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Dynamics of hard-sphere suspensions

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A systematic theory for the dynamics of concentrated hard-sphere suspensions of interacting Brownian particles with both hydrodynamic and direct interactions is presented. An alternative equation for the number density of particles is derived. The volume-fraction dependence of the short- and long-time self-diffusion coefficients is thus explored from a new point of view. Both the short-range and the long-range hydrodynamic interactions are shown to play an important role in both coefficients, while the direct interactions are reduced drastically by the hydrodynamic interactions.

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In recent years a number of experimental [1–5], theoretical [6–12], and numerical [13] attempts have been made to study the dynamics of hard-sphere suspensions of interacting colloidal particles. Most theoretical treatments are restricted to the evaluation of the short-time self-diffusion coefficients, treating the short-range hydrodynamic interactions between the particles at small volume fractions. Its theoretical prediction for higher volume fractions was addressed by Beenakker and Mazur [9]. There are a few theoretical results for the long-time self-diffusion coefficient.

The purpose of this paper is to derive the macroscopic equation for the number density of Brownian particles, which enables us to describe both hydrodynamic and direct interactions between particles for a large range of volume fractions. Thus we can study the dynamics of concentrated hard-sphere suspensions from a unifying point of view, including short- and long-time behavior of the self-diffusion coefficients and their dependence on the volume fraction of the spheres.

We consider a three-dimensional classical system which consists of N identical spherical particles with radius a and position vector $\mathbf{X}_i(t)$ $(i=1,2,\ldots,N)$, and an incompressible fluid with viscosity η. The fluctuating velocity field of the fluid is assumed to be described by the linearized fluctuating Navier-Stokes equation, supplemented by stick boundary conditions at the surfaces of the spheres. The system has then three characteristic lengths: the molecule radius r_0, the particle radius a, and the screening length $l=(6\pi a n_0)^{-1/2}$, within which the hydrodynamic interactions become important. Here l and a are large compared to r_0, and n_0 is the number density of the spheres. Therefore there are five characteristic times: the microscopic time t_0; the relaxation time of the momentum contained in the fluid volume of size a, $\tau_f \sim \rho a^2/\eta$; the relaxation time of the sphere, $\tau_B \sim m/\zeta_0$; the screening time, $\tau_H \sim \tau_f/\phi$, in which the hydrodynamic interactions become important; and the structural-relaxation time, $\tau_D \sim l^2/D_0$, which is a time required for a particle to diffuse over a distance l. Here m is the particle mass, $\zeta_0=6\pi\eta a$ the friction coefficient, ρ the fluid mass density, $\phi=4\pi a^3 n_0/3$ the volume fraction of the spheres, and $D_0=k_B T/\zeta_0$ the single-particle diffusion coefficient, where k_B is Boltzmann's constant and T the temperature. Here τ_B is the same order as τ_f since the mass density of the spheres is assumed to be of the same order as that of the fluid, where the particle mass is much larger than the mass of a molecule of the fluid. For concentrated suspensions τ_H also becomes of the same order as τ_B since l is of order of a. This leads to $t_0 \ll \tau_f \sim \tau_B \sim \tau_H \ll \tau_D$. Depending on the space-time scales, therefore, there are two characteristic stages. One is a kinetic stage [K] where the space-time cutoff (x_c, t_c) is set as $a \sim l \gg x_c \gg r_0$ and $\tau_H \gg t_c \gg t_0$. The other is a suspension-hydrodynamic stage [SH] where $x_c \gg l$ and $\tau_D \gg t_c \gg \tau_H$.

By solving the fluctuating Navier-Stokes equation under the appropriate boundary conditions, one can first derive a set of non-Markov Langevin equations for hard-sphere suspensions in stage [K]. The formulation here bears some similarity with that of Mazur [7]. The difference is that we start from the Navier-Stokes equation, while he started from the quasistatic Stokes equation. On a time scale longer than τ_B, we thus obtain the set of Markov Langevin equations for the velocity $\mathbf{u}_i(t)$ of the particle i

$$m\frac{d}{dt}\mathbf{u}_i(t)=\mathbf{M}_i(t)+\sum_{j(\neq i)}^{N}\mathbf{F}_{ij}(t), \qquad (1)$$

with the force exerted by the fluctuating fluid on particle i

$$\mathbf{M}_i(t)=-\zeta_0\mathbf{u}_i(t)-\sum_{j(\neq i)}^{N}\mathbf{G}(\mathbf{X}_{ij}(t))\cdot\mathbf{M}_j(t)+\mathbf{R}_i(t), \qquad (2)$$

where $\mathbf{X}_{ij}=\mathbf{X}_i-\mathbf{X}_j$, and $\mathbf{F}_{ij}(t)$ is the force between particles i and j. The random force $\mathbf{R}_i(t)$ obeys a Gaussian, Markov process with zero mean and is related to the coefficients ζ_0 and $\mathbf{G}(\mathbf{X}_{ij})$ by the fluctuation-dissipation relation. The tensor

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$\mathbf{G}(\mathbf{X}_{ij})$ gives modifications to the friction coefficient due to the hydrodynamic interactions and consists of two parts, an Oseen part $\mathbf{g}^0_{ij}$ and a dipole part $\mathbf{g}^D_{ij}$; $\mathbf{G}(\mathbf{X}_{ij})=\mathbf{g}^0_{ij}+\mathbf{g}^D_{ij}$ with

$$\mathbf{g}^0_{ij}=\frac{3}{4}\;\frac{a}{X_{ij}}(\mathbf{1}+\hat{\mathbf{x}}_{ij}\hat{\mathbf{x}}_{ij}),\quad \mathbf{g}^D_{ij}=\frac{1}{2}\left(\frac{a}{X_{ij}}\right)^3(\mathbf{1}-3\hat{\mathbf{x}}_{ij}\hat{\mathbf{x}}_{ij}),\tag{3}$$

where $\hat{\mathbf{x}}_{ij}=\mathbf{X}_{ij}/X_{ij}$, and we have retained only these two parts in $\mathbf{G}(\mathbf{X}_{ij})$ since the effects of the higher-order terms in a/X_{ij} are negligible as compared to them.

Equation (1) is an alternative starting equation to study the dynamics of concentrated suspensions of interacting Brownian particles on the space-time scale of order (l,τ_D). The second term of Eq. (2) represents the hydrodynamic interactions between particles separated by a distance of order l and contains the higher-order terms in ϕ. Because of these long-range interactions, it is beyond our capacity to deal with Eq. (1) analytically. Hence we must further reduce it to obtain macroscopic equations, which we can reasonably analyze. In fact, one can first transform Eq. (1) into the hierarchy equations for the particle distribution functions. By employing the systematic expansion method [15], we can expand them in powers of correlation functions in a manner consistent with the expansion in powers of ϕ and then truncate them to obtain the Fokker-Planck equation for the single-particle distribution function, $f(\mathbf{u},\mathbf{x},t)$, with velocity $\mathbf{u}$ and position $\mathbf{x}$, to all orders ϕ. In each order, the coefficients are determined in terms of the short-range hydrodynamic interactions between particles separated by a distance of order a, the long-range hydrodynamic interactions between particles separated by a distance of order l, and the direct interactions between particles. There are two kinds of many-body effects due to the hydrodynamic interactions; a static many-body (screening) effect which is determined only by the single-particle distribution function, and a dynamic many-body (correlation) effect which is determined by the particle correlation functions. We then transform this Fokker-Planck equation into the hierarchy equations for the moment densities of velocity, such as the number density $n(\mathbf{x},t)=\int d\mathbf{u}\, f(\mathbf{u},\mathbf{x},t)$, the velocity density $\mathbf{U}(\mathbf{x},t)=\int d\mathbf{u}\, \mathbf{u}f(\mathbf{u},\mathbf{x},t)$, and so on, where most screening effects are canceled out by the correlation effects. By eliminating moments higher than the first, we obtain up to order ∇^2,

$$\frac{\partial}{\partial t}n(\mathbf{x}_1,t)=\boldsymbol{\nabla}_1\cdot\int d\mathbf{x}_2\mathbf{D}^H_S(\mathbf{x}_1,\mathbf{x}_2,t)\cdot[\boldsymbol{\nabla}_2 n(\mathbf{x}_2,t)-\mathbf{C}(\mathbf{x}_2,t)],\tag{4}$$

where the tensor $\mathbf{D}^H_S$ denotes the self-diffusion coefficient obtained by taking only the hydrodynamic interactions into account, and is given by

$$\begin{aligned}\mathbf{D}^H_S(\mathbf{x}_1,\mathbf{x}_2)&=D_0\delta(\mathbf{x}_1-\mathbf{x}_2)\mathbf{1}-\mathbf{H}_1\cdot\mathbf{D}^H_S(\mathbf{x}_1,\mathbf{x}_2)\\&\quad-\int d\mathbf{x}_3\mathbf{K}_{13}\cdot\mathbf{D}^H_S(\mathbf{x}_3,\mathbf{x}_2).\end{aligned}\tag{5}$$

The nonlocal tensor $\mathbf{K}_{12}(t)$ represents the correlation effects and is given by

$$\begin{gathered}\mathbf{K}_{12}=\mathbf{A}_{12}+2\int d\mathbf{x}_3\mathbf{A}_{13}\cdot\mathbf{K}_{32}-\int\int d\mathbf{x}_3 d\mathbf{x}_4\mathbf{A}_{13}\cdot\mathbf{A}_{34}\cdot\mathbf{K}_{42},\\ \mathbf{A}_{12}=n(\mathbf{x}_1)\mathbf{g}_{12}\cdot\mathbf{g}_{21}\cdot\int d\mathbf{x}_3\mathbf{g}^0_{13}\cdot\mathbf{g}_{32}n(\mathbf{x}_3),\end{gathered}\tag{6}$$

where $\mathbf{g}_{12}(t)$ denotes the renormalized Oseen tensor defined through

$$\mathbf{g}_{12}(t)=\mathbf{g}^0_{12}-\int d\mathbf{x}_3\mathbf{g}^0_{13}\cdot\mathbf{g}_{32}(t)n(\mathbf{x}_3,t).\tag{7}$$

The local tensor $\mathbf{H}_1(t)$consists of three types of interactions, a long-range interaction $\mathbf{H}^L_1$, a short-range interaction $\mathbf{H}^S_1$, and their coupling $\mathbf{H}^C_1$; $\mathbf{H}_1=\mathbf{H}^L_1+\mathbf{H}^S_1+\mathbf{H}^C_1$ with

$$\begin{gathered}\mathbf{H}^L_1=\int d\mathbf{x}_2\left[\int d\mathbf{x}_3\mathbf{B}^0_{32}+\mathbf{H}^L_2\right]\cdot\mathbf{B}_{21},\\ \mathbf{H}^S_1=\int d\mathbf{x}_2[\mathbf{1}+\mathbf{H}^S_2]\cdot\mathbf{J}_{21},\end{gathered}\tag{8}$$

where

$$\mathbf{J}_{21}=n(\mathbf{x}_2)(2\mathbf{g}^0_{12}\cdot\mathbf{g}^D_{21}+\mathbf{g}^D_{12}\cdot\mathbf{g}^D_{21}),$$

$$\mathbf{B}^0_{21}=n(\mathbf{x}_2)\mathbf{g}^0_{12}\cdot\mathbf{g}_{21},$$

$$\mathbf{B}_{21}=n(\mathbf{x}_2)\mathbf{g}_{12}\cdot\mathbf{g}_{21}.$$

The explicit form of the coupling term $\mathbf{H}^C_1$ is planned to be given elsewhere [14].

The term $\mathbf{C}(\mathbf{x},t)$represents the coupled effects of the short-range hydrodynamic and direct interactions and is given by

$$\mathbf{C}(\mathbf{x}_1,t)=\int d\mathbf{x}_2[\mathbf{1}-\mathbf{G}(\mathbf{x}_{12})]\cdot\beta\mathbf{F}_{12}Q(\mathbf{x}_1,\mathbf{x}_2,t)\tag{9}$$

with the pair correlation function

$$\begin{aligned}Q(\mathbf{x}_1,\mathbf{x}_2,t)=\int_0^t ds\ &\exp(sD_0\{\nabla^2_1+\nabla^2_2+(\boldsymbol{\nabla}_2-\boldsymbol{\nabla}_1)\cdot[\mathbf{1}-\mathbf{G}(\mathbf{x}_{12})]\cdot\beta\mathbf{F}_{12}\})\\&\times D_0(\boldsymbol{\nabla}_2-\boldsymbol{\nabla}_1)\cdot[\mathbf{1}-\mathbf{G}(\mathbf{x}_{12})]\cdot\beta\mathbf{F}_{12}n(\mathbf{x}_1,t-s)n(\mathbf{x}_2,t-s),\end{aligned}\tag{10}$$

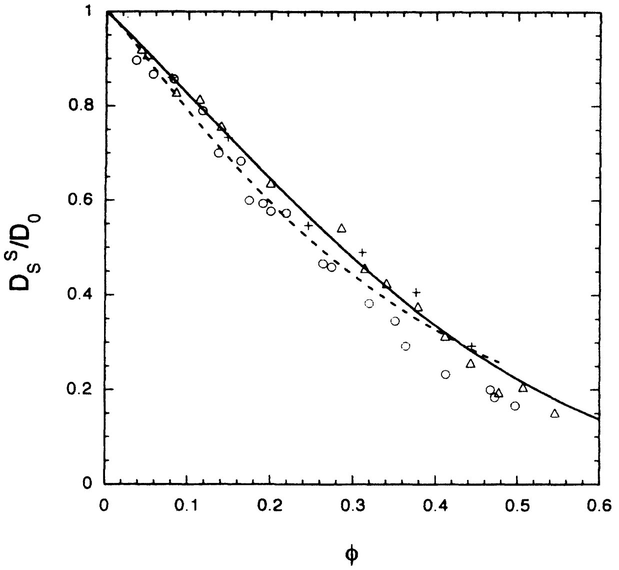

FIG. 1. Volume-fraction dependence of the short-time self-diffusion coefficient, D_S^S/D_0. The solid line represents the present result and the dashed line the theoretical prediction of Ref. [9]. Shown also are the data from Ref. [2] (△), Ref. [3] (+), and Ref. [4] (○).

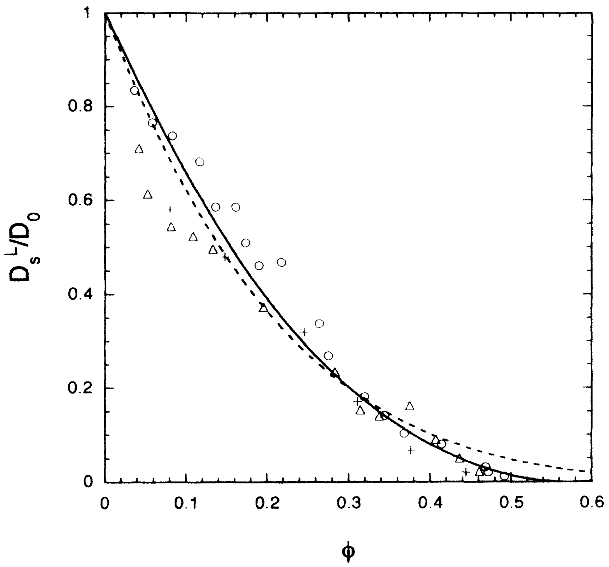

FIG. 2. Volume-fraction dependence of the long-time self-diffusion coefficient, D_S^L/D_0. Details are the same as in Fig. 1, except that the dashed line represents the mean-field results of Ref. [5].

where $\beta=1/k_BT$. In order to derive Eq. (9), we have kept only the binary collisions since the many-body collisions are drastically reduced by the hydrodynamic interactions.

Equation (4) is the mesosocopic equation for $n(\mathbf{x},t)$, which describes the diffusion process characterized by the space-time scale of order (l,τ_D). From this equation one can find the expressions for the self-diffusion coefficient in the short-time region where $\tau_D \gg t \gg \tau_B$ and $|\mathbf{x}| \ll l$. In fact, the configurations of the Brownian particles do not change appreciably due to their Brownian motion. Hence the deviation of the number density $n(\mathbf{x},t)$ from its equilibrium form n_0 may be neglected in the tensor $\mathbf{D}_S^H$. The correlation effects and the direct interactions are also negligible in this region. Therefore the tensor $\mathbf{D}_S^H$ reduces to the simple form $\mathbf{D}_S^H(\mathbf{x}_1,\mathbf{x}_2)=D_S^S\delta(\mathbf{x}_1-\mathbf{x}_2)\mathbf{1}$ with the short-time self-diffusion coefficient

$$D_S^S(\phi)=D_0/[1+H(\phi)], \tag{11}$$

where $H(\phi)$ results from the local tensor $\mathbf{H}_1$ and is given by

$$H(\phi)=\frac{2b^2}{(1-b)}-\frac{c}{(1+2c)}-\frac{bc(2+c)}{(1+c)(1-b+c)}. \tag{12}$$

Here $b(\phi)=(9\phi/8)^{1/2}$, $c(\phi)=11\phi/16$, and the terms in Eq. (12) correspond to the local tensors $\mathbf{H}_1^L$, $\mathbf{H}_1^S$, and $\mathbf{H}_1^C$, respectively.

In stage [SH] we can further expand $n(\mathbf{x}_i,t)$ about $\mathbf{x}_1$. Thus Eq. (4) reduces, to lowest order in ∇, to

$$\frac{\partial}{\partial t}n(\mathbf{x},t)=\nabla\cdot D_S(\Phi(\mathbf{x},t))\cdot\nabla n(\mathbf{x},t) \tag{13}$$

with the self-diffusion coefficient

$$D_S(\Phi)=\frac{D_0(1-9\Phi/32)}{1+H(\Phi)+(\Phi/\phi_0)/(1-\Phi/\phi_0)^2}, \tag{14}$$

where $\phi_0=(4/3)^3/(7\ \ln 3-8\ln 2+2)\approx 0.5718$, and the local volume fraction $\Phi(\mathbf{x},t)$ is given by $\Phi(\mathbf{x},t)=4\pi a^3 n(\mathbf{x},t)/3$. The last term in the denominator of Eq. (14) results from the nonlocal tensor $\mathbf{K}_{12}$, while the last term in the numerator comes from the coupled effect $\mathbf{C}(\mathbf{x},t)$. Equation (13) is the macroscopic equation which describes the diffusion process in stage [SH]. From Eq. (13) we can find the long-time self-diffusion coefficient to be $D_S^L(\phi)=D_S(\phi)$ for the long-time region where $t \gg \tau_D$ and $|\mathbf{x}| \gg l$.

In Figs. 1 and 2 we plot the volume-fraction dependence of D_S^S/D_0 and D_S^L/D_0, respectively, and compare them with recent experimental results by several groups. In both cases the agreement between the present results and experimental results is good. For comparison the theoretical results by Beenakker and Mazur [9] and the mean-field results by Blaaderen *et al.* [5] are also shown in Figs. 1 and 2 by the dashed line, respectively.

In summary, we have shown that both short- and long-range hydrodynamic interactions between particles play an important role in the dynamics of concentrated hard-sphere suspensions for the whole time range. For short times, only the local hydrodynamic interactions become important. For long times, the nonlocal hydrodynamic interactions become important as well as the local ones, while the direct interactions are drastically reduced by the hydrodynamic interactions. The detailed analysis of Eqs. (1), (4), and (13) is planned to be discussed in a separate paper [14].

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