to zero. Therefore in systems without hydrodynamic interactions the short- and long-time collective diffusion coefficients are equal.

On the other hand, when the hydrodynamic interactions cannot be neglected there is a nonzero contribution from the memory effects to D_c. The magnitude of this contribution can be measured by the dimensionless factor Δ[40]

$$\Delta = \frac{D_c^s - D_c^l}{D_c^s} = \int_0^\infty M(t') dt'. \tag{11.12}$$

For a dilute suspension, the memory function may be analyzed by means of the virial expansion in the volume fraction:

$$M(t) = m_1(t) + m_2(t)\phi + m_3(t)\phi^2 + \cdots. \tag{11.13}$$

$$M(t) \equiv \lim_{\mathbf{k}\to 0} M(\mathbf{k},t) = -\frac{1}{y_{jE}} x_{jE}(t). \tag{11.8}$$

Note that in the above formulas both the diffusion coefficients and the memory function are expressed in terms of the fast decaying, short-range kernels. Therefore, they depend only on the local characteristics of the suspension and not on the shape and size of the system. However, there is a price to pay: The expressions for the irreducible terms making up the response kernels become increasingly more complex with the number of particles involved. An example may be found in Ref. 39 where the three particle terms making up the instantaneous response kernel $\mathbf{Y}_{jE}^{irr}$ are analyzed. One of the tools which facilitates the analysis is a diagrammatic technique developed in Ref. 38.

Let us now analyze the memory contribution to long-time diffusion coefficient in some detail. First, by inserting the explicit expressions for the transport kernels given by Eqs. (4.12a) and (4.13a) into the relation (11.8) for the memory function we get

However, the virial expansion of the denominator of Eq. (11.9) is known to be in the form[2,15]

$$\frac{1}{3N\mu_o} \left\langle \sum_{i,j=1}^N \mathrm{Tr}\,\boldsymbol{\mu}_{ij} \right\rangle^{irr} = \beta(1 + e_1\phi + e_2\phi^2 + \cdots). \tag{11.14}$$

For example for hard-sphere suspensions the parameters e_1 and e_2 read[3,6,39,41]

$$e_1 = -6.546, \quad e_2 = 21.918. \tag{11.15}$$

Thus we concentrate on the numerator of Eq. (11.9) and consider the function

$$T(1,2,\ldots,s;t) = \frac{a^2}{3N\beta\mu_o^2} \left[\sum_{i,j,k=1}^s (\boldsymbol{\nabla}_i + \beta\mathbf{F}_{ji})\cdot\boldsymbol{\mu}_{ik} \right]$$
$$\cdot \left[\sum_{l,m,p=1}^s (\boldsymbol{\nabla}_l + \beta\mathbf{F}_{ml})\cdot\boldsymbol{\mu}_{lp}(t) \right]$$
$$s = 1,2\ldots. \tag{11.16}$$

The successive terms in its cluster expansion,

$$T(1,2,\ldots,s;t) = \sum_{i=1}^s \tilde{T}(i;t) + \sum_{i<j} \tilde{T}(i,j;t) + \cdots,$$
$$s = 1,2\ldots, \tag{11.17}$$

determine the subsequent terms in the virial expansion (11.13) of $M(t)$. In particular, one-particle contributions, $\tilde{T}(i;t) = T(i;t)$, vanish since in this case $\boldsymbol{\mu}$ is again of the

form (11.10). To analyze the two-particle term we use following symmetries of two-body hydrodynamic matrices[42]

$$\nabla_1 \cdot \boldsymbol{\mu}_{12} = -\nabla_2 \cdot \boldsymbol{\mu}_{12} = -\nabla_2 \cdot \boldsymbol{\mu}_{21},$$

$$\nabla_1 \cdot \boldsymbol{\mu}_{11} = -\nabla_2 \cdot \boldsymbol{\mu}_{11} = -\nabla_2 \cdot \boldsymbol{\mu}_{22}.$$

The above relations give

$$\sum_{i,k=1}^{2} \nabla_i \cdot \boldsymbol{\mu}_{ik} = 0. \tag{11.18}$$

Moreover, using the symmetries of the two-body mobility matrix and the fact that a sum of interparticle forces in the system vanishes, one gets

$$\sum_{i,j,k=1}^{2} \mathbf{F}_{ji} \cdot \boldsymbol{\mu}_{ik} = 0. \tag{11.19}$$

The two relations (11.18) and (11.19) yield

$$T(i,j;t) = 0. \tag{11.20}$$

Since the one-particle terms $\tilde{T}(i;t)$ vanish one concludes that also $\tilde{T}(i,j;t) = 0$. The above analysis together with relation (11.14) leads to the conclusion that the two lowest terms in the virial expansion of the memory function vanish:

$$m_1(t) = m_2(t) = 0. \tag{11.21}$$

Let us now study the three-particle term. First, we notice that from the fact that the one- and two-particle operators $\tilde{T}(i;t)$ and $\tilde{T}(i,j;t)$ vanish, and from Eq. (11.17), one obtains

$$\tilde{T}(1,2,3;t) = T(1,2,3;t). \tag{11.22}$$

Another useful property of three-particle term is that: *All the nonzero three-particle terms making up* $\langle T(1,2,3;t) \rangle$ *are irreducible and therefore* $\langle T(1,2,3;t) \rangle^{irr} = \langle T(1,2,3;t) \rangle$.

Proof. The kernel $\langle T(1,2,3;t) \rangle$ can be written as $\langle A(1,2,3)e^{\mathcal{L}t}B(1,2,3) \rangle$. However, the sum of all the terms, in which either A or B does not depend on the positions of all three particles but only one or two of them, vanishes because of the symmetries mentioned above. What remains are the terms in which particles (1,2,3) are connected with each other by at least one bond in A and one in B. All such terms are irreducible. □

Thus one could relax the irreducibility condition while calculating the virial coefficient m_3. An explicit expression for this quantity is

$$m_3(t) = \frac{1}{32\pi^2 a^4 \mu_o^2} \int d\mathbf{R}_{12} \int d\mathbf{R}_{13}$$

$$\times \left[\sum_{i,j,k=1}^{3} (\nabla_i + \beta \mathbf{F}_{ji}) \cdot \boldsymbol{\mu}_{ik} \right]$$

$$\cdot \left[\sum_{l,m,p=1}^{3} (\nabla_l + \beta \mathbf{F}_{pl}) \cdot \boldsymbol{\mu}_{lp}(t) \right] e^{-\beta\phi(\mathbf{R}_{12}, \mathbf{R}_{13})}. \tag{11.23}$$

At this time, there is no apparent reason why the above coefficient should vanish. On the contrary, it is relatively

simple to prove that the three-particle contribution is nonzero, for example by calculating an initial value $m_3(0)$ for a hard-sphere gas

$$m_3(0) = \int d\mathbf{R}_2 d\mathbf{R}_3 \left(\sum_{i,j=1}^{3} \nabla_i \cdot \boldsymbol{\mu}_{ij} \right)^2 W(1,2,3), \tag{11.24}$$

where $W(1,2,3)$ is unity for nonoverlapping configurations of the spheres and vanishes otherwise. This integral could be performed numerically using full hydrodynamic interactions involving three spheres, following the scheme presented in Ref. 43. The calculation gives $m_3(0) = 1.42 \pm 0.02$. Interestingly enough, a good estimate of m_3 could be obtained by considering the long interparticle distance asymptotics. It turns out[38] that the main contribution comes from strongly asymmetric configurations in which two of the particles (for example, 1 and 2) are much closer to each other than they are to the third. In this case the integrand function in Eq. (11.24) scales asymptotically as $\mathbf{R}_{23}^{-4}$. The integration of asymptotic terms gives $m_3^{as}(0) \approx 1.9$ which is of the order of $m_3(0)$ itself. The asymmetry of the configuration is the key element here, since the divergence of the mobility matrix summed over all particles

$$\mathbf{d}_i = \sum_j \nabla_j \cdot \boldsymbol{\mu}_{ji}, \tag{11.25}$$

which appears in Eq. (11.24) vanishes for all regular configurations of the particles, such as periodic lattices, and thus can be considered as a measure of asymmetry of the configuration.

XII. NUMERICAL CALCULATION OF THE MEMORY FACTOR

We have numerically estimated the values of the memory factor for hard-sphere suspensions using Brownian dynamics simulations in periodic boundary conditions.

The use of periodic boundary conditions simplifies considerably the expression for the memory function. Namely, as it was mentioned in the Introduction, when deriving the mobility matrix for a periodic system one adds the constraint that the net suspension velocity in whole sample vanishes,[9,10,44] as otherwise the divergences in the fluid velocity field appear. In that way Eq. (1.1) is automatically satisfied which, in turn, implies that we can relax the irreducibility condition in Eq. (11.9) and the expression for $M(t)$ in the case of hard spheres takes a relatively simple form

$$M(t) = \frac{\langle \sum_{i,j,k,l=1}^{N} [\nabla_i \cdot \boldsymbol{\mu}_{ij}(0)] \cdot [\nabla_k \cdot \boldsymbol{\mu}_{kl}(t)] \rangle_{per}}{\beta \langle \sum_{i,j=1}^{N} \text{Tr} \, \boldsymbol{\mu}_{ij} \rangle_{per}}, \tag{12.1}$$

where the symbol $\langle \ \rangle_{per}$ stands for the average over hard-sphere configurations with periodic boundary conditions.

It is reasonable to calculate $M(t)$ in two steps. First one computes an initial value of the memory function $M(t=0)$ and then carries out the calculations of the mean relaxation time $\tau_M = M(t=0)^{-1} \int_0^\infty M(t)dt$. The reason behind this is that $M(0)$ can be calculated with great precision by means of equilibrium averaging only, while the relaxation time requires Brownian dynamic simulations which are much more

TABLE I. The initial values of the memory function $M(t=0)$, mean relaxation time τ_M, and memory factor Δ for hard-sphere suspension of volume fraction ϕ obtained from equilibrium Monte Carlo averaging and Brownian dynamics simulations.

ϕ	$D_o^{-1} a^2 M(t=0)$	$D_o a^{-2} \tau_M$	Δ
0.01	$(1.55 \pm 0.05) \times 10^{-4}$		
0.1	$(1.7 \pm 0.1) \times 10^{-2}$		
0.2	$(9.2 \pm 0.3) \times 10^{-2}$	$(1.25 \pm 0.25) \times 10^{-1}$	$(1.0 \pm 0.3) \times 10^{-2}$
0.3	$(2.4 \pm 0.15) \times 10^{-1}$	$(1.20 \pm 0.25) \times 10^{-1}$	$(3 \pm 1) \times 10^{-2}$
0.4	$(5.4 \pm 0.3) \times 10^{-1}$	$(0.90 \pm 0.2) \times 10^{-1}$	$(5 \pm 1.5) \times 10^{-2}$
0.45	$(6.7 \pm 0.2) \times 10^{-1}$		

expensive numerically. Therefore, as it was noted by Zwanzig and Ailawadi,[45] such a two-step procedure increases considerably an accuracy of the numerically obtained memory function.

The details of the calculations are given elsewhere.[46,47] Here we just point out that the main difficulty we faced turned out to be the calculation of the divergence of mobility matrix $\nabla \cdot \boldsymbol{\mu}$ needed in Eq. (12.1) for the memory function. Although in principle the divergence of $\boldsymbol{\mu}$ may be obtained by a "brute-force" numerical differentiation, such a scheme is not only extremely time consuming and memory consuming but also inaccurate. Instead, we have devised a scheme of calculating the divergence of mobility matrix in an analytical way with use of the multipole expansion method.[47]

The final results of the numerical calculations are given in Table I. They show that the memory factor is nonzero, relatively small, but increases with the volume fraction reaching the value of 5% at the volume fraction $\phi = 0.4$. This result is in qualitative an agreement with experimental data (cf. Ref. 15). The presence of nonzero memory factor disproves the conjecture by Dhont in Ref. 2 that the collective diffusion coefficient is independent of time.

XIII. SUMMARY

We have derived the macroscopic equations governing the long-time dynamics of Brownian suspensions analogous to those derived by Felderhof,[12] Nozières,[11] and Noetinger[5] but with inclusion of memory effects caused by the relaxation of the distribution function. The coefficients in these equations are given by well-defined expressions, free of divergences as the system size goes to infinity. We have applied this formalism to calculation of memory contribution to long-time collective diffusion coefficient and proved that it is nonzero, although relatively small.

APPENDIX A: ZERO NET FLUX CONDITION

Below we present a proof of the zero net flux condition for incompressible fluid placed in a container on the walls of which stick boundary conditions are applied.

The zero net flux condition reads

$$I := \int_V \mathbf{v}(\mathbf{r}) d\mathbf{r} = 0. \tag{A.1}$$

Let us first rewrite the above integral as

$$I = \int_{V_f} \mathbf{v}_f(\mathbf{r}) d\mathbf{r} + \sum_{i=1}^{N} \int_{V_i} \mathbf{u}_i(\mathbf{r}) d\mathbf{r}, \tag{A.2}$$

where V_f denotes the volume occupied by the fluid whereas V_i stands for the volume of the ith particle. Next, $\mathbf{v}_f$ is a fluid flow field, while fields $\mathbf{u}_i(\mathbf{r})$ describe rigid body motion of particle i [cf (3.2)]. However,

$$v_\alpha = \delta_{\alpha\beta} v_\beta = \frac{\partial(x_\alpha v_\beta)}{\partial x_\beta} - x_\alpha \frac{\partial v_\beta}{\partial x_\beta}. \tag{A.3}$$

Since the last term on the right-hand side of the above equations vanishes for incompressible velocity fields, we can rewrite Eq. (A2) in the form

$$I = \oint_{\partial W} \mathbf{v}_f \cdot \mathbf{n r} d\sigma + \sum_{i=1}^{N} \int_{S_i} (\mathbf{u}_i - \mathbf{v}_f) \cdot \mathbf{n r} d\sigma, \tag{A.4}$$

where Gauss theorem has been used to convert the volume integrals to surface integrals. Here W denotes the walls of the container and $\mathbf{n}$ is a unit vector normal to the surface, pointing outwards.

However, since there is no flow through the container walls nor through the surfaces of the spheres and the container is at rest we conclude that all the integrals in Eq. (A4) vanish and finally $I = 0$.

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