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Dynamical properties of hard-sphere suspensions

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We present an alternative approach to the calculation of long-time diffusion coefficients of dense suspensions. The main idea is to approximate friction coefficients rather than the diffusion coefficients. Within this scheme we derive a very simple yet accurate theory of dynamic properties of a hard-sphere suspension: to calculate friction coefficients we keep only the two-particle dynamics while taking the higher-density effects into account via a renormalization of the frequency of the binary encounters by the contact value of the pair-correlation function. Using this theory we calculate the long-time self-friction and self-diffusion coefficients, the time-dependent self-diffusion kernel, and the wave-number-dependent long-time friction coefficients. The explicit results compare reasonably well with Brownian-dynamics simulations.

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I. INTRODUCTION

There has been considerable interest in recent years in dynamic properties of suspensions of interacting colloidal particles [1–5]. A remarkable development of experimental techniques, including methods used to prepare well-defined, stable dispersions and dynamical-light-scattering (photon-correlation-spectroscopy) techniques, made possible quite a detailed investigation of the dynamics of fluctuations in equilibrium dispersions: the basic quantities measured in the dynamical light scattering experiments—the intermediate light scattering function $F(k;t)$ and the tagged-particle scattering function $F_s(k;t)$—are related by the Fourier transform to the autocorrelation functions of macroparticle density fluctuations and tagged macroparticle (tracer) density fluctuations, respectively.

Studies of these scattering functions revealed a very interesting transition in the dynamic behavior of suspensions. The crucial time is the *structural-relaxation time* [5] τ_R, the time a Brownian particle needs in order to diffuse over its radius a,

$$\tau_R = a^2/D_0 , \tag{1}$$

where D_0 is the diffusion coefficient of a single colloidal particle. The relaxation time separates two different regimes: For times shorter than τ_R (but much longer than characteristic decay time of the velocity of the macroparticle), the tagged-particle-scattering function $F_s(k;t)$ is given accurately by

$$F_s(k;t) = \exp(-D_s^S k^2 t) , \tag{2}$$

where D_s^S is the short-time self-diffusion coefficient. For times much longer than τ_R, the situation is not clear. The experimental results of Pusey and Tough [6] could for long times be fitted by an exponential, which constitutes a possible definition of a long-time k-dependent self-diffusion coefficient D_s^L,

$$F_s(k;t) \sim \exp[-D_s^L(k) k^2 t] . \tag{3}$$

The more recent data of Taylor and Ackerson [7] seem to be incompatible with a long-time exponential decay. In the model considered here Eq. (2) always holds, but Eq. (3) is *not* valid at long times, except in the hydrodynamic limit $k \to 0, t \to \infty$, keeping $k^2 t$ constant. Then the fitting parameter in the exponent is the phenomenological self-diffusion coefficient D_s. A different way of analyzing the tagged-particle-scattering function is in terms of time- or frequency-dependent diffusion kernels, also called memory functions. These will be defined below in Sec. II. Diffusion kernels were the subjects of theoretical predictions [1] and were derived from data of real [7] and computer [8] experiments. Similar diffusion coefficients and memory-function representations can be defined for the intermediate scattering function $F(k;t)$. Finding accurate predictions of the tagged-particle-scattering function and the intermediate scattering function is a major goal in the theory of dynamic properties of suspensions.

The dynamics of suspensions of interacting macroparticles is a very complicated problem. Not only the direct interactions between the colloidal particles have to be taken into account, but also so-called hydrodynamic interactions [9] that result from the motion of the fluid in which the particles are dispersed. Including the direct interactions already creates a difficult problem, and an accurate treatment of interacting colloids with hydrodynamic interactions is even more complicated as hydrodynamic interactions are long ranged and not pairwise additive. Both features create great difficulties in particular in combining them into a single theoretical description. Fortunately there exist systems in which the hydrodynamic interactions are much less pronounced: in suspensions of highly charged colloidal particles the strong screened Coulomb repulsion has usually much greater range [10] than the physical radius of the particle, which is the important parameter for determining the strength of the hydrodynamic interactions. One then has to deal with a real system that is dense from the direct-interactions point of view and dilute as far as the hydrodynamic interactions are concerned. For typical experimental situations the relevant volume fractions differ by a few orders of magnitude [11]: $\phi=4(\pi n a^3)/3$ being of the order of 0.1–0.5 and $\phi_h=4(\pi n a_h^3)/3$ being of the order of 10^{-3}, where a and a_h denote the range of the strong screened Coulomb repulsion and the real radius of the colloidal particle, respectively. To make a model system for charged colloids one may therefore ignore the hydrodynamic interactions and keep only direct interactions. This model has been studied before a number of times [1]. Various exact but low-density results were obtained [1,12–14]. Also a number of approximate theories for high densities have been proposed. These use various mode-mode-coupling schemes [1], cluster-expansion techniques [15], and kinetic-theory methods [16]. However, a simple yet satisfactory theory is still needed.

An intriguing question is whether there is an analogy between the dynamics of colloids and the dynamics of atomic fluids, even though the time scales involved differ by nine orders of magnitude. Recently de Schepper *et al.* [17] proposed an analogy between the dynamics of hard-sphere fluids and colloidal suspensions for long-time relaxation. They used it to obtain a simple and reasonably accurate expression for the long-time diffusion coefficient, but they did not present any derivation of it. Here we will present a theory for the dynamics of a hard-sphere suspension that is partly inspired by the hard-sphere Enskog kinetic theory [18].

In this article we present a simple approach to the dynamic properties of a model suspension without hydrodynamic interactions. A main idea of our approach is to formulate a theory that approximates the friction coefficient rather than the diffusion coefficient [19]. Within this scheme we derive a simple theory and apply it to a hard-sphere suspension. The theory is based on ideas of the Enskog kinetic theory [18] of a dense hard-sphere fluid: to calculate approximately the friction coefficients we drop three particle dynamical effects but retain static correlations. Our approximation satisfies the exact short-time limit for a hard-sphere suspension. As for short wavelengths the tagged-particle-scattering function decays very rapidly, also the short-wavelength limit should be exact. The approximation made, and the way to arrive at it, is related to one made in a recent paper on the velocity autocorrelation function of the Lennard-Jones fluid [20].

The paper is organized as follows. In Sec. II we properly define the model system studied, and define time and wave-number-dependent diffusion and friction kernels. In Sec. III we present our theory for the relaxation of the tagged-particle-scattering function. First we give some intuitive arguments leading to the approximate theory. These are followed by a detailed derivation clarifying the approximations made. The detailed presentation is especially important as we are going to use some methods of kinetic theory. These are not particularly difficult in themselves, but probably not well known. We want to emphasize that, although we present explicit calculations for a hard-sphere suspension, the general approach to approximate the friction coefficients rather than the diffusion coefficient is valid for arbitrary interactions between the colloidal particles. In Sec. IV we present numerical results and compare them with the Brownian-dynamics-simulation data of Cichocki and Hinsen [8]. Taking the simplicity of the theory into account, the agreement is quite satisfactory. Concluding remarks are made in Sec. V. In Appendix A we present the corresponding theory for the relaxation of the intermediate scattering function. In Appendix B we summarize literature results for the low-density friction kernels.

II. FORMULATION OF THE PROBLEM

We consider a system of N identical colloidal particles suspended in a fluid solvent. The single-particle diffusion coefficient D_0 is determined by the solvent viscosity and the radius of the hard core of the particle. On a time scale large compared to the relaxation time of the Brownian component of the macroparticle velocity the state of the suspension can be described by the N-particle probability distribution $P_N(\mathbf{R}_1,\ldots,\mathbf{R}_N,t)$. Here $\mathbf{R}_i$ denotes the position of particle i. The time evolution is then given by the Smoluchowski equation

$$\frac{\partial}{\partial t}P_N(\mathbf{R}_1,\ldots,\mathbf{R}_N;t)=\Omega_S P_N(\mathbf{R}_1,\ldots,\mathbf{R}_N;t)\ , \tag{4}$$

where Ω_S is the N-particle Smoluchowski operator

$$\Omega_S=D_0\sum_{i=1}^{N}\frac{\partial}{\partial\mathbf{R}_i}\cdot\left[\frac{\partial}{\partial\mathbf{R}_i}-\beta\sum_{i\,(\neq j)}^{N}\mathbf{F}_{ij}\right]\ . \tag{5}$$

Here $\mathbf{F}_{ij}$ is the force between particles i and j, $\mathbf{F}_{ij}=(\partial/\partial\mathbf{R}_{ij})V(R_{ij})$, and $\beta=1/k_B T$. Actually we are going to consider mainly a hard-sphere suspension. Then a no-flux boundary condition has to be imposed whenever two particles are touching,

$$\frac{\partial}{\partial\mathbf{R}_{ij}}P_N(\mathbf{R}_1,\ldots,\mathbf{R}_N,t)=0 \quad\text{whenever } R_{ij}=2a^{+}\ . \tag{6}$$

Here a is the radius of a hard sphere. However, as it has been shown by Cichocki [22] the evolution equation Eq. (4) still can be used for the hard-sphere suspension if we take

$$\beta\mathbf{F}_{ij}=\hat{\mathbf{R}}_{ij}\delta(R_{ij}-2a)\ , \tag{7}$$

where $\hat{\mathbf{R}}=\mathbf{R}/R$. The boundary conditions Eq. (6) are then incorporated into the evolution equation and need not be considered explicitly. To emphasize the fact that the approach presented in Sec. III B of this paper is valid for arbitrary interactions we will keep the force $\mathbf{F}$ in all equations and only in explicit calculations we will use relation (7).

In the theoretical analysis it is also useful to consider a description of a suspension in terms of reduced distribution functions. To this end we define the k-particle reduced distribution as the average of the microscopic k-particle density over the probability distribution $P_N(t)$. For example, for $k=1,2$ we have

$$n_1(\mathbf{r}_1;t)=\left\langle \sum_{i=1}^{N} \delta(\mathbf{r}_1-\mathbf{R}_i)\right\rangle_t$$

$$=N\int d\mathbf{R}_2\cdots d\mathbf{R}_N P_N(\mathbf{r}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N;t)\ , \tag{8}$$

$$n_2(\mathbf{r}_1,\mathbf{r}_2;t)=\left\langle \sum_{\substack{i=1\\ i\neq j}}^{N} \delta(\mathbf{r}_1-\mathbf{R}_i)\delta(\mathbf{r}_2-\mathbf{R}_j)\right\rangle_t$$

$$=N(N-1)\int d\mathbf{R}_3\cdots d\mathbf{R}_N$$

$$\times P_N(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R}_3,\ldots,\mathbf{R}_N;t)\ . \tag{9}$$

The time evolution of the reduced distributions is given by an infinite hierarchy of equations that can be obtained from the Smoluchowski equation (4). Again, for $k=1,2$ we have

$$\frac{\partial}{\partial t}n_1(\mathbf{r}_1;t)=D_0\nabla_1^2 n_1(\mathbf{r}_1;t)-D_0\nabla_1\cdot\int d\mathbf{r}_2\beta\mathbf{F}_{12}n_2(\mathbf{r}_1,\mathbf{r}_2;t)\ , \tag{10}$$

$$\frac{\partial}{\partial t}n_2(\mathbf{r}_1,\mathbf{r}_2;t)=D_0[\nabla_1^2+\nabla_2^2-(\nabla_1-\nabla_2)\cdot\beta\mathbf{F}_{12}]n_2(\mathbf{r}_1,\mathbf{r}_2;t)$$

$$-D_0\sum_{i=1}^{2}\nabla_i\cdot\int d\mathbf{r}_3\beta\mathbf{F}_{i3}n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)\ . \tag{11}$$

Here $\nabla_i=\partial/\partial\mathbf{r}_i$.

We assume that one of the particles, suppose the first one, is tagged, and study the tagged-particle-scattering function

$$F_s(k;t)=\langle e^{-i\mathbf{k}\cdot\mathbf{R}_1}e^{\Omega_S t}e^{i\mathbf{k}\cdot\mathbf{R}_1}\rangle\ , \tag{12}$$

i.e., the Fourier transform of the tagged-particle density autocorrelation function:

$$F_s(k;t)=\int d\mathbf{r}_{10}e^{-i\mathbf{k}\cdot\mathbf{r}_{10}}V\langle\delta(\mathbf{r}_1-\mathbf{R}_1)e^{\Omega_S t}\delta(\mathbf{r}_0-\mathbf{R}_1)\rangle\ . \tag{13}$$

Here V is the volume of the system (thermodynamic limit is always understood), $\delta(\mathbf{r}_1-\mathbf{R}_1)$ is the microscopic density of the tagged particle at point $\mathbf{r}_1$, and brackets $\langle\ \rangle$ without subscript t denote the equilibrium ensemble average. We take the convention that the equilibrium distribution $P_N^{\mathrm{eq}}\sim\exp[-\sum_{i\neq j}V(r_{ij})/k_BT]$ is formally represented by the ket vector $\cdots\rangle$. Note that in Eqs. (12) and (13) the evolution operator Ω_S acts on everything to its right, also on the equilibrium distribution P_N^{eq}, which is relevant since the operator is not equal to its adjoint operator. We will also present results concerning the intermediate scattering function

$$F(k;t)=\frac{1}{N}\left\langle\sum_{i=1}^{N}e^{-i\mathbf{k}\cdot\mathbf{R}_i}e^{\Omega_S t}\sum_{j=1}^{N}e^{i\mathbf{k}\cdot\mathbf{R}_j}\right\rangle\ . \tag{14}$$

In the main text we only consider the tagged-particle problem, the calculations for nontagged particles are relegated to Appendix A.

To proceed with the theoretical analysis it is useful to note that the time-dependent correlation functions in equilibrium [as, for example, $F_s(k;t)$] can be expressed in terms of nonequilibrium reduced distributions with a suitable initial condition. Namely, for the tagged-particle density autocorrelation function we have

$$V\langle\delta(\mathbf{r}_1-\mathbf{R}_1)e^{\Omega_S t}\delta(\mathbf{r}_0-\mathbf{R}_1)\rangle=n_s(\mathbf{r}_1;t)\ , \tag{15}$$

where $n_s(\mathbf{r}_1;t)=\langle\delta(\mathbf{r}_1-\mathbf{R}_1)\rangle_t$ is the density of the tagged particle calculated for the following nonequilibrium ensemble:

$$P_N(R_1,\ldots,R_N;t)=e^{\Omega_S t}\delta(\mathbf{r}_0-\mathbf{R}_1)VP_N^{\mathrm{eq}}(R_1,\ldots,R_N)\ , \tag{16}$$

or, equivalently, $n_s(\mathbf{r}_1;t)$ is the solution of the infinite hierarchy of equations for the tagged-particle problem with the initial condition that follows from the form of the distribution P_N, Eq. (16) at $t=0$ (see Sec. III B).

We discuss everything in both the time domain, as this, perhaps, yields a more microscopic picture, but also in the frequency or Laplace domain as calculations then can be more easily performed. The Laplace transform for a quantity A is defined as

$$A(z)=\int_0^\infty dt\, e^{-zt}A(t)\ . \tag{17}$$

Usually the tagged-particle-scattering function F_s is interpreted in terms of a (time-dependent) self-diffusion kernel in the expectation that this will yield a simplified description and a useful quantity for other cases as well. The time Laplace transform of the self-diffusion kernel is defined through

$$F_s(k,z)=\frac{1}{z+D_s(k,z)k^2} \tag{18}$$

or equivalently in the time domain

$$\frac{d}{dt}F_s(k,t)=-k^2\int_0^t dt' D_s(k,t')F_s(k,t-t')\ . \tag{19}$$

To zeroth order in density the diffusion is entirely determined by the solvent and we have

$$D_s(k,t)=D_0\delta(t-0^+)+O(n)\ . \tag{20}$$

Equation (1) follows from the observation that this is also the exact short-time diffusion kernel.

We separate the self-diffusion kernel into a solvent part and an interaction part

$$D_s(k,t)=D_0\delta(t-0^+)+D_{s,I}(k,t)\ . \tag{21}$$

Obviously, it is the interaction part we are after. For a hard-sphere suspension the interaction part has a $t^{-1/2}$ contribution for short times (Sec. III A); there are no δ functions in it.

A starting point different from the diffusion coefficient picture just described is to consider forces and fluxes. The Fourier transform of the flux density $\mathbf{j}_s$ is defined through

$$\frac{d}{dt}n_s(k,t)=-i\mathbf{k}\cdot\mathbf{j}_s(k,t)\ , \tag{22}$$

and the driving force for self-diffusion is the osmotic pressure resulting from a tagged-particle density gradient, or the external force:

$$\mathbf{f}_s(k,t) = -i\mathbf{k}k_BTn_s(k,t) + \mathbf{F}^{(\mathrm{ext})}n_s(k,t) \tag{23}$$

(for the tagged particle the derivative of the tagged-particle osmotic pressure with respect to the density of that particle gives k_BT). In itself considering a nonequilibrium fluid as is done in Eqs. (22) and (23) is entirely different from the equilibrium fluctuation approach on which the definition of the diffusion kernel is based. By making the Onsager assumption that equilibrium fluctuations decay in the same way as a nonequilibrium state we can relate the two. Taking the initial condition $n_s(k,t=0)=1$ we find that the flux is related to the force density as

$$\mathbf{j}_s(k,t) = \frac{1}{k_BT}\int_0^t dt' D_s(k,t')\mathbf{f}_s(k,t-t') \tag{24}$$

with the same self-diffusion kernel D_s appearing in Eq. (18). In the long-wavelength, long-time limit we obtain from (23) and (24) the familiar phenomenological relation with the self-diffusion coefficient $D_s = \lim_{z\to 0}\lim_{k\to 0} D_s(k;z)$. This can again be decomposed into the solvent part D_0 and the interaction part $D_{s,I} = \lim_{z\to 0}\lim_{k\to 0} D_{s,I}(k;z)$.

We would like to point out a particularly transparent approach towards deriving the self-diffusion coefficient of a suspension as given by Lekkerkerker and Dhont [14]: Assume that we apply a constant force on the tagged particle. The local surrounding of the particles will then change since particles will pile up in front of the tagged particles, thus reducing the average current (velocity) of the tagged particle. Our theory as written below can be used to perform the calculations needed for this interpretation. We give an expression for the two-particle distribution function as a function of the tagged-particle flux. We do not pursue this approach here any further than these comments.

We define the self-friction kernel as the inverse of Eq. (24), the relation between the force given the flux

$$\mathbf{f}_s(k,t) = \int_0^t dt' \xi_s(k,t')\mathbf{j}_s(k,t-t') . \tag{25}$$

Again, we can separate the solvent and the interaction part of the self-friction kernel:

$$\xi_s(k,t) = \xi_0\delta(t-0^+) + \xi_{s,I}(k,t) , \tag{26}$$

and define the long-wavelength, long-time self-friction coefficients: $\xi_s = \lim_{z\to 0}\lim_{k\to 0}\xi_s(k;z)$, $\xi_{s,I} = \lim_{z\to 0}\lim_{k\to 0}\xi_{s,I}(k;z)$. In the following we will mainly discuss the friction coefficients. It will turn out that the self-friction coefficient is a much nicer quantity to approximate as the collision-induced friction has the same sign as the solvent or back-ground friction. We expect that at high densities D_s is close to zero, hence $D_{s,I} \simeq -D_0$, whereas at high densities $\xi_{s,I}$ is only expected to be large. Making a small mistake for $D_{s,I}$ will yield a poor approximation for D_s, which does not hold for $\xi_{s,I}$. Approximations for $\xi_{S,I}$ are expected then to yield better results. We would like to emphasize that Eq. (25) is the *definition* of the self-friction kernel. For a very heavy particle in a sea of light particles Kirkwood [19] already derived an expression for the friction coefficient. Unfortunately, when the mass ratio is finite there are no workable expressions, only expressions with projected dynamics; see Ref. [21] and also Sec. III B.

In the Fourier-Laplace domain the relation between the friction and diffusion kernels is

$$D_s(k,z) = \frac{k_BT}{\xi_s(k,z)} . \tag{27}$$

Note that the same relation holds for the solvent contributions: $D_0 = k_BT/\xi_0$. In the time domain we have the following relation between the interaction part of the diffusion and friction kernels:

$$D_{s,I}(k,t) = -D_0\xi_{s,I}(k,t)/\xi_0 - \int_0^t dt' D_{s,I}(k,t-t')\xi_{s,I}(k,t')/\xi_0 , \tag{28}$$

as can be verified by substitution of Eq. (25) into (27).

III. APPROXIMATION

A. Intuitive derivation

One way of formulating the basic idea of the paper is to state that we insist on binary collisions throughout. This in order to keep the problems tractable; to fully treat three or more particle dynamics is both technically unattractive and yields a rather opaque microscopic model. Our aim is to find out what can be understood in terms of binary collisions. Obviously this picture is going to fail at a certain density. In particular we do not expect to get reasonable results for the glass transition. Nevertheless, quite useful results are obtained by wisely applying binary collisions.

In this subsection we will consider hard spheres exclusively, the derivation as presented in Sec. III B can be applied for arbitrary interactions. For low densities everything is clear. We only need to solve the two-particle Smoluchowski equation for $F_s(k,t)$, and extract the interaction part of the friction function. In the context of suspensions the first calculations have been done by Ackerson and Fleishman [12]. For tagged particles the result is

$$\xi_{s,I}(k,t) = \frac{n}{k_BTV}\int d\mathbf{r}_1 \int d\mathbf{r}_2 e^{-i\mathbf{k}\cdot\mathbf{r}_1}(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})e^{\Omega_2 t} \times(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})e^{i\mathbf{k}\cdot\mathbf{r}_1} + O(n^2) . \tag{29}$$

In Eq. (29) V is the volume of the system (again, thermodynamic limit is understood), operator Ω_2 is the two-particle Smoluchowski operator

$$\Omega_2 = D_0[\nabla_1^2 + \nabla_2^2 - (\nabla_1 - \nabla_2)\cdot\beta\mathbf{F}_{12}] . \tag{30}$$

In Appendix B there are some explicit formulas for the interaction friction kernel $\xi_{s,I}$, and also its extension to nontagged particles. A peculiarity of colloids is that already the two-particle interaction is time dependent. The physical origin is that whenever two particles are close at $t=0$ they will be close for some time after, and may recollide a number of times before diffusing out to infinity.

As $\xi_{s,I}$ and $D_{s,I}$ are proportional to the density, for low densities the interaction term is small. At higher densities this term will be more important. One thing that is going to happen if we go to higher density is that particles will be compressed against each other, and the interaction contribution will be larger than just proportional to ϕ. The idea, due to Enskog in the end, is to use the first term on the right-hand side of Eq. (29), where we insert an additional prefactor χ. Considering results for short times supports the idea that a good choice is to take $\chi=g(2a)$: An exact statement at all densities is that for short times

$$\xi_{s,I}(k,t)=4\phi g(2a)\xi_0\left[\frac{D_0}{2\pi a^2 t}\right]^{1/2}, \tag{31}$$

whereas Eq. (29) gives the same result except for the prefactor $g(2a)$ (see Appendix B). We can arrive at Eq. (31) by the following argument. For short times we have $\xi_{s,I}=-D_{s,I}$. Taking the second time derivative of $F_s(k,t)$ we find a two-particle contribution and a three-particle contribution. The three-particle contribution is a regular, smooth function of time and starts out as a constant. The two-particle contribution for hard spheres is a recollision probability, as is obviously the case in the low-density limit. For short times, third particles do not significantly change the dynamics. When considering higher density the only thing that is left to note is that as particles are compressed onto each other the number of particles initially close is enhanced by an additional factor of $g(2a)$. Using the explicit result Eq. (B3) we arrive at Eq. (31).

Let us compare this approximation to the corresponding approximation in the case of Enskog kinetic theory, where we study the Liouville equation, particles moving ballistically with hard-sphere collisions. In the Enskog theory collisions are instantaneous; two hard spheres can only collide once, third particles are needed in order to have recollisions. In a suspension the solvent causes recollisions to take place. In our simple theory only recollisions of the tagged particle with the same, nontagged particle are kept. Therefore in both approaches three and more particle dynamics is entirely ignored.

Another main point of difference is that of time scales. In a suspension there is a universal time scale that is relevant until the density gets too high: the time a particle needs to diffuse over a hard-sphere radius $t_0=a^2/D_0$. At higher density the motion will be "interaction dominated" and a different time scale is needed. The interaction contribution to the diffusion will decay on this time scale. For kinetic particles there is no density independent time for which the velocity autocorrelation function will decay, for hard spheres the mean free time is proportional to $1/\phi g(2a)$. The reason for this distinction is that kinetic particles only change their velocity when colliding, a diffusing particle changes its velocity all the time. For kinetic particles interactions are "everything."

However, the techniques that are used to derive closed kinetic equations can be used with some modifications to suspensions. Mainly the interpretation has to be reconsidered.

B. Formal derivation

The starting point of the formal derivation are the first two equations of the hierarchy for the tagged-particle problem:

$$\frac{\partial}{\partial t}n_s(\mathbf{r}_1;t)=D_0\nabla_1^2 n_s(\mathbf{r}_1;t)-D_0\nabla_1\cdot\int d\mathbf{r}_2\beta\mathbf{F}_{12}n_2(\mathbf{r}_1,\mathbf{r}_2;t)\ , \tag{32}$$

$$\frac{\partial}{\partial t}n_2(\mathbf{r}_1,\mathbf{r}_2,t)=D_0[\nabla_1^2+\nabla_2^2-(\nabla_1-\nabla_2)\cdot\beta\mathbf{F}_{12}]n_2(\mathbf{r}_1,\mathbf{r}_2;t) -D_0\sum_{i=1}^{2}\nabla_i\cdot\int d\mathbf{r}_3\beta\mathbf{F}_{i3}n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)\ . \tag{33}$$

In this section $n_2(\mathbf{r}_1,\mathbf{r}_2;t)$ and $n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)$ denote the joint distribution function of the tagged particle at $\mathbf{r}_1$ and of nontagged particles at $\mathbf{r}_2$, and $\mathbf{r}_2$ and $\mathbf{r}_3$, respectively. The initial conditions for the tagged-particle hierarchy follow from the distribution (16),

$$\begin{aligned} &n_s(\mathbf{r}_1;t=0)=\delta(\mathbf{r}_1-\mathbf{r}_0)\ ,\\ &n_2(\mathbf{r}_1,\mathbf{r}_2;t=0)=\delta(\mathbf{r}_1-\mathbf{r}_0)ng_2^{\mathrm{eq}}(r_{12})\ ,\\ &n_s(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t=0)=\delta(\mathbf{r}_1-\mathbf{r}_0)n^2g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\ . \end{aligned} \tag{34}$$

Here n is the density of nontagged particles and g_2^{eq} and g_3^{eq} denote the equilibrium pair and triple distribution, respectively $g_2^{\mathrm{eq}}(r_{12})=n_2^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2)/n^2$, $g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=n_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)/n^3$.

The traditional approach of kinetic theory is to somehow close Eq. (33) and then to solve the resulting equation with initial condition Eq. (34) and the boundary condition $\lim_{r_{12}\to\infty}n_2(\mathbf{r}_1,\mathbf{r}_2;t)=n$ (see Ref. [14] for a low-density calculation along these lines). In this way one calculates the diffusion coefficient directly. However, as was indicated in Sec. II, this approach is very sensitive to the quality of the approximations made and it is better to approximate first the friction coefficient and then to calculate the diffusion coefficient using the Einstein relation [23].

To calculate the friction coefficient we rewrite the hierarchy (32) and (33). First, we separate n_2 and n_3 into the *local-equilibrium* contributions, i.e., contributions of the form of Eq. (34), and the remaining parts that can be called nonequilibrium dynamical correlations:

$$\begin{aligned} &n_2(\mathbf{r}_1,\mathbf{r}_2;t)=n_s(\mathbf{r}_1;t)ng_2^{\mathrm{eq}}(r_{12})+\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\ ,\\ &n_3(\mathbf{r}_1,\mathbf{r}_2,r_3;t)=n_s(\mathbf{r}_1;t)n^2g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)+\delta n_3(\mathbf{r}_1,\mathbf{r}_2,r_3;t)\ . \end{aligned} \tag{35}$$

Comparing the continuity equation

$$\frac{\partial}{\partial t}n_s(\mathbf{r}_1;t)=-\nabla_1\cdot\mathbf{j}_s(\mathbf{r}_1;t) \tag{36}$$

with the first hierarchy Eq. (32) we express the current density in terms of the reduced distributions

$$\mathbf{j}_s(\mathbf{r}_1;t)=-D_0\nabla_1 n_s(\mathbf{r}_1;t)+\beta D_0\int d\mathbf{r}_2\mathbf{F}_{12}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\ . \tag{37}$$

Note that due to the symmetry properties of the equilibrium pair distribution g_2^{eq}, the local equilibrium contribution $n_s(\mathbf{r}_1;t)ng_2^{\text{eq}}$ does not contribute to the current.

The relation Eq. (37) can rewritten in the following way:

$$\xi_0\mathbf{j}_s(\mathbf{r}_1;t)-\int d\mathbf{r}_2\mathbf{F}_{12}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)=-k_BT\nabla_1 n_s(\mathbf{r}_1;t)\ . \tag{38}$$

The right-hand side is the osmotic (or entropic) force. If we now are able to express δn_2 in terms of the current density then by a comparison with the definition Eq. (25) we can extract the friction kernel. Note that the first term on the left-hand side of Eq. (38) represents the friction due to the solvent and the second term is the interaction contribution to the friction.

To obtain the equation relating dynamical correlations δn_2 and δn_3 and the tagged-particle current density $\mathbf{j}_s$ we substitute Eq. (35) into the second hierarchy Eq. (33):

$$\begin{aligned}ng_2^{\text{eq}}(r_{12})\frac{\partial}{\partial t}n_s(\mathbf{r}_1;t)+\frac{\partial}{\partial t}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)={}&D_0[\nabla_1^2+\nabla_2^2-(\nabla_1-\nabla_2)\cdot\beta\mathbf{F}_{12}][n_s(\mathbf{r}_1;t)ng_2^{\text{eq}}(r_{12})+\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)]\\&-D_0\sum_{i=1}^{2}\nabla_i\cdot\int d\mathbf{r}_3\beta\mathbf{F}_{i3}[n_s(\mathbf{r}_1;t)ng_3^{\text{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)+\delta n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)]\ .\end{aligned} \tag{39}$$

Equation (39) can be simplified with help of the second equation of the Yvon-Born-Green hierarchy [24]:

$$-\nabla_1 g_2^{\text{eq}}(r_{12})+\beta\mathbf{F}_{12}g_2^{\text{eq}}(r_{12})+n\int d\mathbf{r}_3\mathbf{F}_{13}g_3^{\text{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=0\ . \tag{40}$$

Namely, using Eq. (40) we obtain from Eq. (39) the following equation:

$$\begin{aligned}ng_2^{\text{eq}}(r_{12})\frac{\partial}{\partial t}n_s(\mathbf{r}_1;t)+\frac{\partial}{\partial t}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)={}&n\nabla_1[g_2^{\text{eq}}(r_{12})\cdot D_0\nabla_1 n_s(\mathbf{r}_1;t)]+D_0[\nabla_1^2+\nabla_2^2-(\nabla_1-\nabla_2)\cdot\beta\mathbf{F}_{12}]\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\\&-D_0\sum_{i=1}^{2}\nabla_i\cdot\int d\mathbf{r}_3\beta\mathbf{F}_{i3}\delta n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)\ .\end{aligned} \tag{41}$$

Finally we eliminate the density of the tagged particle using the continuity Eq. (36) and the relation Eq. (38). In this way we obtain the required relation between the dynamical correlations and the tagged-particle current:

$$\begin{aligned}\frac{\partial}{\partial t}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)={}&-n[\nabla_1 g_2^{\text{eq}}(r_{12})]\cdot\mathbf{j}_s(\mathbf{r}_1;t)+D_0[\nabla_1^2+\nabla_2^2-(\nabla_1-\nabla_2)\cdot\beta\mathbf{F}_{12}]\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\\&+n\nabla_1\cdot\left[g_2^{\text{eq}}(r_{12})\int d\mathbf{r}_3\beta\mathbf{F}_{13}\delta n_2(\mathbf{r}_1,\mathbf{r}_3;t)\right]-D_0\sum_{i=1}^{2}\nabla_i\cdot\int d\mathbf{r}_3\beta\mathbf{F}_{i3}\delta n_3(\mathbf{r}_1,\mathbf{r}_2\mathbf{r}_3;t)\ .\end{aligned} \tag{42}$$

Note that up to now we did not make any approximations. Moreover, Eq. (42) is valid for arbitrary interactions between the colloidal particles.

The evolution Eq. (42) for the dynamical correlations δn_2 can be interpreted in the following way: At $t=0$ there are no dynamical correlations, $\delta n_2=0$. However, the local-equilibrium form $n_s(\mathbf{r}_1,t)ng_2^{\text{eq}}$ of n_2 is not preserved by the dynamical evolution and new nonequilibrium correlations are created. The source of these correlations is the average motion of the tagged-particle represented in Eq. (42) by the current density $\mathbf{j}_s$. This motion disturbs the state of the nontagged particles. The tagged particle acts on them with the *mean force* [24]: The first term at the right-hand side of Eq. (42), i.e., the source term, can be rewritten as

$$\begin{aligned}&-n[\nabla_1 g_2^{\text{eq}}(r_{12})]\cdot\mathbf{j}_s(\mathbf{r}_1;t)\\&\qquad=n[g_2^{\text{eq}}(r_{12})\nabla_1\beta V^{\text{eff}}(r_{12})]\cdot\mathbf{j}_s(\mathbf{r}_1;t)\ ,\end{aligned} \tag{43}$$

where V^{eff} is the potential of the effective mean force, $\beta V^{\text{eff}}(r_{12})=-\ln g_2^{\text{eq}}(\mathbf{r}_{12})$. The last three terms at the right-hand side of Eq. (42) describe decay of the dynamical correlations. This evolution is different from the evolution given by the hierarchy (32) and (33). The difference in the evolution corresponds to the fact that the Green-Kubo expression for the self-friction coefficient contains the projected evolution operator [21]. Note that the Eq. (42) has to be solved with the boundary condition $\lim_{r_{12}\to\infty}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)=0$.

Equation (42) is not closed—to get any explicit result we have to make some approximations. As it was stated in Sec. III A we want here, first, to keep the two-particle dynamics only, and, second, to take into account the enhanced probability of binary encounters. With this end in view we neglect the three-particle dynamical correlations δn_3 completely, omit the third term at the right-hand side, and replace the potential of the effective mean force V^{eff} in the source term Eq. (43) by its low-density limit V. There are some arguments to why these steps should be taken all at the same time. This we will discuss in a future publication [25].

We obtain the following evolution equation:

$$\frac{\partial}{\partial t}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)=-ng_2^{\mathrm{eq}}(r_{12})\beta\mathbf{F}_{12}\cdot\mathbf{j}_s(\mathbf{r}_1;t)+D_0[\nabla_1^2+\nabla_2^2-(\nabla_1-\nabla_2)\cdot\beta\mathbf{F}_{12}]\times\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\;. \tag{44}$$

The continuity Eq. (36); the relation Eq. (38) between the current density, the dynamical correlations, and the tagged-particle density gradient; and the evolution Eq. (44) constitute a closed system of equations. Using them we can calculate the self-friction coefficient, the self-diffusion coefficient, and the whole time evolution of the tagged-particle scattering function. For the interaction contribution to the self-friction kernel we find

$$\xi_{s,I}(k,t)=\frac{n}{k_BTV}\int d\mathbf{r}_1\int d\mathbf{r}_2 e^{-i\mathbf{k}\cdot\mathbf{r}_1}(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})\times e^{\Omega_2 t}(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})e^{i\mathbf{k}\cdot\mathbf{r}_1}g(r_{12})\;, \tag{45}$$

where V is the volume of the system (thermodynamic limit is understood). In the hard sphere limit this becomes identical to Eq. (29), except for a prefactor $g(2a)$, which is what we wanted.

IV. RESULTS

To get explicit results from Eq. (45) we have to solve the two-particle Smoluchowski equation. For hard spheres this can be done analytically. Actually, it has already been done many times and we simply resume the results taken from the literature in Appendix B. Below we use these expressions to derive the results of our theory.

Using Eq. (B1) in the limits $k\rightarrow 0$ and $z\rightarrow 0$ we obtain for the interaction part of the self-friction coefficient

$$\xi_{s,I}=2\phi g(2a)\xi_0\;. \tag{46}$$

In Fig. 1 we compare this simple expression with the Brownian-dynamics-simulation results of Cichocki and Hinsen [8]. The accuracy is quite satisfactory, better than the mode-coupling-like calculation of Medina-Noyola [26]; the deviations are reminiscent of what is found for atomic fluids, where the Enskog theory also gives too-high results for intermediate densities and too-low results near the crystallization density [24].

Having calculated the self-friction coefficient we can immediately get the long-time self-diffusion coefficient using the Einstein relation

$$D_s=\frac{D_0}{1+2\phi g(2a)}\;. \tag{47}$$

As it was anticipated in the Introduction for high densities, the self-diffusion is very small (at $\phi=0.5$ we find $D_s=0.14D_0$)—the single-particle (solvent) contribution and the interaction contribution cancel to a large extent.

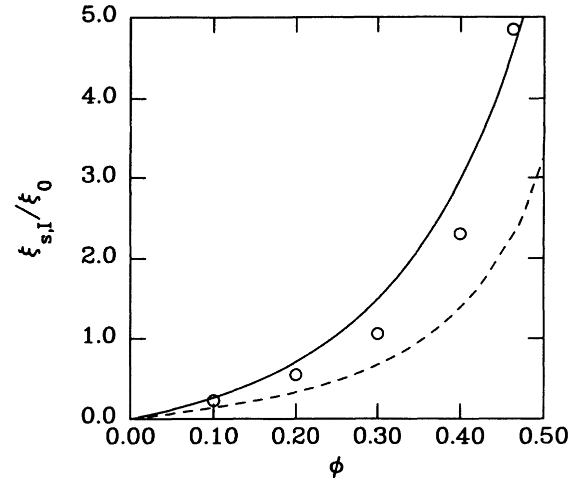

FIG. 1. The interaction contribution to the self-friction coefficient $\xi_{s,I}$ normalized by the solvent (zeroth order in density) friction ξ_0 as a function of the volume fraction $\phi=4\pi na^3/3$. Solid line, present theory; circles, simulation data of Cichocki and Hinsen [8]; dashed line, mode-mode-coupling theory of Medina-Noyola [26].

The time dependence of the self-diffusion kernel at $k=0$ can be calculated using the formulas of Sec. II and Appendix B. Before presenting the numerical results we make some analytical predictions. We consider the characteristic time of interaction as defined by Cichocki and Hinsen (see Fig. 2). In our notation this time τ is defined as

$$\tau=\frac{\int_0^\infty dt\, tD_{s,I}(t)}{\int_0^\infty dt\, D_{s,I}(t)}\;. \tag{48}$$

The time τ can be expressed through the Laplace transform of the self-diffusion kernel as

$$\tau=-\frac{d}{dz}\ln D_{s,I}(z)\;. \tag{49}$$

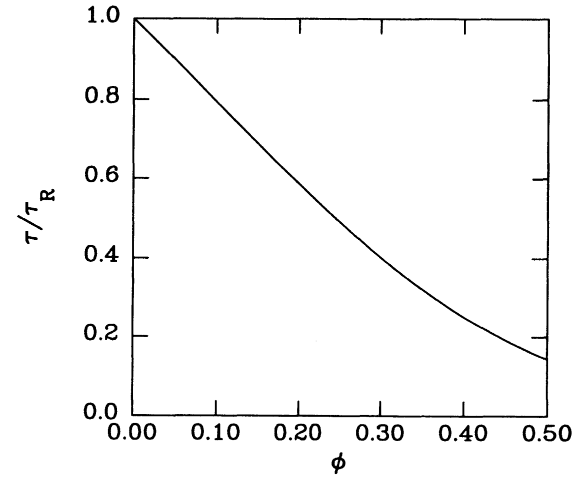

FIG. 2. The characteristic time of interaction as defined by Cichocki and Hinsen [8] normalized by its low-density limit $\tau_R=a^2/D_0$ as a function of the volume fraction ϕ.

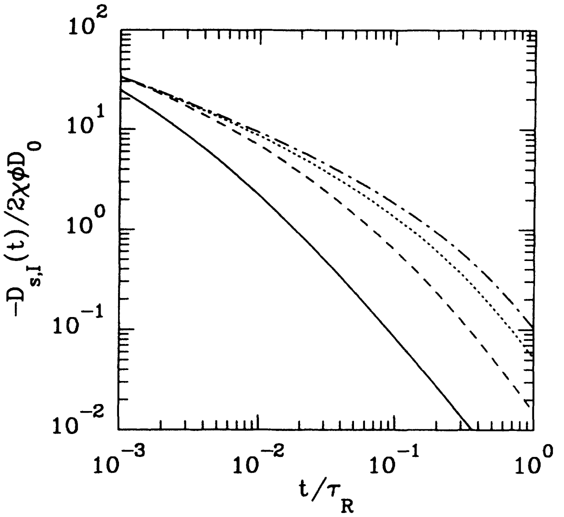

FIG. 3. The interaction contribution to the long-wavelength self-diffusion kernel $-D_{s,I}(k=0;t)$ divided by $2\chi\phi D_0$ as a function of time in units $\tau_R=a^2/D_0$, $\chi=g(2a)$. Dash-dotted line, low-density limit $\phi=0$; dotted line, volume fraction $\phi=0.14$, which corresponds to $\chi\phi=0.2$; dashed line, $\phi=0.3$, which corresponds to $\chi\phi=0.75$; solid line, $\phi=0.5$, which corresponds to $\chi\phi=3$.

Using the Laplace transform of Eq. (28) we find the following exact relation between the interaction time τ and the corresponding interaction time τ_f for the friction kernel:

$$\tau=\tau_f\frac{D_s}{D_0}\ . \tag{50}$$

In our theory τ_f is independent of density. Using Eq. (B1) we find $\tau_f=\tau_R=a^2/D_0$. For the diffusion interaction time we then find

$$\tau=\frac{a^2}{D_0}\frac{1}{1+2\phi g(2a)}\ . \tag{51}$$

We do not compare this expression with the Brownian-dynamics-simulation results as there is no reliable data available [27]. In Fig. 3 we present the numerical results for the interaction part of the self-diffusion kernel. Note that for short times the kernel diverges as $t^{-1/2}$, the coefficient of the dominant term agrees with the exact short-time result, and for long times there is an algebraic tail decaying as $t^{-5/2}$.

Additional information can be obtained from the wave-number-dependent self-friction kernel integrated

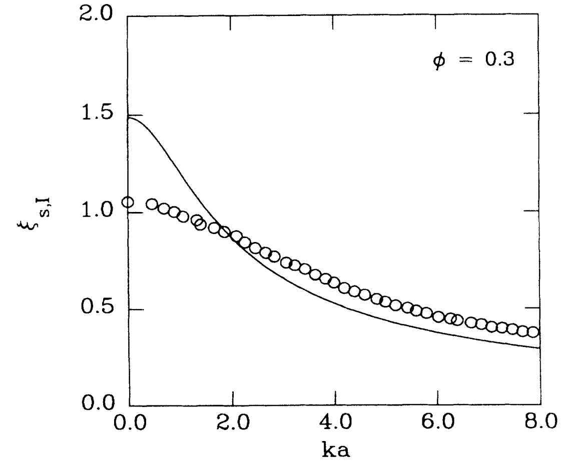

FIG. 4. The interaction contribution to the self-friction kernel integrated over time $\xi_{s,I}(k;z=0)$ divided by the solvent friction ξ_0 as a function of wave number in units a^{-1} for volume fraction $\phi=0.3$. Solid line, theory; circles, simulations of Cichocki and Hinsen [8].

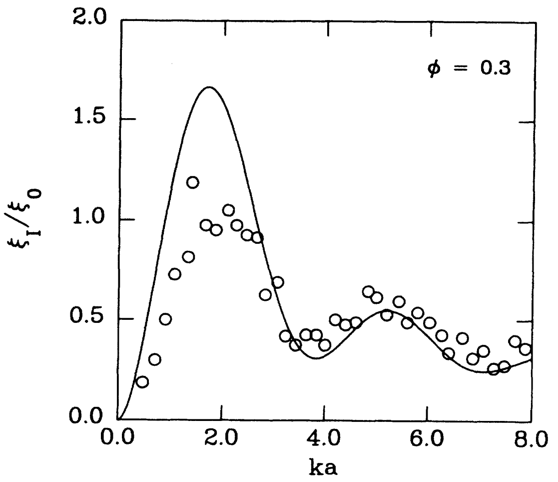

FIG. 5. The interaction contribution to the friction kernel integrated over time $\xi_I(k;z=0)$ divided by the solvent friction ξ_0 as a function of wave number in units a^{-1} for volume fraction $\phi=0.3$. Solid line, theory; circles, simulations of Cichocki and Hinsen [8].

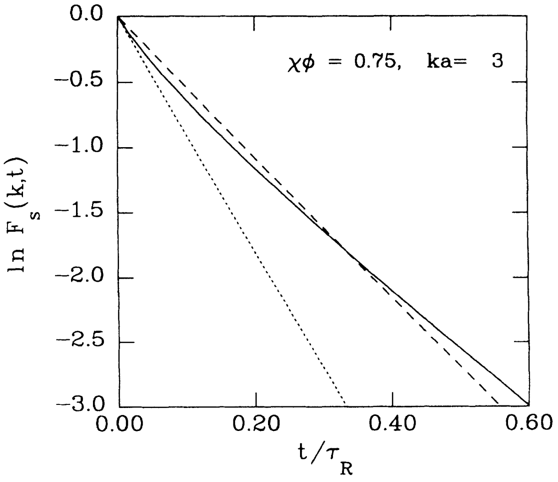

FIG. 6. Solid line, the tagged-particle scattering function $F_s(k;t)$ calculated using the present theory as a function of time in units $\tau_R=a^2/D_0$ for volume fraction $\phi=0.3$, which corresponds to $\chi\phi=0.75$ and wave number $ka=3$; the dotted line is an extrapolation of the initial slope, the dashed line is an exponential with the "long-time" self-friction coefficient $\xi_{s,I}(k;z=0)$ for $ka=3$.

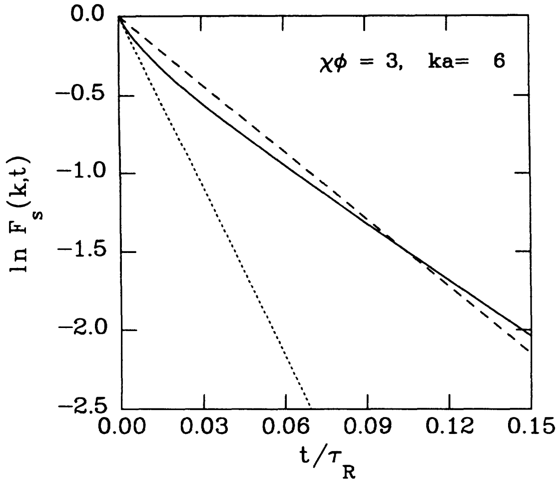

FIG. 7. Solid line, the tagged-particle scattering function $F_s(k;t)$ calculated using the present theory as a function of time in units $\tau_R=a^2/D_0$ for volume fraction $\phi=0.5$, which corresponds to $\chi\phi=3$ and wave number $ka=6$; the dotted line is an extrapolation of the initial slope, the dashed line is an exponential with the "long-time" self-friction coefficient $\xi_{s,I}(k;z=0)$ for $ka=6$.

over time, i.e., $\xi_{s,I}(k;z=0)$, and from the friction kernel for the non-tagged-particle problem, i.e., $\xi_I(k;z=0)$. These are graphed for a typical intermediate volume fraction $\phi=0.3$ in Figs. 4 and 5. We find that the present theory overestimates the interaction part, in particular for $ka<\pi$, but reproduces the general structure quite well. Actually, as we anticipated in the Introduction, for high wave numbers we have very good agreement with the simulation results.

We have also calculated the intermediate scattering function $F(k,t)$ for some volume fractions. In Fig. 6 we graphed $F(k,t)$ calculated using our theory for density $\phi=0.3$ for which $g(2a)=\chi=2.48$ ($\chi\phi\approx0.75$), for a wave number for which the theory, according to Fig. 3, is reasonably accurate. Notice that the change from short- to long-time regime is quite rapid, but definitely noticeable. More structure is found by going to very high volume fractions, $\phi=0.5$ for which $g(2a)=6$ and $\chi\phi=3$. A typical wave number is graphed in Fig. 7. At this volume our theory is not really expected to be accurate though. We notice that since our friction kernel decays algebraically at long times, also the self-intermediate scattering function decays algebraically. This can easily be shown by considering the Laplace transform $F(k,z)$.

V. CONCLUDING REMARKS

We presented an alternative approach to the dynamical phenomena of suspensions of interacting colloidal particles. The model suspension without hydrodynamic interactions was considered, the actual calculations were done for the hard-sphere interaction potential. The main idea was to approximate the friction coefficients and then to obtain the diffusion coefficients using the Einstein relation. To this end we rewrote the hierarchy of equations describing the time dependence of the reduced distribution functions. We obtained the evolution equation for the dynamical correlations. These were created due to the average motion of the tagged particle, i.e., the source term was essentially the current. Within this scheme we derived a very simple theory of dynamical behavior of a hard-sphere suspension. To calculate the friction coefficients only the two-particle dynamics was kept. However, the renormalization of the frequency of the binary encounters due to the static correlations was retained. Thus this simple theory is very similar to the Enskog kinetic theory that describes quite well the dynamical behavior of the hard-sphere fluid. However, it is much more advanced than the mode-mode–coupling theories. For the tagged-particle problem an infinite number of recollisions of the tagged particle with the same, nontagged particle is effectively summed whereas in the mode-coupling theories only one recollision is kept. In this way overlapping configurations are avoided here that are admitted by the mode-mode–coupling theories. As earlier studies of the pair dynamics [28] or depolarized light scattering [29] shows this is very relevant for obtaining satisfactory quantitative results.

Using our very simple theory we calculated the self-friction coefficient, the self-diffusion coefficient, the time-dependent self-diffusion kernel, and the wave-number-dependent friction kernels. The theoretical predictions were compared against the Brownian-dynamics-simulation results. We get quite reasonable agreement, especially taking the simplicity of the theory into account. In particular we got very satisfactory agreement for the wave-number-dependent friction kernels for high wave numbers.

We would like to point out that our simple theory gives by no means the final answer, even for a simple model suspension without hydrodynamic interactions. Its deficiencies are similar to those of the Enskog kinetic theory of dense hard-sphere fluid [30]. First, the simple theory does not take into account correlated encounters and slightly overestimates the friction coefficients for intermediate densities. Moreover, it does not include collective "cage" effects and therefore fails to predict slowing down of structural relaxation for very high densities, $\phi>0.45$. While the first deficiency is relatively easy to cure (we will return to this problem in a future publication [31]), tackling the second one seems to be more complicated. Finally, one should always keep in mind that in order to describe really concentrated suspensions also hydrodynamic interactions between colloidal particles have to be included. This problem is left for future study.

Note added in proof. Our attention has been drawn to the paper of Sonnenburg *et al.* [Mol. Phys. **72**, 873 (1991)], who have also approximated the friction coefficient rather than the diffusion coefficient. They use a completely different closure based on the direct correlation force idea. While superficially their Eq. (75) resembles our Eq. (47), their result is exact but formal and requires an approximation for g_{ab}, for which they use a nonequilibrium version of the Percus-Yevick equation. In contrast our Eq. (47) is approximate but explicit.

Their figure for the long-time zero-wave-number self-diffusion coefficient is different from our result.

ACKNOWLEDGMENTS

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APPENDIX A: COLLECTIVE CASE

In this Appendix we derive the approximate evolution equation for the intermediate scattering function. The derivation presented here is entirely analogous to that given in Sec. III B, but quite a lot more complicated. For clarity we have written out the derivation in considerable detail.

First, we express the intermediate scattering function in terms of nonequilibrium reduced distributions with a suitable initial condition. To this end we start with rewriting the definition (14)

$$F(k;t)=\frac{1}{N}\left\langle \sum_{i=1}^{N} e^{-i\mathbf{k}\cdot\mathbf{R}_i} e^{\Omega_S t} \sum_{j=1}^{N} e^{i\mathbf{k}\cdot\mathbf{R}_j} \right\rangle$$
$$=\int d\mathbf{r}_{10} e^{-i\mathbf{k}\cdot\mathbf{r}_{10}} \left\langle \sum_{i=1}^{N} \delta(\mathbf{r}_1-\mathbf{R}_i) e^{\Omega_s t} \sum_{j=1}^{N} [\delta(\mathbf{r}_0-\mathbf{R}_1)-n] \right\rangle . \tag{A1}$$

Then we note that the density correlation function

$$\left\langle \sum_i \delta(\mathbf{r}_1-\mathbf{R}_i)\exp(\Omega_s t) \sum_j [\delta(\mathbf{r}_0-\mathbf{R}_j)-n] \right\rangle$$

is equal to the one-particle density for a particular nonequilibrium ensemble:

$$\left\langle \sum_{i=1}^{N} \delta(\mathbf{r}_1-\mathbf{R}_i) e^{\Omega_s t} \sum_{j=1}^{N} [\delta(\mathbf{r}_0-\mathbf{R}_1)-n] \right\rangle = n_1(\mathbf{r}_i;t) , \tag{A2}$$

where $n_1(\mathbf{r}_1;t)=\langle \sum_{i=1}^{N} \delta(\mathbf{r}_1-\mathbf{R}_i) \rangle_t$ is the one-particle density calculated for the nonequilibrium ensemble

$$P_N(R_1,\ldots,R_N;t)$$
$$=e^{\Omega_s t} \sum_{j=1}^{N} [\delta(\mathbf{r}_0-\mathbf{R}_1)-n] P_N^{\mathrm{eq}}(R_1,\ldots,R_N) . \tag{A3}$$

Equivalently, $n_1(\mathbf{r}_1;t)$ is the solution of the infinite hierarchy of equations for the reduced distributions with the initial conditions that follow from the form of distribution (A3). We will need the first two equations of this hierarchy, namely Eqs. (10) and (11) and the initial conditions for the first three reduced distributions:

$$n_1(\mathbf{r}_1;t=0)=n\delta(\mathbf{r}_1-\mathbf{r}_0)+n^2[g_2^{\mathrm{eq}}(r_{12})-1] ,$$
$$n_2(\mathbf{r}_1,\mathbf{r}_2;t=0)=[\delta(\mathbf{r}_1-\mathbf{r}_0)+\delta(\mathbf{r}_2-\mathbf{r}_0)]n^2 g_2^{\mathrm{eq}}(r_{12})$$
$$+n^3[g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)-g_2^{\mathrm{eq}}(r_{12})] , \tag{A4}$$
$$n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t=0)$$
$$=[\delta(\mathbf{r}_1-\mathbf{r}_0)+\delta(\mathbf{r}_2-\mathbf{r}_0)+\delta(\mathbf{r}_3-\mathbf{r}_0)]n^3 g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$$
$$+n^4[g_4^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)-g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)] .$$

Here n is the density of colloidal particles and g_2^{eq}, g_3^{eq}, and g_4^{eq} denote the equilibrium pair, triple, and quadrupule distribution, respectively: $g_2^{\mathrm{eq}}(r_{12})=n_2^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2)/n^2$, $g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=n_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)/n^3$, and $g_4^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)=n_4^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)/n^4$. For further analysis it is convenient to express the initial conditions for the two- and three-particle density as a functional of the initial condition for the one-particle density:

$$n_2(\mathbf{r}_1,\mathbf{r}_2;t=0)=\int d\mathbf{r}_3 Q_2(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)n_1(\mathbf{r}_3;t=0) ,$$
$$n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t=0)=\int d\mathbf{r}_3 Q_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3|\mathbf{r}_4)n_1(\mathbf{r}_4;t=0) . \tag{A5}$$

The kernels Q_2 and Q_3 are defined as

$$Q_2(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)=\left.\frac{\delta n_2(\mathbf{r}_1,\mathbf{r}_2)}{\delta n(\mathbf{r}_3)}\right|_{\mathrm{eq}} ,$$
$$Q_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3|\mathbf{r}_4)=\left.\frac{\delta n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{\delta n(\mathbf{r}_4)}\right|_{\mathrm{eq}} . \tag{A6}$$

These derivatives can be defined by introducing an external potential [32]. Explicitly the Q kernels are given by

$$Q_2(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)=\int d\mathbf{r}_4\{[\delta(\mathbf{r}_1-\mathbf{r}_4)+\delta(\mathbf{r}_2-\mathbf{r}_4)]n^2 g_2^{\mathrm{eq}}(r_{12})+n^3[g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_4)-g_2^{\mathrm{eq}}(r_{12})]\}[n^{-1}\delta(\mathbf{r}_4-\mathbf{r}_3)-c(r_{43})] ,$$
$$Q_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3|\mathbf{r}_4)=\int d\mathbf{r}_5\{[\delta(\mathbf{r}_1-\mathbf{r}_5)+\delta(\mathbf{r}_2-\mathbf{r}_5)+\delta(\mathbf{r}_3-\mathbf{r}_5)]n^3 g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$$
$$+n^4[g_4^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_5)-g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)]\}[n^{-1}\delta(\mathbf{r}_5-\mathbf{r}_4)-c(r_{54})] . \tag{A7}$$

In Eqs. (A7) $c(r_{12})$ denotes the Ornstein-Zernike direct correlation function [24].

To calculate the generalized friction coefficient for the intermediate scattering function we rewrite the hierarchy Eqs. (10) and (11). First, we separate n_2 and n_3 into the *local-equilibrium* contributions, i.e., contributions of the form of Eq. (A5), and the remaining parts that represent nonequilibrium dynamical correlations

$$\begin{aligned} n_2(\mathbf{r}_1,\mathbf{r}_2;t)&=\int d\mathbf{r}_3 Q_2(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)n_1(\mathbf{r}_3;t)+\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\ ,\\ n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)&=\int d\mathbf{r}_3 Q_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3|\mathbf{r}_4)n_1(\mathbf{r}_4;t)\\ &\quad+\delta n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)\ . \end{aligned} \tag{A8}$$

This is the proper generalization of Eq. (35), as is clear from the definition of the Q kernels Eq. (A6). Comparing the continuity equation

$$\frac{\partial}{\partial t}n_1(\mathbf{r}_1;t)=-\nabla_1\cdot\mathbf{j}(\mathbf{r}_1;t) \tag{A9}$$

with the first hierarchy equation Eq. (10), we express the current density in terms of the reduced distributions

$$\begin{aligned} \mathbf{j}(\mathbf{r}_1;t)&=-D_0\nabla_1 n(\mathbf{r}_1;t)\\ &\quad+\xi_0^{-1}\int d\mathbf{r}_2\mathbf{F}_{12}\int d\mathbf{r}_3 Q_2(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)n_1(\mathbf{r}_3;t)\\ &\quad+\xi_0^{-1}\int d\mathbf{r}_2\mathbf{F}_{12}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\ . \end{aligned} \tag{A10}$$

The relation Eq. (A10) can be rewritten in the following way:

$$\begin{aligned} &\xi_0\mathbf{j}(\mathbf{r}_1;t)-\int d\mathbf{r}_2\mathbf{F}_{12}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\\ &\quad=-k_BT\nabla_1 n_1(\mathbf{r}_1;t)\\ &\qquad-\xi_0^{-1}\int d\mathbf{r}_2\mathbf{F}_{12}\int d\mathbf{r}_3 Q_2(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)n_1(\mathbf{r}_3;t)\ . \end{aligned} \tag{A11}$$

The second term on the right-hand side of Eq. (A11) can be simplified using the second equation of the Yvon-Born-Green hierarchy Eq. (40) and the Ornstein-Zernike equation [24]:

$$g_2^{\mathrm{eq}}(r_{12})-1=c(r_{12})+n\int d\mathbf{r}_3 c(r_{13})[g_2^{\mathrm{eq}}(r_{32})-1]\ . \tag{A12}$$

Namely, using Eqs. (40) and (A12) we can rewrite the relation Eq. (A11) in the following form:

$$\begin{aligned} &\xi_0\mathbf{j}(\mathbf{r}_1;t)-\int d\mathbf{r}_2\mathbf{F}_{12}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\\ &\quad=-k_BT\int d\mathbf{r}_2[\delta(\mathbf{r}_1-\mathbf{r}_2)-nc(r_{12})]\nabla_2 n_1(\mathbf{r}_2;t)\ . \end{aligned} \tag{A13}$$

The right-hand side of Eq. (A13) is the osmotic pressure gradient, suitably generalized to the nonuniform state. If we now express δn_2 in terms of the current density and substitute into Eq. (A13), then by a comparison with the definition Eq. (25) we can extract the friction kernel (now the derivative of the osmotic pressure of the colloidal particles with respect to their density is, in general, different than k_BT). Again, the first term on the left-hand side of Eq. (A13) represents the friction due to the solvent and the second term is the interaction contribution.

To obtain the equation relating dynamical correlations δn_2 and δn_3 and the current density $\mathbf{j}$ we substitute Eq. (A8) into the second hierarchy Eq. (11):

$$\begin{aligned} &\int d\mathbf{r}_3 Q_2(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)\frac{\partial}{\partial t}n_1(\mathbf{r}_3;t)+\frac{\partial}{\partial t}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\\ &\quad=D_0[\nabla_1^2+\nabla_2^2-(\nabla_1-\nabla_2)\cdot\beta\mathbf{F}_{12}]\left[\int d\mathbf{r}_3 Q_2(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)n_1(\mathbf{r}_3;t)+\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\right]\\ &\qquad-D_0\sum_{i=1}^{2}\nabla_i\cdot\int d\mathbf{r}_3\beta\mathbf{F}_{i3}\left[\int d\mathbf{r}_3 Q_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3|\mathbf{r}_4)n_1(\mathbf{r}_4;t)+\delta n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)\right]\ . \end{aligned} \tag{A14}$$

Again, Eq. (A14) can be greatly simplified with help of Eq. (40), the Ornstein-Zernike equation (A12), and the third equation of the Yvon-Born-Green hierarchy [24]:

$$-\nabla_1 g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)+\beta\mathbf{F}_{12}g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)+\beta\mathbf{F}_{13}g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)+n\int d\mathbf{r}_4\mathbf{F}_{14}g_4^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)=0\ . \tag{A15}$$

Namely, using Eqs. (40), (A12), and (A15), we obtain from Eq. (A14)

$$\begin{aligned} &\int d\mathbf{r}_3 Q_2(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)\frac{\partial}{\partial t}n_1(\mathbf{r}_3;t)+\frac{\partial}{\partial t}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\\ &\quad=n\nabla_1\cdot\left[g_2^{\mathrm{eq}}(r_{12})\int d\mathbf{r}_3[\delta(\mathbf{r}_1-\mathbf{r}_3)-nc(r_{13})]D_0\nabla_3 n_s(\mathbf{r}_3;t)\right]+n\nabla_2\cdot\left[g_2^{\mathrm{eq}}(r_{12})\int d\mathbf{r}_3[\delta(\mathbf{r}_2-\mathbf{r}_3)-nc(r_{23})]D_0\nabla_3 n_s(\mathbf{r}_3;t)\right]\\ &\qquad+D_0[\nabla_1^2+\nabla_2^2-(\nabla_1-\nabla_2)\cdot\beta\mathbf{F}_{12}]\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)-D_0\sum_{i=1}^{2}\nabla_i\cdot\int d\mathbf{r}_3\beta\mathbf{F}_{i3}\delta n_3(\mathbf{r}_1,\mathbf{r}_2\mathbf{r}_3;t)\ . \end{aligned} \tag{A16}$$

Finally we eliminate the one-particle density using the continuity equation Eq. (A9) and the relation Eq. (A13). In this way we obtain the required relation between the dynamical correlations and the current density:

$$\frac{\partial}{\partial t}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)=-n[\nabla_{12}g_2^{\mathrm{eq}}(r_{12})]\cdot[\mathbf{j}(\mathbf{r}_1;t)-\mathbf{j}(\mathbf{r}_2;t)]$$
$$+n^2\int d\mathbf{r}_3\{Q(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)-n[\delta(\mathbf{r}_1-\mathbf{r}_3)+\delta(\mathbf{r}_2-\mathbf{r}_3)]g_2^{\mathrm{eq}}(r_{12})\}\nabla_3\cdot\mathbf{j}(\mathbf{r}_3;t)$$
$$+D_0[\nabla_1^2+\nabla_2^2-(\nabla_1-\nabla_2)\cdot\beta\mathbf{F}_{12}]\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)+n\nabla_1\cdot\left[g_2^{\mathrm{eq}}(r_{12})\int d\mathbf{r}_3\beta\mathbf{F}_{13}\delta n_2(\mathbf{r}_1,\mathbf{r}_3;t)\right]$$
$$+n\nabla_2\cdot\left[g_2^{\mathrm{eq}}(r_{12})\int d\mathbf{r}_3\beta\mathbf{F}_{23}\delta n_2(\mathbf{r}_2,\mathbf{r}_3;t)\right]-D_0\sum_{i=1}^{2}\nabla_i\cdot\int d\mathbf{r}_3\beta\mathbf{F}_{i3}\delta n_3(\mathbf{r}_1,\mathbf{r}_2\mathbf{r}_3;t)\;. \tag{A17}$$

Note that up to now we did not make any approximations. Moreover, Eq. (A17) is valid for arbitrary interactions between the colloidal particles. It can be interpreted in a way similar to the corresponding equation for the tagged-particle problem.

Again, the evolution equation Eq. (A17) is not closed and we still have to make some approximations. As it was stated in Sec. III A we want here, first, to keep the two particle dynamics only and, second, to take into account the enhanced probability of binary encounters. With this end in view we neglect the three-particle dynamical correlations δn_3 completely, omit the forth and fifth terms on the right-hand side, and replace the source term by its low-density limit. We keep the equilibrium pair distribution g_2^{eq} in the source term. In this way we obtain the following evolution equation:

$$\frac{\partial}{\partial t}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)$$
$$=-ng_2^{\mathrm{eq}}(r_{12})\beta\mathbf{F}_{12}\cdot[\mathbf{j}(\mathbf{r}_1;t)-\mathbf{j}(\mathbf{r}_2;t)]$$
$$+D_0[\nabla_1^2+\nabla_2^2-(\nabla_1-\nabla_2)\cdot\beta\mathbf{F}_{12}]\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)\;. \tag{A18}$$

Again, the continuity equation Eq. (A9); the relation Eq. (A13) between the current density, the dynamical correlations, and the osmotic pressure gradient; and the evolution equation Eq. (A18) constitute the closed system of equations. Using them we can calculate the friction coefficient, the diffusion coefficient, and the whole time evolution of the intermediate scattering function.

For the friction kernel we get the following expression:

$$\xi_I(k,t)=\frac{n}{k_BTV}\int d\mathbf{r}_1\int d\mathbf{r}_2 e^{-i\mathbf{k}\cdot\mathbf{r}_1}(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})e^{\Omega_2 t}(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})$$
$$\times(e^{i\mathbf{k}\cdot\mathbf{r}_1}-e^{i\mathbf{k}\cdot\mathbf{r}_2})g(r_{12})\;, \tag{A19}$$

where V is the volume of the system (thermodynamic limit is understood). For hard spheres the low-density result is recovered, up to a prefactor $g(2a)$. The low-density interaction friction ξ_I is given explicitly in Appendix B. Then using the continuity equation Eq. (A9) and the relation Eq. (A13) between the current density and the osmotic pressure gradient we find the diffusion kernel

$$D(k,z)=\frac{k_BT}{S(k)[\xi_0+\xi_I(k,z)]}\;. \tag{A20}$$

Since for $k\to 0$ the low-density friction kernel vanishes (see Appendix B), in the long-wavelength limit we recover the exact result $D_0/S(k)$. Using the expression Eq. (A20) and the initial condition $F(k;t=0)=S(k)$ we get the final formula for the intermediate scattering function:

$$F(k,z)=\frac{S(k)}{z+k^2D(k,z)}\;. \tag{A21}$$

APPENDIX B: EXPLICIT EXPRESSION FOR ξ_I

Here we give a summary of literature results for the interaction parts of the friction kernel. The results quoted here are arrived at by solving the two particle Smoluchowski equation, and inserting appropriate prefactors [12]. In the frequency domain we have

$$\xi_{s,I}(k,z)=12\phi\xi_0\sum_{l=0}^{\infty}(2l+1)\frac{[j_l'(ka)]^2k_l(\mu a)}{-\mu a k_l'(\mu a)}\;, \tag{B1}$$

where j_l and k_l are spherical Bessel functions and modified spherical Bessel functions, primes denote derivative with respect to argument, and $\mu=(k^2+2z/D_0)^{1/2}$. For the collective friction function the sum has to be taken over even l only, and the prefactor 12 has to be replaced by 24.

In the time domain we find

$$\xi_{s,I}(k,t)=12\phi\xi_0\left[\frac{D_0}{a^2}e^{-D_0k^2t/2}\right]$$
$$\times\sum_{l=0}^{\infty}(2l+1)[j_l'(ka)]^2H_l\left[\frac{D_0t}{a^2}\right]\;, \tag{B2}$$

where the $e^{-D_0k^2t/2}$ originates from the center of mass motion, and the solution of the relative Smoluchowski equation enters through the function H_l,

$$H_l(s)=\frac{1}{\pi}\int_0^{\infty}d\kappa\frac{e^{-\kappa^2 s/2}}{\kappa^2\{[n_l'(\kappa)]^2+[j_l'(\kappa)]^2\}}\;, \tag{B3}$$

where j_l and n_l are spherical Bessel functions. The collective version of (B2) is arrived at in the same way as above.

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