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Long-time self-diffusion coefficients of suspensions

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We present a theory for calculation of the long-time self-diffusion coefficient of suspensions of interacting colloidal particles without hydrodynamic interactions. The theory follows the idea put forward in the preceding paper [Jan A. Leegwater and Grzegorz Szamel, Phys. Rev. A **46**, 4999 (1992)]: The self-friction coefficient is calculated approximately and the self-diffusion coefficient can be obtained using the Einstein relation. To calculate the friction coefficient, we retain the part of the three-particle dynamical correlations that can be expressed in terms of the two-particle dynamical correlations. In this way we renormalize the two-particle dynamics. To get explicit results for hard spheres, we introduce a decoupling approximation for the long-time contributions to the friction coefficient. For intermediate densities the predictions of our theory agree very well with Brownian-dynamics simulation.

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I. INTRODUCTION

In the preceding paper [1], hereafter referred to as I, we presented a microscopic theory for the dynamic properties of a model suspension without hydrodynamic interactions. There are two reasons for studying this model: First, the results can be used to describe suspensions of highly charged colloidal particles (see, however, [2]). Second, a comparison (Ref. [3], Sec. V.I.5) of experimental data and Brownian-dynamics simulation results shows that at least for not too low densities quite a reasonable way to account for the hydrodynamic interactions is to introduce an effective diffusion constant such that the short time properties are reproduced (see also [4]). Hence the present work can also be relevant for understanding dynamic properties of suspensions of noncharged particles.

The main idea of our approach was to formulate a theory that approximates the friction coefficient rather than the diffusion coefficient. The diffusion coefficient can then be calculated using the Einstein relation. Within this scheme we derived a very simple theory and applied it to a hard-sphere suspension. The theory was based on ideas of the Enskog kinetic theory [5] of a dense hard-sphere fluid: to calculate approximately the friction coefficients we dropped three-particle dynamical effects but retained static correlations. The theory of I satisfies the exact short-time limit for a hard-sphere suspension. Also the long-time properties were reproduced reasonably well. In the case of the so-called long-time self-friction coefficient the deviations between the predictions of our theory and Brownian-dynamics results were reminiscent of what is found for atomic fluids, where the Enskog theory gives too high results for intermediate densities and too low results near the crystallization density [6]. For atomic fluids it is known that the main source of the deviations for intermediate densities is that in the Enskog theory one completely neglects correlated collisions.

Here we present a more advanced theory. The present theory is based on ideas of an approximate hard-sphere kinetic theory of Resibois and Lebowitz [7] that was proposed to improve on the Enskog kinetic theory while staying in the same spirit.

We follow I in that the friction coefficient is approximated rather than the diffusion coefficient. We propose a closure approximation. Next, we make a decoupling approximation for a part of the rather complicated expression obtained from the closure. The main difference with I is that the theory of this paper includes correlated "collision" sequences in a certain approximate way. For intermediate densities the present theory reproduces very well Brownian-dynamics results for the long-time self-friction coefficient: for all volume fractions up to $\phi=0.4$ the difference between the theory and simulation is less than 5% ($\phi=4\pi na^3/3, n$ is the density of colloidal particles, and a is particle radius). The results for the time-integrated wave-vector-dependent self-friction kernel are somewhat less accurate.

The theory is not restricted to the hard-sphere interaction. We study hard spheres because we can use simple, approximate formulas for the static correlation functions that are known to reproduce the equilibrium properties very well [6]. Furthermore, Brownian-dynamics simulations have been performed for this model system [8,9] and we can test our theoretical predictions against those results. In this way we avoid the difficulties connected with the additional approximations involved when comparing real colloidal suspensions to our calculations. Also, for hard spheres it is much easier to arrive at analytical expressions.

The paper is organized as follows: In Sec. II we present a closure approximation and derive an expression for the time-integrated wave-vector-dependent friction coefficient. In Sec. III we formulate a decoupling approximation. In Sec. IV we present predictions of the theory and compare them with Brownian-dynamics results. We summarize the results in Sec. V. Some theoretical considerations leading to the closure approximation are relegated to the Appendix.

II. APPROXIMATE CLOSURE

In the preceding paper we derived a formalism that enables calculation of the self-friction kernel $\xi_s(k;z)$. Here we use the same notation as in that paper. The formalism can be briefly summarized as follows: First the difference δn_2 between the nonequilibrium pair distribution function and the local equilibrium pair distribution function can be exactly expressed in terms of the tagged-particle current density $\mathbf{j}_s$ as the solution of the following evolution equation [Eq. (42) of I; hereafter equations of the preceding paper are referred to as (I.42) and so on]:

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

Then in order to arrive at the friction coefficient we substitute δn_2 into relation (I.38) between the current density $\mathbf{j}_s$, the dynamical correlations δn_2, and the gradient of the tagged-particle density $\nabla_1 n_s$:

$$\xi_0\mathbf{j}_s(\mathbf{r}_1;t)-\int d\mathbf{r}_2\mathbf{F}_{12}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)=-k_BT\nabla_1 n_s(\mathbf{r}_1;t)\ . \qquad (2)$$

Finally we get the self-friction kernel comparing the result with the following constitutive relation that can be obtained from (I.23) and (I.25):

$$\xi_s(k;z)\mathbf{j}_s(k;z)=-i\mathbf{k}k_BTn_s(k;z)\ . \qquad (3)$$

Note that the left-hand side is the friction force acting on the tagged particle and the right-hand side is the osmotic (or entropic) force.

Equation (1) is not closed—to get any explicit result we have to make some approximations for the three-particle dynamical correlations δn_3. In I our aim was as follows: first, to keep the two-particle dynamics only, and, second, to take into account the enhanced probability of binary encounters. Here we want to include that part of the three-particle dynamical correlations δn_3 that can be expressed in terms of the two-particle dynamical correlations δn_2. In a sense we want to renormalize also the two-particle *dynamics* by the static correlations. To this end one has to separate δn_3 into two parts. The first one will be expressed in terms of δn_2 and the second one, to be neglected in the end, will be called the three-particle *irreducible* dynamical correlations. The separation of δn_3 into two parts is a generalization of the separation (I.35) of n_2 and n_3 into local equilibrium parts that are expressed in terms of the tagged-particle density n_s and the remaining parts describing the nonequilibrium dynamical correlations. There are a number of ways to arrive at the required separation. In the main text we just present the result and give a brief physical interpretation. This point is discussed at some length in the Appendix.

We separate the three-particle dynamical correlations in the following way:

$$\delta n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)=\int d\mathbf{r}_4\{n^2 g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)[\delta(\mathbf{r}_{24})+\delta(\mathbf{r}_{34})]+n^3[g_4^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)-g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)g_2^{\mathrm{eq}}(r_{14})]\}$$
$$\times\int d\mathbf{r}_5\left\{\frac{\delta(\mathbf{r}_{45})}{ng_2^{\mathrm{eq}}(r_{14})}-d(\mathbf{r}_1;\mathbf{r}_4,\mathbf{r}_5)\right\}\delta n_2(\mathbf{r}_1,\mathbf{r}_5;t)+\delta n_3^{\mathrm{irr}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)\ . \qquad (4)$$

Here function $d(\mathbf{r}_1;\mathbf{r}_2,\mathbf{r}_3)$ is defined as a solution of the generalized Ornstein-Zernike equation (A13).

The physical interpretation of the separation (4) is as follows: the first term in (4) describes the part of the three-particle correlations in a *nonequilibrium* state that has the same form as the *equilibrium* correlations in a system in external two-particle potential, the potential being chosen in such a way that the actual two-particle density is recovered (for further discussion see the Appendix). As the two-particle potential can influence the correlations very profoundly, we hope that the closure $\delta n_3^{\mathrm{irr}}=0$ retains a major part of the nonequilibrium correlations.

Substituting form (4) of the three-particle dynamical correlations into evolution equation (1) we obtain a rather complicated evolution equation. This equation can be simplified with use of the second and the third equations of the equilibrium Yvon-Born-Green hierarchy [6]. The explicit calculations are rather lengthy but relatively simple and need not be presented here. The final form of the evolution equation reads

$$\begin{aligned}\frac{\partial}{\partial t}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)=&-n[\nabla_1 g_2^{\mathrm{eq}}(r_{12})]\cdot\mathbf{j}_s(\mathbf{r}_1;t)\\&+D_0\nabla_1\int d\mathbf{r}_3\{ng_2^{\mathrm{eq}}(r_{12})\delta(\mathbf{r}_{23})+n^2[g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)-g_2^{\mathrm{eq}}(r_{12})g_2^{\mathrm{eq}}(r_{13})]\}\\&\quad\times\nabla_1\int d\mathbf{r}_4\left\{\frac{\delta(\mathbf{r}_{34})}{ng_2^{\mathrm{eq}}(r_{13})}-d(\mathbf{r}_1;\mathbf{r}_3,\mathbf{r}_4)\right\}\delta n_2(\mathbf{r}_1,\mathbf{r}_4;t)\\&+D_0\nabla_2 ng_2^{\mathrm{eq}}(r_{12})\cdot\nabla_2\int d\mathbf{r}_4\left\{\frac{\delta(\mathbf{r}_{24})}{ng_2^{\mathrm{eq}}(r_{12})}-d(\mathbf{r}_1;\mathbf{r}_2,\mathbf{r}_4)\right\}\delta n_2(\mathbf{r}_1,\mathbf{r}_4;t)-D_0\sum_{i=1}^{2}\nabla_i\cdot\int d\mathbf{r}_3\beta\mathbf{F}_{i3}\delta n_3^{\mathrm{irr}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t).\end{aligned} \tag{5}$$

The evolution equation is not closed yet. The *closure approximation* of the theory presented here is to neglect the three-particle irreducible correlations, $\delta n_3^{\mathrm{irr}}=0$. In this way we obtain from (5) a closed evolution equation that is the starting point of the further analysis.

Note that closure $\delta n_3^{\mathrm{irr}}=0$ is exact at short times: for continuous potentials we reproduce exactly the second time derivative of $F_s(k;t)$. For the hard-sphere potential the dominant short-time term proportional to $t^{3/2}$ is reproduced exactly (see I). Further analysis is needed to investigate whether also the term proportional to t^2 is correctly retained in this case.

Using the evolution equation (5) with closure $\delta n_3^{\mathrm{irr}}=0$ we can express the dynamical correlations δn_2 in terms of the tagged-particle current $\mathbf{j}_s$

$$\delta n_2(\mathbf{r}_1,\mathbf{r}_2;z)=-n\frac{1}{z-\Omega_2^{\mathrm{ren}}}[\nabla_1 g_2^{\mathrm{eq}}(r_{12})]\cdot\mathbf{j}_s(\mathbf{r}_1;t)\ . \tag{6}$$

Here Ω_2^{ren} denotes the renormalized two-particle Smoluchowski operator that acts on a function $f(\mathbf{r}_1,\mathbf{r}_2)$ in the following way:

$$\begin{aligned}\Omega_2^{\mathrm{ren}}f(\mathbf{r}_1,\mathbf{r}_2)=&D_0\nabla_1\int d\mathbf{r}_3\{ng_2^{\mathrm{eq}}(r_{12})\delta(\mathbf{r}_{23})+n^2[g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)-g_2^{\mathrm{eq}}(r_{12})g_2^{\mathrm{eq}}(r_{13})]\}\\&\quad\times\nabla_1\int d\mathbf{r}_4\left\{\frac{\delta(\mathbf{r}_{34})}{ng_2^{\mathrm{eq}}(r_{13})}-d(\mathbf{r}_1;\mathbf{r}_3,\mathbf{r}_4)\right\}f(\mathbf{r}_1,\mathbf{r}_4)\\&+D_0\nabla_2 ng_2^{\mathrm{eq}}(r_{12})\cdot\nabla_2\int d\mathbf{r}_4\left\{\frac{\delta(\mathbf{r}_{24})}{ng_2^{\mathrm{eq}}(r_{12})}-d(\mathbf{r}_1;\mathbf{r}_2,\mathbf{r}_4)\right\}f(\mathbf{r}_1,\mathbf{r}_4)\ .\end{aligned} \tag{7}$$

Substituting the expression (6) into the relation (2) between the tagged-particle gradient, the dynamical correlations, and the tagged-particle current, Fourier transforming and comparing the formula with constitutive relation (3), we obtain the approximate expression for the interaction part of the self-friction kernel:

$$\xi_{s,I}(k;z)=\frac{n}{V}\int d\mathbf{r}_1\int d\mathbf{r}_2 e^{-i\mathbf{k}\cdot\mathbf{r}_1}(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})\frac{1}{z-\Omega_2^{\mathrm{ren}}}[\hat{\mathbf{k}}\cdot\nabla_1 g_2^{\mathrm{eq}}(r_{12})]e^{i\mathbf{k}\cdot\mathbf{r}_1}\ . \tag{8}$$

Here V denotes the volume of the system (the thermodynamic limit is understood) and to get the expression (8) we used the fact that the self-friction kernel is translationally invariant.

The expression for the wave-vector-dependent self-friction kernel $\xi_{s,I}(k)$ can be rewritten in a more symmetric way. Using the second equation of the Yvon-Born-Green hierarchy [6] and the Ornstein-Zernike-like equation (A13), we can write the expression (8) for $z=0$ in the following form:

$$\xi_{s,I}(k)=-\frac{n^2k_BT}{V}\int d\mathbf{r}_1\int d\mathbf{r}_2 e^{-i\mathbf{k}\cdot\mathbf{r}_1}[\hat{\mathbf{k}}\cdot\nabla_1 g_2^{\mathrm{eq}}(r_{12})](\tilde{\Omega}_2^{\mathrm{ren}})^{-1}[\hat{\mathbf{k}}\cdot\nabla_1 g_2^{\mathrm{eq}}(r_{12})]e^{i\mathbf{k}\cdot\mathbf{r}_1}\ . \tag{9}$$

Here $\tilde{\Omega}_2^{\mathrm{ren}}$ is a symmetrized renormalized two-particle Smoluchowski operator:

$$\begin{aligned}\tilde{\Omega}_2^{\mathrm{ren}}f(\mathbf{r}_1,\mathbf{r}_2)=&D_0\nabla_1\int d\mathbf{r}_3\{ng_2^{\mathrm{eq}}(r_{12})\delta(\mathbf{r}_{23})+n^2[g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)-g_2^{\mathrm{eq}}(r_{12})g_2^{\mathrm{eq}}(r_{13})]\}\cdot\nabla_1 f(\mathbf{r}_1,\mathbf{r}_3)\\&+D_0\nabla_2 ng_2^{\mathrm{eq}}(r_{12})\cdot\nabla_2 f(\mathbf{r}_1,\mathbf{r}_2)\ .\end{aligned} \tag{10}$$

Note that if the distance r_{12} is much larger than the static correlation length, renormalized two-particle operator $\tilde{\Omega}_2^{\text{ren}}$ reduces to the sum of two one-particle Smoluchowski operators.

The expression (9) is the main formal result of the present paper. The only approximation that was made up to now was the closure $\delta n_3^{\text{irr}}=0$.

III. DECOUPLING APPROXIMATION

To get explicit results from Eq. (9) one has to solve the integro-differential equation

$$\tilde{\Omega}_2^{\text{ren}} f(\mathbf{r}_1,\mathbf{r}_2)=\hat{\mathbf{k}}\cdot\nabla_1 g_2^{\text{eq}}(r_{12})e^{i\mathbf{k}\cdot\mathbf{r}_1} \tag{11}$$

involving the triple distribution g_3^{eq}. This is a rather complicated task and requires a considerable computational effort. Here we instead propose a simple approximation that is based on the observation made in I that Enskog-like theory reproduces the transport properties surprisingly well.

Let us consider the self-friction coefficient. We start with rewriting Eq. (9) in the following form:

$$\xi_{s,I}=\xi_{s,I}^{\text{short time}}+(\xi_{s,I}-\xi_{s,I}^{\text{short time}}) \ . \tag{12}$$

Here $\xi_{s,I}^{\text{short time}}$ is the Enskog-like result of I:

$$\xi_{s,I}^{\text{short time}} = -\frac{n}{k_B TV}\int d\mathbf{r}_1\int d\mathbf{r}_2(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})(\Omega_2)^{-1}(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})g(r_{12}) \ , \tag{13}$$

and superscript "short time" has been added to emphasize that (13) results from time-integrating of the expression (I.45) that is exact at short times for the hard-sphere interaction (for continuous potentials it is essentially a binary-interaction result and it should contain most of the exact short-time contributions except at high densities; this remark applies also to arguments that follow below). In Eq. (13) Ω_2 denotes the two particle Smoluchowski operator, i.e., the low density limit of Ω_2^{ren}. For the hard-sphere potential $\xi_{s,I}^{\text{short time}}=2\phi g_2^{\text{eq}}(2a)\xi_0$.

As the first term at the right-hand side of Eq. (12) correctly takes the short-time processes into account, the rest should correspond to long-time processes. Then it is plausible that the dominant contribution to the difference at the right-hand side of Eq. (12) comes from the processes in which particles are well separated. Therefore we expect that a calculation of the terms in parentheses at the right-hand side of Eq. (12) in the *decoupling* approximation should give quite reasonable results. The additional justification is one of simplicity: we know that the first term is the dominant one. Then even if we make an error in estimating the terms in parentheses we are going to make a much smaller relative error in the sum.

To get the decoupling approximation we replace the renormalized two-particle Smoluchowski operator and the two-particle Smoluchowski operator in the terms in parentheses at the right-hand side of Eq. (12) by the sum of two one-particle Smoluchowski operators:

$$(\xi_{s,I}-\xi_{s,I}^{\text{short time}})_{\text{decoupling}}=-\frac{nk_BT}{V}\int d\mathbf{r}_1\int d\mathbf{r}_2[\hat{\mathbf{k}}\cdot\nabla_1 g_2^{\text{eq}}(r_{12})](\Omega_2^{\text{dec}})^{-1}[\hat{\mathbf{k}}\cdot\nabla_1 g_2^{\text{eq}}(r_{12})]$$
$$-\left[-\frac{n}{k_BTV}\right]\int d\mathbf{r}_1\int d\mathbf{r}_2(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})(\Omega_2^{\text{dec}})^{-1}(\hat{\mathbf{k}}\cdot\mathbf{F}_{12})g(r_{12}) \ , \tag{14}$$

and Ω_2^{dec} is given by the relation

$$\Omega_2^{\text{dec}} f(\mathbf{r}_1,\mathbf{r}_2)=D_0[\nabla_1^2+\nabla_2^2]f(\mathbf{r}_1,\mathbf{r}_2) \ . \tag{15}$$

We would like to point out that the first term at the right-hand side of Eq. (14) is the result obtained by Medina-Noyola [4] using a mode-coupling-like theory,

$$(\xi_{s,I})_{\text{decoupling}}=n\xi_0\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{[k_z h(k)]^2}{2k^2} \ . \tag{16}$$

Here $h(k)=[1-S(k)]/n$ with $S(k)$ being the static structure factor [6].

The approach presented above can be easily generalized to calculation of wave-number-dependent self-friction kernel $\xi_{s,I}(k)$.

IV. RESULTS AND DISCUSSION

For the hard-sphere potential the second term at the right-hand side of Eq. (14) can be easily calculated. It is equal to the low-density mode-coupling result $4/3\phi\xi_0$ "renormalized" by the pair distribution at contact $g_2^{\text{eq}}(2a)$. Hence for hard-sphere suspensions the Enskog-like theory and decoupling approximation (14) give together the following result:

$$\xi_{s,I}=\tfrac{2}{3}\phi g_2^{\text{eq}}(2a)\xi_0+(\xi_{s,I})_{\text{decoupling}} \ . \tag{17}$$

In Fig. 1 we compare simple expression (17) with the Brownian-dynamics simulation results of Cichocki and Hinsen [9,10]. The accuracy is very satisfactory: for all volume fractions up to $\phi=0.4$ the difference between the theory and simulation is less than 5%. For a comparison we also plotted the results of simple Enskog-like theory of I. For not too high volume fractions, up to $\phi=0.4$ the present theory represents a significant improvement in comparison to the Enskog-like theory. This could have been expected as the decoupling approximation includes correlated "collision" sequences; it is reminiscent of the ring approximation of the kinetic theory of atomic fluids.

We also made a comparison with predictions of the mode-coupling-like calculation of Ref. [4] and results of a mode-coupling theory along the lines of Ref. [10]. In the

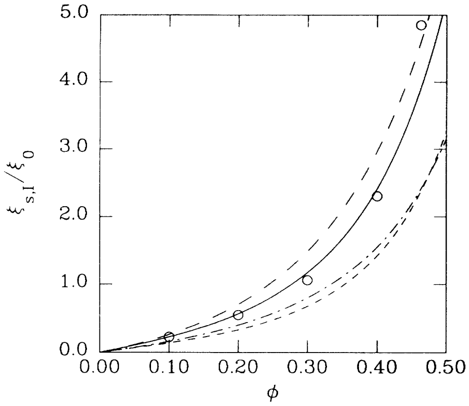

FIG. 1. The interaction contribution to the self-friction coefficient $\xi_{s,I}$ normalized by the solvent (zeroth order in density) friction ξ_0 as a function of the volume fraction $\phi=4\pi na^3/3$. Solid line: present theory; circles: simulation data of Cichocki and Hinsen [9]; long-dashed line: Enskog-like theory of Ref. [1]; dot-dashed line: mode-coupling theory of Hess and Klein [10] with short-time "propagators"; dashed line: mode-coupling-like theory of Medina-Noyola [4].

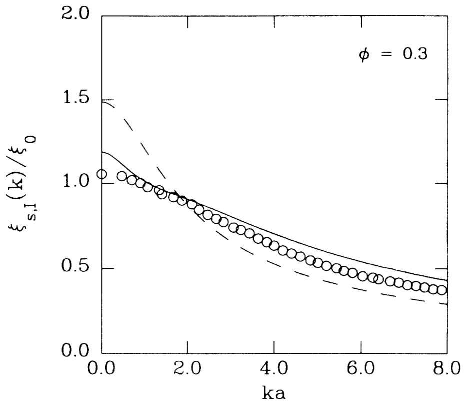

FIG. 2. The interaction contribution to the self-friction kernel integrated over time $\xi_{s,I}(k)$ divided by the solvent friction ξ_0 as a function of wave vector in units a^{-1} for volume fraction $\phi=0.3$. Solid line: present theory; circles: simulations of Cichocki and Hinsen [9]; dashed line: Enskog-like theory of Ref. [1].

latter case we used expression (10.11) of [10] and adopted a short-time form of the "propagators." The results of both calculations deviate substantially from the simulation results. One can argue that a self-consistent mode-coupling theory may give better results. Such a theory is, however, much more complicated from the calculational point of view than the rather simple approach presented here. Furthermore, even within the self-consistent mode-coupling approach one decouples also the short-time contributions to the self-friction coefficient, which is a rather crude approximation.

It is worth noting that our final result [(12) and (14)] is somewhat similar to the expression proposed by Cichocki and Hinsen [8]. Their expression involves memory functions in a self-consistent way and hence numerical evaluation requires a large computational effort. The other point is that our Enskog-like theory is the dominant contribution in (12) whereas their Enskog-like approximation gives the low-density result $2\phi\xi_0$ for the interaction part of the self-friction coefficient.

For very high volume fractions $\phi>0.4$ the present theory, i.e., Eq. (9) *with* the decoupling approximation (14), does not reproduce Brownian-dynamics simulation results. It is possible that the agreement can be improved by solving Eq. (11) instead of resorting to the decoupling approximation. However, to get satisfactory results for the highest densities one needs to include collective "cage" effects. It is not clear whether they are taken into account in Eq. (9). If not, a more refined closure approximation may work.

Finally we compare the results for wave-number-dependent self-friction kernel $\xi_{s,I}(k)$. One should expect that the agreement with Brownian-dynamics simulation results is not that good in this case since finite k corresponds to small distances and then the decoupling approximation cannot be expected to hold. In Fig. 2 we show that this is indeed the case: the agreement between wave-number-dependent self-friction kernel $\xi_{s,I}(k)$ and Brownian-dynamic data of Ref. [8] is somewhat less satisfactory. In particular, one may expect the Enskog-like theory to give essentially exact results in the high-k limit [it is exact for short times and only short times are expected to contribute to $\xi_{s,I}(k)$ in the high-k limit], and there is a systematic difference between the present theory and Enskog-like result of I. Clearly the decoupling approximation should be refined to get more satisfactory results for large wave numbers.

V. SUMMARY

We considered the motion of a test particle in a model suspension without hydrodynamic interactions; the actual calculations were done for the hard-sphere suspension. We followed the idea of our previous investigation: we derived a theory that approximates the self-friction coefficient and the self-diffusion coefficient can be obtained using the Einstein relation. To calculate the self-friction coefficient we closed the hierarchy of equations describing the time dependence of the reduced distribution functions on the level of the second hierarchy equation. However, we kept the part of the three-particle dynamical correlations that can be expressed in terms of the two-particle ones. In this way we renormalized the two-particle dynamics. To reduce the amount of computational effort required to get explicit results we introduced a decoupling approximation for the difference between the Enskog-like result and the full expression. In this way we took care of the dominant short-time contributions that cannot be adequately described within the decoupling approximation. For intermediate densities the predictions of our theory for the self-friction coefficient agree very well with the Brownian-dynamics simulation results. For very high densities, $\phi>0.4$, the theory underestimates the self-friction coefficient. For the wave-vector-dependent self-friction kernel we got somewhat less satisfactory agreement. We argued that in this case the decoupling approximation may be expected to be much less accurate.

The present theory can with less difficulty be generalized to the collective diffusion problem. However, it is more difficult to obtain explicit results in this case because even within a decoupling approximation one needs the equilibrium triple distribution.

A different direction is to study systems with more realistic potentials, i.e., a screened Coulomb potential. This is now the subject of the authors' research.

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APPENDIX: REDUCIBLE THREE-PARTICLE CORRELATIONS

Here we discuss the separation (4) of the three-particle dynamical correlations δn_3 into a reducible part that can be expressed in terms of the two-particle dynamical correlations δn_2 and the rest that is called the irreducible three-particle dynamical correlations $\delta n_3^{\mathrm{irr}}$. Our presentation draws heavily upon Refs. [7] and [11]. For different approaches to this problem see Ref. [12] and references cited therein.

Our starting point is the N-particle nonequilibrium distribution (I.16) describing exactly the state of the system:

$$P_N(\mathbf{R}_1,\ldots,R_N;t)=e^{\Omega_s t}\delta(\mathbf{r}_0-\mathbf{R}_1)VP_N^{\mathrm{eq}}(R_1,\ldots,R_N)\ . \tag{A1}$$

Here Ω_S is the N-particle Smoluchowski operator (I.5). At $t=0$ distribution (A1) reduces to

$$P_N(\mathbf{R}_1,\ldots,\mathbf{R}_N;t=0)=\delta(\mathbf{r}_0-\mathbf{R}_1)VP_N^{\mathrm{eq}}(\mathbf{R}_1,\ldots,\mathbf{R}_N)\ . \tag{A2}$$

It can be interpreted in the following way: distribution (A2) is a product of the equilibrium distribution of $N-1$ untagged particles in the external field of the tagged particle

$$P_{N-1}^{\mathrm{eq}}(\mathbf{R}_2,\ldots,\mathbf{R}_N|V(R_{1i}))\sim\exp\left\{-\beta\left[\sum_{i=2}^{N}V(R_{1i})+\sum_{i\neq j=2}^{N}V(R_{ij})\right]\right\} \tag{A3}$$

and of a distribution of the tagged particle

$$P_s(\mathbf{R}_1;t=0)=\delta(\mathbf{R}_1-\mathbf{r}_0)\ . \tag{A4}$$

Note that distribution (A3) is a conditional distribution of the untagged particles under the condition that the tagged particle is at $\mathbf{R}_1$. Hence the product of (A3) and (A4) is a well-defined joint distribution for a composite system of 1 tagged particle and $N-1$ untagged ones.

The dynamical evolution will change the distribution (A2). Our aim here is to find approximate forms of the nonequilibrium distributions at later times. Consider a certain time t. Let the distribution of the tagged particle be $n_s(\mathbf{r}_1;t)$, and the joint two- and three-particle densities be $n_2(\mathbf{r}_1,\mathbf{r}_2;t)$ and $n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)$, respectively. Let us try to find approximate forms for the nonequilibrium distribution (A2) at time t in such a way that the following are true.

(1) Successive approximations reproduce correctly successive many-particle densities.

(2) All the approximations stick as closely as possible to the equilibrium distribution in an external field for $N-1$ untagged particles.

As a first approximation let us try to keep form (A3) of the distribution of the untagged particles and to modify only the distribution of the tagged particle (A4) such that the actual distribution $n_s(\mathbf{r}_1;t)$ is recovered. In this way we obtain the following approximate form for the nonequilibrium distribution:

$$P_N(\mathbf{R}_1,\ldots,\mathbf{R}_N;t)\approx P_N^1(\mathbf{R}_1,\ldots,\mathbf{R}_N;t)=n_s(\mathbf{R}_1;t)P_{N-1}^{\mathrm{eq}}(\mathbf{R}_2,\ldots,\mathbf{R}_N|V(R_{1i}))\ . \tag{A5}$$

For untagged particles distribution (A5) is the equilibrium distribution in the external field, or local equilibrium distribution. Hence we called the first approximations (I.35) for the joint two- and three-particle densities that are obtained from (A5)

$$\begin{aligned}&n_2(\mathbf{r}_1,\mathbf{r}_2;t)\approx n_s(\mathbf{r}_1;t)ng_2^{\mathrm{eq}}(r_{12})\ ,\\&n_3(\mathbf{r}_1,\mathbf{r}_2,r_3;t)\approx n_s(\mathbf{r}_1;t)n^2g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\ ,\end{aligned} \tag{A6}$$

the local equilibrium contributions to the joint densities.

At $t=0$ distribution (A5) reproduces nonequilibrium distribution (A1). However, for $t>0$ it misses a very important face: as the tagged particle is moving, its local surrounding will change since particles will pile up in front of the tagged particles. In other words, there are new dynamical correlations between the tagged particle and the untagged ones that are not taken into account by local equilibrium distribution (A5). These correlations cause the self-friction coefficient to grow up from its $t=0$ low-density value. With the second approximation we try to include the dynamical correlations on the two-particle level exactly. This will generate an approximate form of the three-particle dynamical correlations.

As the second approximation let us try the following distribution:

$$P_N(\mathbf{R}_1,\ldots,\mathbf{R}_N;t) \approx P_N^1(\mathbf{R}_1,\ldots,\mathbf{R}_N;t)+P_N^2(\mathbf{R}_1,\ldots,\mathbf{R}_N;t)\ , \tag{A7}$$

where P_N^1 is given by Eq. (A5) and P_N^2 has the following form:

$$P_N^2(\mathbf{R}_1,\ldots,\mathbf{R}_N;t)=n_s(\mathbf{R}_1;t)P_{N-1}^2(\mathbf{R}_2,\ldots\mathbf{R}_N|\mathbf{R}_1;t)\ , \tag{A8}$$

$$P_{N-1}^2(\mathbf{R}_2,\ldots,\mathbf{R}_N|\mathbf{R}_1;t)=P_{N-1}^{\mathrm{eq}}(\mathbf{R}_2,\ldots,\mathbf{R}_N|V(R_{1i}))\left[-\beta\sum_{i=2}^{N}V_2(\mathbf{R}_1,\mathbf{R}_i;t)+\left\langle\beta\sum_{i=2}^{N}V_2(\mathbf{R}_1,\mathbf{R}_i;t)\right\rangle_{N-1}\right]\ . \tag{A9}$$

In Eq. (A9) brackets $\langle\ \rangle_{N-1}$ denote the average over $N-1$ particle local equilibrium distribution (A3) and time-dependent potential $V_2(\mathbf{R}_1,\mathbf{R}_2;t)$ is assumed to be chosen in such a way that joint two-particle density n_2 calculated with distribution (A7) coincides with actual two-particle density $n_2(\mathbf{r}_1,\mathbf{r}_2;t)$.

One can arrive at the form (A9) by the following reasoning: we need the distrbution that reproduces the difference $n_2-n_s n g_2^{\mathrm{eq}}$ between the actual two-particle density and the local equilibrium approximation and we want this distribution to be as similar to the local equilibrium distribution as possible. The easiest way to do that is to adopt the distribution of the form (A5) but with an $N-1$ particle distribution in a time-dependent external field $V(R_{1i})+V_2(\mathbf{R}_1,\mathbf{R}_i;t)$:

$$P_{N-1}^2(\mathbf{R}_2,\ldots,\mathbf{R}_N|\mathbf{R}_1;t)\sim\exp\left\{-\beta\left[\sum_{i=2}^{N}[V(R_{1i})+V_2(\mathbf{R}_1,\mathbf{R}_i;t)]+\sum_{i\neq j=2}^{N}V(R_{ij})\right]\right\}\ . \tag{A10}$$

Actually since we want to reproduce only the difference $n_2-n_s n g_2^{\mathrm{eq}}$, we take the difference between distribution (A10) and the local equilibrium distribution (A3). Moreover, since the $N-1$ particle system is close to the local equilibrium state (we have essentially linear displacement from local equilibrium) we keep only the terms linear in $V_2(\mathbf{R}_1,\mathbf{R}_i;t)$. In this way we obtain expression (A9).

Using distribution (A7) we reproduce exactly the two-particle dynamical correlations

$$\begin{aligned}\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)&=n_2(\mathbf{r}_1,\mathbf{r}_2;t)-n_s(\mathbf{r}_1;t)n g_2^{\mathrm{eq}}(r_{12})\\&=n g_2^{\mathrm{eq}}(r_{12})[-n_s(r_1;t)\beta V_2(\mathbf{r}_1,\mathbf{r}_2;t)]+n^2\int d\mathbf{r}_3[g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)-g_2^{\mathrm{eq}}(r_{12})g_2^{\mathrm{eq}}(r_{13})][-n_s(\mathbf{r}_1;t)\beta V_2(\mathbf{r}_1,\mathbf{r}_3;t)]\ ,\end{aligned} \tag{A11}$$

and obtain an approximation for the three-particle dynamical correlations

$$\begin{aligned}\delta n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)&=n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)-n_s(\mathbf{r}_1;t)n g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\\&\approx n^2 g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)[-n_s(\mathbf{r}_1;t)\beta V_2(\mathbf{r}_1,\mathbf{r}_2;t)-n_s(\mathbf{r}_1;t)\beta V_2(\mathbf{r}_1,\mathbf{r}_3;t)]\\&\quad+n^3\int d\mathbf{r}_4[g_4^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)-g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)g_2^{\mathrm{eq}}(r_{14})][-n_s(\mathbf{r}_1;t)\beta V_2(\mathbf{r}_1,\mathbf{r}_4;t)]\ .\end{aligned} \tag{A12}$$

Approximate expression (A12) for the three-particle correlations can be rewritten in terms of the two-particle ones. To this end one has to invert relation (A11) and express time-dependent potential $V_2(\mathbf{r}_1,\mathbf{r}_2;t)$ in terms δn_2. Let us define a three-particle direct correlation function $d(\mathbf{r}_1;\mathbf{r}_4,\mathbf{r}_3)$ as a solution of the following integral equation:

$$\begin{aligned}&g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)-g_2^{\mathrm{eq}}(r_{12})g_2^{\mathrm{eq}}(r_{13})\\&\quad=g_2^{\mathrm{eq}}(r_{12})g_2^{\mathrm{eq}}(r_{13})d(\mathbf{r}_1;\mathbf{r}_2,\mathbf{r}_3)+n g_2^{\mathrm{eq}}(r_{13})\int d\mathbf{r}_4[g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_4)-g_2^{\mathrm{eq}}(r_{12})g_2^{\mathrm{eq}}(r_{14})]d(\mathbf{r}_1;\mathbf{r}_4,\mathbf{r}_3)\ .\end{aligned} \tag{A13}$$

As was argued in Ref. [7] Eq. (A13) is essentially an Ornstein-Zernike equation in the external field of the tagged particle. In the limit $r_{12}\rightarrow\infty$ the integral equation (A13) reduces to the usual Ornstein-Zernike equation and the direct correlation function in the external field of the tagged particle $d(\mathbf{r}_1;\mathbf{r}_2,\mathbf{r}_3)$ tends to the two-particle, or Ornstein-Zernike direct correlation function $c(r_{23})$. With the help of the direct correlation function we can construct the inverse of relation (A11). Namely, a straightforward calculation shows that Ornstein-Zernike-like equation (A13) is equivalent to the following equation:

$$\int d\mathbf{r}_3\{n g_2^{\mathrm{eq}}(r_{12})\delta(\mathbf{r}_{23})+n^2[g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)-g_2^{\mathrm{eq}}(r_{12})g_2^{\mathrm{eq}}(r_{13})]\}\left\{\frac{\delta(\mathbf{r}_{34})}{n g_2^{\mathrm{eq}}(r_{13})}-d(\mathbf{r}_1;\mathbf{r}_3,\mathbf{r}_4)\right\}=\delta(\mathbf{r}_{14})\ . \tag{A14}$$

Using integral equation (A14) we can invert relation (A11) and express time-dependent potential $V_2(\mathbf{r}_1,\mathbf{r}_2;t)$ in terms δn_2:

$$-n_s(\mathbf{R}_1;t)\beta V_2(\mathbf{r}_1,\mathbf{r}_2;t)=\frac{\delta n_2(\mathbf{r}_1,\mathbf{r}_2;t)}{n g_2^{\mathrm{eq}}(r_{12})}-\int d\mathbf{r}_3 d(\mathbf{r}_1;\mathbf{r}_2,\mathbf{r}_3)\delta n_2(\mathbf{r}_1,\mathbf{r}_3;t)\ . \tag{A15}$$

Then substituting relation (A15) into Eq. (A12) we obtain the following expression for the three-particle dynamical correlations:

$$\begin{aligned}\delta n_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;t)\approx\int d\mathbf{r}_4\{&n^2 g_3^{eq}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)[\delta(\mathbf{r}_{24})+\delta(\mathbf{r}_{34})]\\&+n^3[g_4^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)-g_3^{\mathrm{eq}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)g_2^{\mathrm{eq}}(r_{14})]\}\int d\mathbf{r}_5\left\{\frac{\delta(\mathbf{r}_{45})}{n g_2^{\mathrm{eq}}(r_{14})}-d(\mathbf{r}_1;\mathbf{r}_4,\mathbf{r}_5)\right\}\delta n_2(\mathbf{r}_1,\mathbf{r}_5;t)\ .\end{aligned} \tag{A16}$$

The part of three-particle dynamical correlations described by (A16) we call the *reducible* part. The rest is called the *irreducible* three-particle correlations.

It is worth emphasizing at this moment that with second approximation (A7) we can reproduce exact two-particle dynamical correlations at any single t. However, the three- and higher-order dynamical correlations are included only in an approximate way. Hence if we use formula (A16) to close the second hierarchy equation the time derivatives of two-particle dynamical correlations are not in general exact.

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