Nonequilibrium effects on slow dynamics in concentrated colloidal suspensions

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(Received 7 March 1996)

An alternative stochastic diffusion equation is proposed to study the dynamics of nonequilibrium density fluctuations in concentrated hard-sphere suspensions of interacting Brownian particles with both hydrodynamic and direct interactions among particles. The singularity of the correlation effect of the many-body hydrodynamic interactions is shown to drastically influence the qualitative behavior of the relaxation of nonequilibrium density fluctuations, and thus to cause the two different slow relaxations whose time scales, t_β and t_α, diverge as the volume fraction of Brownian particles approaches the critical value $\phi_c=(\frac{4}{3})^3/(7\ln 3-8\ln 2+2)$; $t_\beta\sim(1-\phi/\phi_c)^{-1}$ and $t_\alpha\sim(1-\phi/\phi_c)^{-2}$. [S1063-651X(96)51908-2]

PACS number(s): 82.70.Dd, 05.40.+j, 51.10.+y

Although there has been a growing interest in the dynamic properties of concentrated colloidal suspensions, more experimental, theoretical, and numerical studies are still needed to obtain a deeper understanding of the dynamics of density fluctuations over the whole time range [1–6]. In order to study the self-diffusion process in concentrated suspensions, Tokuyama and Oppenheim [7] have recently proposed an alterative diffusion equation for the average number density of interacting Brownian particles and found that the generalized self-diffusion coefficient consists of two kinds of many-body hydrodynamic interactions among particles; the screening effect, which mainly contributes to the short-time self-diffusion process, and the correlation effect, which dominates the self-diffusion process after the short-time region, exhibiting a singularity at the critical volume fraction ϕ_c. In this paper, therefore, we study the dynamics of nonequilibrium density fluctuations in concentrated suspensions based on their theory. We first propose a Langevin equation for the nonequilibrium density fluctuations $\delta n(\mathbf{x},t)$ around the average number density $n(\mathbf{x},t)$ and then discuss the asymptotic properties of the self-intermediate-scattering function $F_s(k,t)$. Thus, we first show that the singularity of the correlation effects plays an important role in the relaxations of the nonequilibrium density fluctuations, leading to slow relaxations near the critical volume fraction ϕ_c.

We consider a colloidal suspension with the particle volume fraction $\phi=4\pi a_0{}^3 n_0/3$, which consists of N identical spherical particles with radius a_0 and an incompressible fluid with viscosity η_0 in the volume V, where $n_0=N/V$ is the equilibrium number density of the spheres. In this paper we focus only on a suspension-hydrodynamic stage [7], where the space-time cutoffs (x_c,t_c), which are the minimum wavelength and time of the dynamic process of interest, are set as $x_c\gg l$ and $t_D\gg t_c\gg t_B$. Here l denotes the screening length given by $l=(6\pi a_0 n_0)^{-1/2}=a_0(9\phi/2)^{-1/2}$, in which the hydrodynamic interactions becomes important, $t_B=m/(6\pi\eta_0 a_0)$ the Brownian relaxation time of the sphere, and $t_D=l^2/2\pi D_S^S$ the structural-relaxation time which is a time required for a particle to diffuse over a distance l, where $D_S^S(\phi)$ denotes the short-time self-diffusion coefficient. As was shown in Ref. [7], the averaged number density $n(\mathbf{x},t)$ obeys the alternative diffusion equation

$$\frac{\partial}{\partial t}n(\mathbf{x},t)=\nabla\cdot[D_S(\Phi(\mathbf{x},t))\nabla n(\mathbf{x},t)] \tag{1}$$

with the self-diffusion coefficient

$$D_S(\Phi)=D_S^S(\phi)(1-u\Phi/\phi_c)/[1+\hat{D}_S^S(\phi)K(\Phi)], \tag{2}$$

where $\Phi(\mathbf{x},t)=\phi n(\mathbf{x},t)/n_0$ denotes the local volume fraction and satisfies the conservation law

$$(1/V)\int d\mathbf{x}\;\Phi(\mathbf{x},t)=\phi. \tag{3}$$

The term $(u\Phi/\phi_c)$ in the numerator of Eq. (2) gives the coupled effect between the short-range hydrodynamic and direct interactions among particles. We note here that the coupling factor u is reduced from $2\phi_c$ to $(9/32)\phi_c$ by the short-range hydrodynamic interactions, where $2\phi_c$ is obtained by the direct interactions only [8].

As is seen from Eq. (2), the two kinds of many-body effects due to the hydrodynamic interactions play a crucial role in the self-diffusion process. One is a static many-body (screening) effect $L(\phi)$ due to the local many-body hydordynamic interactions between particles, which becomes important for the short-time region $t_B\ll t\ll t_D$, and is given by

$$L(\phi)=\frac{2B^2}{1-B}-\frac{C}{1+2C}+\frac{D}{E}\left[\frac{8D(E+D)}{(E+4D)(E+2D)}-\frac{2+C}{1+C}+\frac{DC^2(2E+2CE-D)}{(1+C)(E+CE-2D)(E+CE-D)}\right], \tag{4}$$

where $D=BC$, $E=1-B+C$, $B(\phi)=(9\phi+8)^{1/2}$, $C=11\phi/16$, and D_0 is the single-particle diffusion coefficient. Then, the short-time self-diffusion coefficient $D_S^S(\phi)$ is given by

$$D_S^S(\phi)=\hat{D}_S^S(\phi)D_0=D_0/[1+L(\phi)]. \tag{5}$$

The first term in Eq. (4) is the most dominant term due to the long-range hydrodynamic interactions. The second and third terms in Eq. (4) are just corrections due to the short-range hydrodynamic interactions and the coupling between the short- and long-range hydrodynamic interactions, respectively. The other is a dynamic many-body (correlation) effect $K(\Phi)$ due to the nonlocal long-range hydrodynamic interactions, which plays an important role in the intermediate-time region $t \geqslant t_D$, and is given by

$$K(\Phi)=(\Phi/\phi_c)/(1-\Phi/\phi_c)^{\kappa}, \tag{6}$$

where $\kappa=2$ here.

Equation (1) is the generalized diffusion equation which describes the causal motion of the self-diffusion process in concentrated hard-sphere suspensions. For the short-time region $t_B \ll t \ll t_D$, the direct interaction and the correlation effect are negligible. Hence the self-diffusion coefficient $D_S(\Phi(\mathbf{x},t))$ reduces to $D_S^S(\phi)$, and the number density $n(\mathbf{x},t)$ is described by the short-time diffusive motion given by $n^S(x,t)=\exp(-tD_S^S\nabla^2)n(\mathbf{x},0)$. For the long-time region $t_D \ll t$, the number density $n(\mathbf{x},t)$ becomes constant to be n_0. Hence $D_S(\Phi(\mathbf{x},t))$ reduces to the long-time self-diffusion coefficient.

$$D_S^L(\phi)=D_S(\phi)=D_S^S(\phi)(1-\mu\hat{\phi})\sigma^2/[\hat{D}_S^S(\phi)\hat{\phi}+\sigma^2], \tag{7}$$

where $\sigma=\hat{\phi}-1$, and $\hat{\phi}=\phi/\phi_c$. Thus, D_S^L vanishes quadratically as $D_S^L \sim D_0\sigma^2$ near ϕ_c because of the singularity of the correlation effect. For the intermediate-time region, the behavior of the number density becomes more complicated because of the singularity of the correlation effect $K(\Phi)$ near ϕ_c. In fact, such a singularity is expected to play an important role in the relaxation of the nonequilibrium density fluctuations as a cage effect which causes a structural arrest, leading to slow relaxations near ϕ_c. We will investigate this next.

We now discuss the fluctuations $\delta n(\mathbf{x},t)$ around the causal motion $n(\mathbf{x},t)$. In most cases, they are small as compared to the causal motion $n(\mathbf{x},t)$. However, they are important since they are experimentally observable through the scattering function by dynamic light scattering measurements [9]. When the relative magnitude of the fluctuations to the causal motion is small, $|\delta n(\mathbf{x},t)/n(\mathbf{x},t)| \ll 1$, one can linearize Eq. (1) around $n(\mathbf{x},t)$ and add a fluctuating force to obtain a linear Langevin equation for $\delta n(\mathbf{x},t)$ [10]

$$\frac{\partial}{\partial t}\delta n(\mathbf{x},t)=\nabla^2[D_S(\Phi(\mathbf{x},t))\delta n(\mathbf{x},t)]+R(\mathbf{x},t), \tag{8}$$

where $R(\mathbf{x},t)$ denotes a Gaussian, Markov random force with zero mean and satisfies

$$\overline{R(\mathbf{x},t)\delta n(\mathbf{x}',0)}=0. \tag{9}$$

Here the bar denotes the average over a suitable initial statistical ensemble, where $\overline{\delta n(\mathbf{x},t)}=0$.

Equation (9) is a linear stochastic equation which describes a linear relaxation process around the time-dependent nonequilibrium state determined by Eq. (1). In order to discuss the stochastic properties of the random force, one has to derive Eq. (8) from first principles. This is not easy to do in general. In the equilibrium state, however, the correlation function of the random forces is easily obtained from Eq. (8). In fact, from Eq. (8) we obtain, in the limit $t\to\infty$,

$$\overline{R(\mathbf{x},t)R(\mathbf{x}',t')}=-2n_0D_S^L(\phi)\delta(t-t')\nabla^2\delta(\mathbf{x}-\mathbf{x}'). \tag{10}$$

Thus, Eq. (10) satisfies the usual fluctuation-dissipation relation of the second kind.

In terms of the Fourier components

$$\delta n_k(t)=\int d\mathbf{x}\,\exp(i\mathbf{k}\cdot\mathbf{x})\,\delta n(\mathbf{x},t), \tag{11}$$

Eq. (8) takes the form

$$\frac{\partial}{\partial t}\delta n_k(t)=-k^2D_S^L(\phi)\delta n_k(t)-\sum_q M_{kq}(t;\phi)\delta n_q(t)+R_k(t) \tag{12}$$

with the memory function

$$M_{kq}(t;\phi)=k^2D_S^S\int\frac{d\mathbf{x}}{V}e^{i\mathbf{k}\cdot\mathbf{x}}\frac{(1-z)[\hat{D}_S^S+u\sigma^2(1-\hat{\phi}z)^2-\hat{D}_S^S\hat{\phi}^2z\{1+u(1-\sigma-\hat{\phi}z)\}]}{(\hat{D}_S^S+\sigma^2/\hat{\phi})[\hat{D}_S^S\hat{\phi}z+(1-\hat{\phi}z)^2]}e^{-i\mathbf{q}\cdot\mathbf{x}}, \tag{13}$$

where $z(\mathbf{x},t)=\Phi(\mathbf{x},t)/\phi=n(\mathbf{x},t)/n_0$. It is convenient to introduce a correlation function $F_{kq}(t)$ by

$$F_{kq}(t)=\overline{\delta n_k(t)\delta n_q^*(0)}/N. \tag{14}$$

Use of Eqs. (9), (12), and (14) then leads to

$$\frac{\partial}{\partial t}F_{kk}(t)=-k^2D_S^L(\phi)F_{kk}(t)-\sum_q M_{kq}(t;\phi)F_{qk}(t). \tag{15}$$

The intermediate scattering function $F(k,t)$ is given by $F(k,t)=F_{kk}(t)$ and can be separated into a self-part $F_S(k,t)$, which describes the average self-motion of individual particles, and a cross part $F_C(k,t)$, which describes the average relative motion between different particles; $F(k,t)=F_S(k,t)+F_C(k,t)$ [9]. For a scattering vector much larger than the maximum position k_m of the structure factor $S(k)=F(k,0)$, the cross part $F_C(k,t)$ can be neglected and hence $F(k,t)$ reduces to the self-intermediate-scattering function $F_S(k,t)$ with $F_S(k,0)=S(k)=1$. From Eq. (15), we thus obtain

$$F_S(k,t)=f(k,t;\phi)\exp(-k^2D_S^Lt) \quad (16)$$

with the singular part

$$f(k,t;\phi)=\left[\exp_-\left\{-\int_0^t \mathbf{m}(s;\phi)ds\right\}\right]_{kk}, \quad (17)$$

where $\mathbf{m}(t;\phi)$ denotes the matrix whose ($\mathbf{k}$,$\mathbf{q}$) component is given by

$$m_{kq}(t;\phi)=\exp(k^2D_S^Lt)M_{kq}(t;\phi)\exp(-q^2D_S^Lt). \quad (18)$$

Here $\exp_-$ is a time-ordered exponential, ordered from the left, and in order to obtain Eq. (16), we have used the fact that $F_{kq}(0)=\delta_{k,q}$. Here we should mention from Eq. (16) that the scattering function $F_S(k,t)$ is decoupled into a singular part $f(k,t)$ and a long-time part.

In order to study the relaxation process of the density fluctuations around the nonequilibrium state, one must solve the diffusion equation (1) under appropriate initial conditions and then calculate Eq. (16) self-consistently. In the following, however, we only discuss the asymptotic properties of $F_S(k,t)$ and show how the singularity of the correlation effect causes the slow relaxation of the nonequilibrium density fluctuations. For the short-time region of order $t_\gamma=2\pi/k^2D_S^S(\phi)$, from Eq. (16), the relaxation obeys the short-time decay

$$F_S^S(k,t)=[\exp_-\{-\mathbf{m}(0;\phi)t\}]_{\mathbf{kk}} \quad (t_B\ll t\leq t_\gamma), \quad (19)$$

which depends on the initial conditions for $z(\mathbf{x},0)$. For the long-time region of order $t_\alpha=2\pi/k^2D_S^L$, the local volume fraction $\Phi(\mathbf{x},t)$ becomes constant to be ϕ [or $z(\mathbf{x},t)=1$], and the self-diffusion coefficient D_S reduces to the long-time self-diffusion coefficient D_S^L, where $M_{kq}(t;\phi)=0$. Hence the relaxation is described by the long-time decay

$$F_S^L(k,t)=\exp(-k^2D_S^Lt) \quad (t_\gamma\ll t_\alpha\leq t). \quad (20)$$

Near the critical volume fraction ϕ_c, the time t_α is scaled with the separation parameter σ as

$$t_\alpha\sim(k^2D_0)^{-1}|\sigma|^{-2}. \quad (21)$$

Therefore, there exists a crossover from the short-time relaxation process to the long-time relaxation process, where the intermediate-time region is expected to be extended. We next discuss this.

Let $t_e(\phi)$ ($\gg t_\gamma$) denote a characteristic time over which the system nearly reaches an equilibrium state where $z(\mathbf{x},t)=1$. From Eq. (13), we then obtain $M_{kq}(t;\phi)\simeq 0$ for $t\geq t_e$. For the intermediate times $t\geq t_e$, therefore, Eq. (16) can be approximately written as

$$F_S(k,t)\simeq f(k,t_e;\phi)\exp(-k^2D_S^Lt) \quad (t_e\leq t). \quad (22)$$

At the critical volume fraction ϕ_c, the scattering function $F_S(k,t)$ thus becomes the plateau with the height $f_k^C=f(k,t_e;\phi_c)$, while near the critical volume fraction ϕ_c, it is expected to become the plateau for the time region $t_e\leq t\ll t_\alpha$ and then to decay to zero. Let $t_\beta(\sigma)$ denote a crossover time from the plateau f_k^C to the long-time decay $F_S^L(k,t)$,

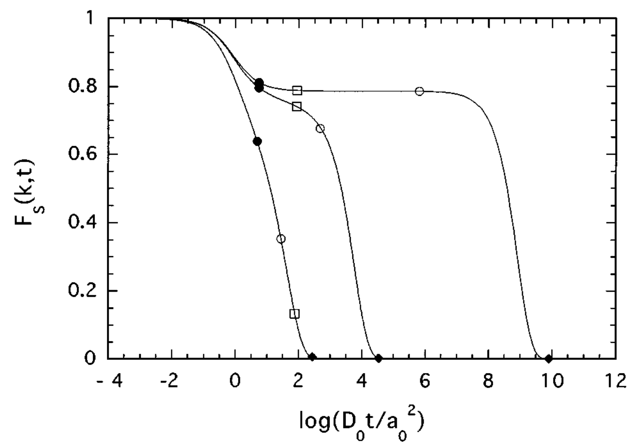

FIG. 1. Schematic behavior of the self-intermediate-scattering function $F_S(k,t)$ at $ka_0=2.8$ for different volume fractions (from left to right): 0.543, 0.569, and 0.571 84. The symbols indicate the time scales; t_γ (●), t_e (□), t_β (○), and t_α (♦). Figures were obtained by using the asymptotic solution for $\Phi(\mathbf{x},t)$, which was found by solving Eq. (1) in an approximate manner [10].

where $t_e\ll t_\beta\ll t_\alpha$. By expanding Eq. (13) in powers of $\sigma(1-z)$, one can approximately write the memory function $m_{kq}(t;\phi)$ as

$$m_{kq}(t;\phi)\simeq-2\sigma(1-u)k^2D_0[\delta_{k,q}-z_{k-q}(t)/V] + O(\sigma^2(1-z)^2). \quad (23)$$

This is combined with Eqs. (17) and (22) to obtain

$$F(k,t)\simeq\exp[2\sigma(1-u)k^2D_0c_k(t_e)-k^2D_S^Lt], \quad (24)$$

where the positive constant $c_k(t_e)$ is a function of $\mathbf{k}$ to be determined, and $\sigma\leq 0$. Since the second term $k^2D_S^Lt$ in Eq. (24) becomes the same order as the first term in Eq. (24) at $t=t_\beta$, we thus find

$$t_\beta\sim 2c_k(t_e)|\sigma|^{-1}. \quad (25)$$

For small volume fractions where $t_\beta\leq t_e$, therefore, the plateau disappears and the scattering functions decay quickly to zero, obeying Eq. (16). As the volume fraction increases and t_β becomes larger than t_e, however, the shape of the scattering functions is expected to become very sensitive to the volume fraction for longer times $t\gg t_\gamma$, forming a shoulder, which becomes a plateau with the height f_k^C at the critical volume fraction ϕ_c. Figure 1 shows schematically how the scattering function $F_S(k,t)$ evolves in time as ϕ increases [10].

Near the critical volume fraction ϕ_c the singularity of the correlation effect $K(\Phi(\mathbf{x},t))$ thus causes the two different slow relaxations concerned with t_α and t_β in the nonequilibrium fluid state ($\sigma<0$) for the intermediate-time region; the first decay towards the plateau for the time region $t_e<t<t_\beta$ and the second decay away from the plateau for $t_\beta<t<t_\alpha$, where both times t_β and t_α diverge at the critical volume fraction ϕ_c. As was predicted in Ref. [10], therefore, in the nonequilibrium fluid state near ϕ_c the relaxation proceeds in the following four time stages: The first is the early stage for $t_B\ll t\leq t_\gamma$, where the relaxation obeys Eq. (19).

The second is the so-called β-relaxation stage for $t_\gamma \ll t \ll t_\beta$, where the relaxation is expected to obey a power-law decay. The third is the so-called α-relaxation stage for $t_\beta \ll t \ll t_\alpha$, where the relaxation is expected to obey the von Schweidler type power-law decay. The last is the late stage for $t_\alpha \ll t$, where the relaxation obeys Eq. (20).

In this paper we have proposed an alternative stochastic diffusion equation (8) to study the dynamics of nonequilibrium density fluctuations in concentrated colloidal suspensions and then investigated the qualitative behavior of the self-intermediate-scattering function. We have shown that the singularity of the correlation effect given by Eq. (6) causes the two different slow relaxations for the intermediate times near the critical volume fraction ϕ_c if the initial state is nonequilibrium. If the initial state is equilibrium from the beginning, that is, $z(\mathbf{x},t=0)=1$, the shoulder disappears and the scattering function just obeys the long-time decay given by Eq. (20). Hence we emphasize that the nonequilibrium effects do change the qualitative behavior of the relaxation process, leading to the slow dynamics. This situation agrees with a recent computer simulation of a supercooled polymer system [11].

By solving the coupled equations (1) and (8) self-consistently under appropriate initial conditions, one can obtain the detailed properties of slow relaxation processes, including the power-law behavior, the temporal exponents, and the crossovers. This calculation is now in progress, showing that a qualitative behavior of $F_S(k,t)$ is quite similar to that in Fig. 1. This will be discussed elsewhere together with a comparison with experiments.

The author is grateful to Professor W. Van Megen and Professor D. J. Evans for valuable comments. This work was supported by the Tohwa Institute for Science, Tohwa University.

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