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Slow Dynamics of Supercooled Colloidal Fluids: Spatial Heterogeneities and Nonequilibrium Density Fluctuations

M. Tokuyama

Statistical Physics Division, Tohwa Institute for Science, Tohwa University, Fukuoka 815, Japan.

Abstract. How the idea of the dynamic anomaly of the self-diffusion coefficient recently proposed by the present author works on the study of equilibrium and nonequilibrium supercooled colloidal liquids is discussed for two kinds of model suspensions, neutral and charged hard-sphere suspensions. Near colloidal glass transition, the long-lived, spatially heterogeneous glassy domains are shown to be formed for intermediate times in equilibrium and nonequilibrium systems. Those spatial heterogeneities are responsible for the slow relaxation of the density fluctuations. In fact, the long-known phenomena similar to those in glass-forming materials, such as the stretching of the α process and the von Schweidler law, can be explained by the existence of those spatial structure. In the equilibrium system, however, those heterogeneities must be difficult to be observed since their sizes and magnitude are quite small compared to those in the nonequilibrium system.

INTRODUCTION

In recent years there has been a growing interest in the dynamics of a supercooled liquid and the mechanism for the liquid-glass transition in colloidal suspensions.¹⁻³ Although the considerable studies have been made for structural glass transitions, our understanding is still incomplete. Hence the colloidal systems are expected to serve as valuable models for the study of the atomic systems. Pusey and van Megen² first recovered the existence of the long-known phenomena similar to those in glass-forming materials, such as the stretching of the α process. Since then, the dynamical properties of equilibrium colloidal suspensions near the colloidal glass transition have been extensively studied experimentally and theoretically. With the recent development of the mode-coupling theory (MCT)⁴⁻⁶ for the dynamics of supercooled fluids, however, much of the recent experimental studies in colloidal fluids have been designed around

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the predictions of MCT. The most striking feature of MCT is the prediction of two distinct slow relaxation processes, α and β , with the relaxation times t_α and t_β , respectively, which diverge as the separation parameter $\sigma = \phi / \phi_g - 1$ approaches zero; $t_\beta \sim |\sigma|^{-\delta}$ and $t_\alpha \sim |\sigma|^{-\eta}$, where ϕ_g denotes the colloidal glass transition volume fraction, and δ and η are time exponents to be determined. Here MCT predicts $\phi_g \approx 0.516$, $\delta = 1.60$ and $\eta = 2.46$ for concentrated hard-sphere suspensions.⁶ Although MCT was the origin of all later works on the structural relaxation in glassy liquids, we find three simple questions in its basic viewpoints for hard-sphere suspensions. The first question is why the transition point 0.516 predicted by MCT is quite different from the value around 0.572 obtained by the experiments.⁷ As is discussed later, this question may be closely related to the fact that MCT deals with only direct interactions between particles. The second one is why the equilibrium density fluctuations obey a nonlinear stochastic equation. The glass transition is not a critical phenomenon because there is no correlation length diverging at the transition point. As long as the system is away from a critical point, therefore, the relative magnitude of the density fluctuations to the mean density should be small even near the glass transition point. Hence the density fluctuations should obey a linear stochastic equation. Finally, the long-time self-diffusion coefficient satisfies the power law $D_s^L(\phi) \propto |\sigma|^\gamma$ with an exponent γ . Then, MCT predicts that the time exponent η of the α relaxation process and the exponent γ should be the same. However, the long-time self-diffusion process should be different from the α relaxation process because the former obeys an exponential decay with D_s^L , while the latter obeys a stretched exponential decay around t_α . Hence $\eta \neq \gamma$. This was also shown in the recent computer simulations of a binary supercooled Lennard-Jones liquid.^{8,9} In this paper we explore those problem from a new viewpoint.

Recently, a new theory based on the idea of the dynamic anomaly of the self-diffusion coefficient has been proposed by the present author¹⁰ to study the dynamics of self-diffusion processes in nonequilibrium colloidal suspensions. The dynamics of spatial heterogeneities of colloidal suspensions is described by the average local volume fraction $\Phi(\mathbf{r}, t) = 4\pi a^3 n(\mathbf{r}, t) / 3$, where $n(\mathbf{r}, t)$ is the average number density of colloids, and a the particle radius. On the other hand, the dynamics of nonequilibrium density fluctuations can be measured by dynamic light scattering through the intermediate scattering function¹¹ which is given by the Fourier transform, $F(\mathbf{k}, t)$, of the autocorrelation function of the density fluctuations $F(\mathbf{r}, t) = \overline{\delta n(\mathbf{r}, t) \delta n(\mathbf{0}, 0)} / N$, where $\delta n(\mathbf{r}, t)$ denotes the density fluctuations around $n(\mathbf{r}, t)$, the bar represents the average over an appropriate initial ensemble, and N is the total number of colloids. For scattering vectors much larger than the maximum position k_m of the structure factor

$S(\mathbf{k}) = F(\mathbf{k}, 0)$, the scattering function $F(\mathbf{k}, t)$ reduces to the self-intermediate scattering function $F_s(\mathbf{k}, t)$, where $F_s(\mathbf{k}, 0) = 1$. In nonequilibrium colloidal suspensions, therefore, one can start with the following coupled diffusion equations already described elsewhere:¹⁰

$$\frac{\partial}{\partial t} \Phi(\mathbf{r}, t) = \nabla \cdot [D_s(\Phi(\mathbf{r}, t)) \nabla \Phi(\mathbf{r}, t)], \quad (1)$$

$$\frac{\partial}{\partial t} F_s(\mathbf{k}, t) = -k^2 \sum_{\mathbf{q}} D_s(\mathbf{k} - \mathbf{q}, t) F_s(\mathbf{q}, t) \quad (2)$$

with the Fourier transform, $D_s(\mathbf{k}, t)$, of the self-diffusion coefficient $D_s(\Phi)$. The most important feature of this theory is that the self-diffusion coefficient $D_s(\Phi)$ becomes dynamically anomalous near ϕ_g as

$$D_s(\Phi(\mathbf{r}, t)) \sim D_0 \left| 1 - \frac{\Phi(\mathbf{r}, t)}{\phi_g} \right|^\gamma, \quad (3)$$

where γ is a time exponent to be determined, and $\gamma = 2$ for the hard-sphere suspensions.¹² This dynamic anomaly results from the many-body correlations between particles. Suppose that we start from a completely random initial configuration. Then, smoothing process of $\Phi(\mathbf{r}, t)$ starts to occur, following Eq.(1), and $\Phi(\mathbf{r}, t)$ finally reaches the equilibrium volume fraction ϕ for long times. As is seen in Fig. 1, for intermediate times there exist glassy regions with inhomogeneous local volume fractions larger than ϕ_g . Since $D_s(\Phi) = 0$ at $\Phi(\mathbf{r}, t) = \phi_g$ and the diffusion coefficients in the glassy regions become much smaller in time than those in the liquid regions with inhomogeneous local volume fractions less than ϕ_g , there are two relaxation regions, slow relaxation regions (glassy regions) and fast relaxation regions (liquid regions).¹³ Thus, the glassy regions freeze for intermediate times, forming the long-lived, finite-sized, irregularly shaped domains, and they disappear for very long times. Those slowly-varying glassy domains do influence the relaxations of the density fluctuations. In fact, a divergence of relaxation times t_α and t_β , at ϕ_g with the exponents δ and $\eta(z_0)$, a two-step relaxation around t_β , including von Schweidler decay, and also the Kohlrausch-Williams-Watts formula (KWW) with the exponent $\beta(z_0) = \gamma / \eta(z_0)$ around t_α were found in the supercooled colloidal state for $\phi_\beta(z_0, ka) \leq \phi < \phi_g$, where ϕ_β denotes the crossover volume fraction¹⁰ over which the shoulder of $F_s(k, t)$ appears. Here z_0 measures how the initial state of the system

is spatially nonuniform and is given by $z_0 = z(t=0)$, where the state parameter $z(t)$ is given by

$$z(t) = 1 - \int \frac{dr}{V} \left| 1 - \frac{\Phi(r,t)}{\phi} \right|, \quad (4)$$

V being the total volume of the system. Thus, the slow relaxation in the supercooled colloidal state turns out to be caused by the existence of long-lived, spatial heterogeneous structure, which results from the dynamic anomaly of the self-diffusion coefficient. In this paper we first present the two different, nonequilibrium suspensions and show how the idea of the dynamic anomaly works on them. Next we discuss how this idea works even in equilibrium suspensions.

NONEQUILIBRIUM SUSPENSIONS

We consider the following two kinds of model suspensions. The first is the concentrated, neutral hard-sphere suspension with both the hydrodynamic and the direct interactions between particles. The second is the highly, charged hard-sphere suspension with the interactions between macroions and counterions.

Depending on the space-time scales, there exist two characteristic stages. One is a kinetic stage, where the space-time cutoff (r_c, t_c) is set as $r_0 \ll r_c \ll \ell$ and $t_0 \ll t_c \ll t_B$. Here ℓ is the characteristic length, r_0 the microscopic length, t_B the Brownian relaxation time, and t_0 the microscopic time. The other is a suspension-hydrodynamic stage, where

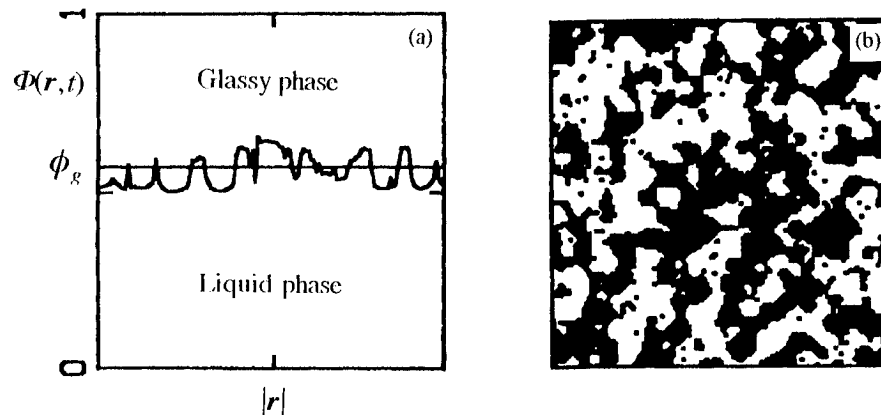


FIGURE 1. Schematic plot of the slow and fast relaxation processes. (a) $\Phi(r,t)$ vs $|r|$. (b) A snapshot, projected onto a plane, of a typical configuration of glassy domains. The glassy phase is colored black.

$r_c \gg \ell$ and $t_c \gg t_B$. In the kinetic stage, the position $X_i(t)$ and the velocity $\mathbf{u}_i(t)$ of the i th particle at time t are described by a set of Langevin equations¹²

$$\frac{d}{dt} X_i(t) = \mathbf{u}_i(t), \quad m \frac{d}{dt} \mathbf{u}_i(t) = \mathbf{M}_i(t) + \sum_{j(\neq i)}^N \mathbf{F}_{ij}(t) \quad (5)$$

with the force exerted by the fluctuating fluid on sphere i

$$\mathbf{M}_i(t) = -\zeta \mathbf{u}_i(t) - \sum_{j(\neq i)} \mathbf{G}_{ij} \cdot \mathbf{M}_j(t) + \mathbf{R}_i(t), \quad (6)$$

where the tensor \mathbf{G}_{ij} represents the Oseen tensor, and ζ is the friction coefficient. Here \mathbf{F}_{ij} is the force between particles i and j , where i and j denote either macroion or counterion for charged case, and the random force $\mathbf{R}_i(t)$ obeys a Gaussian, Markov process. The second term of Eq.(6) represents the hydrodynamic interactions between particles and contains long-range interactions. For charged case the Coulomb force \mathbf{F}_{ij} is also long range. Because of those long-range nature, it is beyond our capacity to deal with Eqs.(5) analytically. Hence we must further reduce it to obtain more macroscopic equations, which we can reasonably analyze.

It is convenient to introduce the probability distribution function of n particles by $f_n(\mathbf{r}_1, \mathbf{u}_1, \dots, \mathbf{r}_n, \mathbf{u}_n; t) = A(\mathbf{r}_1, \mathbf{u}_1, t) \cdots A(\mathbf{r}_n, \mathbf{u}_n, t)$ with the particle number density

$$A(\mathbf{r}, \mathbf{u}, t) = \sum_{i=1}^N \delta(\mathbf{r} - X_i(t)) \delta(\mathbf{u} - \mathbf{u}_i(t)) = f(\mathbf{r}, \mathbf{u}, t) + \delta A(\mathbf{r}, \mathbf{u}, t), \quad (7)$$

where $f(\mathbf{r}, \mathbf{u}, t) = \overline{A(\mathbf{r}, \mathbf{u}, t)}$ is a causal part and $\delta A(\mathbf{r}, \mathbf{u}, t)$ is a fluctuating part. Here the relative magnitude of the fluctuations to the causal part is small; $|\delta A / f| \ll 1$. One can now transform Eqs.(5) into the hierarchy equations for f_n . For charged case the similar hierarchy equations are also derived for counterions. By employing the space-time coarse-graining in an appropriate manner together with expansions in the small parameters and also in $|\delta A / f|$, one can thus derive a nonlinear deterministic nonlinear equation for $f(\mathbf{r}, \mathbf{u}, t)$ and a linear equation for the variance $\overline{\delta A(\mathbf{r}, \mathbf{u}, t) \delta A(\mathbf{r}', \mathbf{u}', t)}$. We note here that in the above formulation all the direct correlation functions were neglected for simplicity. Therefore, the resulting equations are restricted only to the description of the self-diffusion process.

In the suspension-hydrodynamic stage, the relevant variable is the slowly-varying, local volume fraction given by

$$\hat{\Phi}(\mathbf{r}, t) = \int d\mathbf{v} A(\mathbf{r}, \mathbf{v}, t) = \Phi(\mathbf{r}, t) + \delta\phi(\mathbf{r}, t) \quad (8)$$

with the average local volume fraction $\Phi(\mathbf{r}, t)$ and the fluctuation $\delta\phi(\mathbf{r}, t)$, where $|\delta\phi/\Phi| \ll 1$, and $(1/V) \int d\mathbf{r} \Phi(\mathbf{r}, t) = \phi$. By taking expansions in the spatial gradient $\partial/\partial \mathbf{r}$, the slowness parameter $\partial/\partial t$, and the relative magnitude $|\delta\phi/\Phi| \ll 1$, one can then derive the nonlinear deterministic diffusion equation (1) from the equation for $f(\mathbf{r}, \mathbf{u}, t)$ and the linear equation (2) from the linear variance equation for the fluctuations.

We now discuss the analytical results for two kinds of nonequilibrium suspensions. The first is the neutral, hard-sphere suspension (HS) with both the hydrodynamic and the direct interactions between particles. The self-diffusion coefficient is given by¹²

$$D_s(\Phi(\mathbf{r}, t)) = D_s^s(\Phi) \frac{(1 - 9\Phi(\mathbf{r}, t)/32)}{[1 + (\Phi(\mathbf{r}, t)D_s^s(\Phi)/\phi_g D_0)(1 - \Phi(\mathbf{r}, t)/\phi_g)^{-\gamma}]} \quad (9)$$

with $\gamma = 2$, where D_0 is the single-particle diffusion coefficient, $D_s^s(\Phi)$ the short-time self-diffusion coefficient (see Ref. 12 for details), and $\phi_g = (4/3)^3 / (7\ln 3 - 8\ln 2 + 2) \approx 0.57184 \dots$. Here the second singular term in the denominator of Eq.(9) results from the many-body correlations between particles due to the long-range hydrodynamic interactions, while the numerator of Eq.(9) results from the coupling between the direct and the short-range hydrodynamic interactions between particles. For short times $t \ll t_\gamma \sim a^2/D_s^s(\phi)$, $D_s(\Phi)$ reduces to the short-time self-diffusion coefficient $D_s^s(\phi)$ since the direct interactions and the correlations are negligible. On the other hand, for long times $t \gg t_L \sim a^2/D_s^L(\phi)$, it reduces to the long-time self-diffusion coefficient $D_s^L(\phi)$ since $\Phi(\mathbf{r}, t)$ reaches ϕ . As was shown in Ref. 12, a good agreement is also seen between the theoretical diffusion coefficients and the experimental data. Thus, there exists a crossover from a short-time diffusion process to a long-time diffusion process for intermediate times where the dynamic anomaly plays an important role.

It is interesting to notice here that the transition point $0.57184 \dots$, which results from the long-range hydrodynamic interactions between particles, is very close to the experimental value. If the hydrodynamic interactions are neglected completely from the beginning, the diffusion coefficient (9) reduces, within the bilinear approximation, to

$$D_s(\Phi(\mathbf{r}, t)) = D_0 [1 - 2\Phi(\mathbf{r}, t)] . \quad (10)$$

From the idea of the dynamic anomaly, we then find $\phi_g = 0.5$ and $\gamma = 1$. The transition point 0.5 is quite close to the value 0.516 obtained by MCT. This may suggest that the transition point predicted by MCT is closely related to the direct interactions

between particles through the two-body correlations within the bilinear approximation. Hence we emphasize that in order to obtain a reasonable value of the transition point, the hydrodynamic interactions are indispensable.

The second is the highly, charged hard-sphere suspension (CS) with the macroions of radius a and charge Ze , and the counterions of radius a_c and charge qe , where $Z \gg q$ and $a \gg a_c$. Up to lowest order in ϕ and q/Z , we obtain¹⁴

$$\begin{aligned} D_s(\Phi) &= D_s^s(\Phi) [1 - \sqrt{3} \Gamma^{3/2} \Phi^{1/2} + (\sqrt{(3/2)^3} \Gamma^{3/2} - 1/\phi_g^{HS}) \Phi], \\ &= D_s^s(\Phi) [1 - (\Phi/\phi_g)^{1/2}] [1 - (\Phi/\phi_0)^{1/2}], \end{aligned} \quad (11)$$

where $\phi_0 = (4/3)/[\Gamma^{3/2} - \sqrt{\Gamma^3 - \sqrt{6} \Gamma^{3/2} + 4/(3\phi_g^{HS})}]^2$, $D_s^s(\Phi) = D_0(1 - 25\Phi/16)$, $\Gamma = Zq \ell_B/a$, and ϕ_g^{HS} denotes the transition point in case (HS), ℓ_B being the Bjerrum length. Using the idea of the dynamic anomaly, one then finds $\gamma = 1$ and $\phi_g(\Gamma) = (4/3)/[\Gamma^{3/2} + \sqrt{\Gamma^3 - \sqrt{6} \Gamma^{3/2} + 4/(3\phi_g^{HS})}]^2$. The terms with $\Gamma^{3/2}$ in Eq.(11) result from the pair correlation between macroions and counterions due to the long-range, attractive Coulomb interactions, while the last term in Eq.(11) results from the long-range hydrodynamic interactions between macroions. We note here that we have neglected the terms obtained by the repulsive Coulomb interactions between macroions because they lead to corrections for the highly charged suspensions with $\Gamma \geq 2$. Hence the above result is valid for $\Gamma \geq 2$ at small volume fractions. In Fig. 2, the long-time self-diffusion coefficient $D_s^L(\phi) = D_s(\phi)$ is shown versus the separation parameter σ for different values of Γ . For comparison $D_s^L(\phi)$ in case (HS) is also shown.

Although the time exponent γ and the transition point ϕ_g are different from each other for the above suspensions, their long-time relaxation behavior seems not to depend on those qualitatively. In fact, the self-intermediate scattering function $F_s(k, t)$ can be written in the Gaussian form as^{13,14}

$$F_s(k, t) = \exp \left[-\frac{k^2}{2d} M_2(t) \right] \quad (12)$$

with the mean-square displacement

$$M_2(t) = 2d \int_0^t ds \int \frac{d\mathbf{r}}{V} D_s(\Phi(\mathbf{r}, s)), \quad (13)$$

where d is a spatial dimensionality. There are four characteristic time stages in the

supercooled colloidal state for $\phi_\beta(z_0, ka) \leq \phi < \phi_g$. The first is the early stage with $t \leq t_\gamma$, where the density fluctuations obey the short-time exponential decay $F_s(k, t) = \exp[-k^2 D_s^s(\phi)t]$. The second is the β -relaxation stage on the time scale of order $t_\beta \sim |\sigma|^{1/2}$, where $F_s(k, t)$ obeys the von Schweidler decay for $t_\beta \leq t \leq t_\alpha$. The third is the α -relaxation stage with $t_\alpha \leq t \leq t_L$. $\Phi(\mathbf{r}, t)$ can be scaled near ϕ_g as¹³

$$\Phi(\mathbf{r}, t) = \phi[1 + \varepsilon(t^\mu \mathbf{r})], \quad (14)$$

where $\mu(z_0)$ is an exponent to be determined, and $\int d\mathbf{r} \varepsilon(\mathbf{r}) = 0$. Here the exponent $\mu(z_0)$ can be calculated numerically since $1 - z(t) \sim t^{-d\mu}$ from Eqs. (4) and (14). Use of Eqs. (9), (11) and (13) then leads, to lowest order in σ and $|\varepsilon|$, to

$$M_z(t) = m^i(z_0) + |\sigma|^y m_L^i(t), \quad (i = HS, CS) \quad (15)$$

with

$$m^{CS}(\Gamma, z_0) = (d/4) \int_0^{t_\alpha} ds \int \frac{d\mathbf{r}}{V} D_s^s(\Phi(\mathbf{r}, s)) [1 - (\Phi(\mathbf{r}, s)/\phi_0)^{1/2}] \varepsilon(\mathbf{r}, s)^2, \quad (16)$$

$$m_L^{CS}(t) = d \int_0^t ds \int \frac{d\mathbf{r}}{V} D_s^s(\Phi(\mathbf{r}, s)) [1 - (\Phi(\mathbf{r}, s)/\phi_0)^{1/2}]. \quad (17)$$

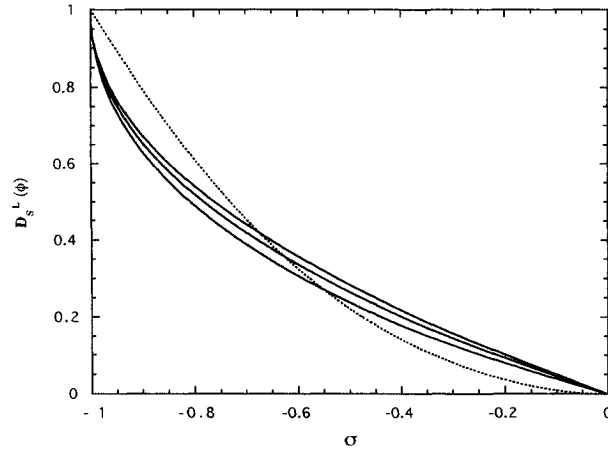


FIGURE 2. Long-time self-diffusion coefficient versus separation parameter σ for $\Gamma=2, 3$, and 6 (from left to right). The dotted line represents $D_s^L(\phi)$ in case (HS).

where we have used the fact that $|\varepsilon| \ll 1$ for $t \geq t_\alpha$, and for case (HS) the details of the terms m^{HS} and m_2^{HS} are shown in Ref. 13. The functions $m_L^i(t)$, ($i = HS, CS$), describes a α -relaxation process. In fact, use of Eq.(14) leads to $m_L^i(t) \sim |\sigma|^\gamma t^\beta$ with the exponent $\beta(z_0) = 1 - d\mu(z_0)$. Thus, one finds the KWW function

$$F_S(k, t) \sim \exp[-(t/t_\alpha)^\beta] \quad (18)$$

with the α -relaxation time $t_\alpha \propto (k|\sigma|)^{-\eta}$, where $\eta(z_0) = \gamma/\beta(z_0)$. For case (HS), $\gamma = 2$, $\phi_\beta(0.8, 3.5) \approx 0.56$, $\phi_g = 0.57184 \dots$, $\beta(0.8) = 0.586$, and $\eta(0.8) = 3.41$, while for case (CS), $\gamma = 1$, $\phi_\beta(0.8, 1.3, \Gamma) \approx 7.609 \times 10^{-3}$, $\phi_g(\Gamma) = 7.9 \times 10^{-3}$, $\beta(0.8) = 0.59$, and $\eta(0.8) = 1.695$ at $\Gamma = 3.684$. The last is the late stage with $t \geq t_L$, where $F_S(k, t)$ obeys the long-time exponential decay $F_S(k, t) = \exp[-k^2 D_S^L(\phi)t]$. In Fig. 3 we show the time evolution of (a) $F_S(k, t)$ and (b) $M_2(t)$ at $\phi = 0.571$ and $ka = 3.5$ (case (HS)), and $\phi = 7.899 \times 10^{-3}$, $\Gamma = 3.684$, and $ka = 1.3$ (case (CS)). Apart from the early stage, the two suspensions thus turn out to give rise to the similar relaxation behavior. Finally, we note that in the nonequilibrium case the charged suspension shows the α and β relaxation processes even at the very low volume fractions near ϕ_g .

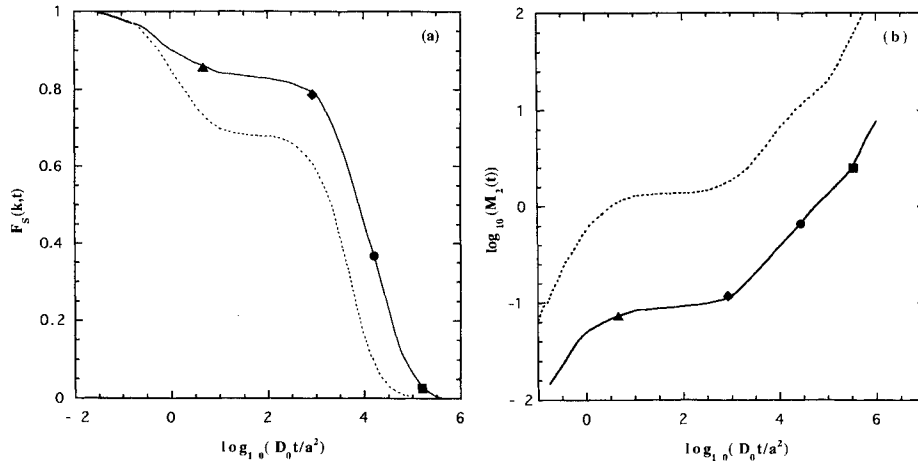


FIGURE 3. Time evolution of (a) $F_S(k, t)$ and (b) $M_2(t)$. The solid lines indicate the results in case (HS) at $\phi = 0.571$ and $ka = 3.5$, while the dotted lines indicate the results in case (CS) at $\phi = 7.899 \times 10^{-3}$, $\Gamma = 3.684$, and $ka = 1.3$. The symbols indicate the time scales: t_γ (\blacktriangle), t_β (\blacklozenge), t_α (\bullet), and t_L (\blacksquare).

EQUILIBRIUM SUSPENSIONS

In this section we discuss the equilibrium suspensions, where the local volume fraction $\hat{\Phi}(\mathbf{r}, t)$ is given by $\hat{\Phi}(\mathbf{r}, t) = \phi + \delta\phi(\mathbf{r}, t)$ with $|\delta\phi/\phi| \ll 1$. In the following, we focus only on case (HS) for simplicity. As was shown in Ref. 10, one can formally derive a nonlinear stochastic diffusion equation for $\hat{\Phi}(\mathbf{r}, t)$, which is similar to Eq.(1), except that the random force $\xi(\mathbf{r}, t)$ now appears. Hence one can assume that the diffusion coefficient is identical to that in the nonequilibrium case, except that $\Phi(\mathbf{r}, t)$ is now replaced by $\hat{\Phi}(\mathbf{r}, t)$. Near ϕ_g , one can then write Eq.(9) approximately as

$$D_s(\hat{\Phi}) \approx D_0 [\sigma + \delta\phi(\mathbf{r}, t) / \phi_g]^2. \quad (19)$$

Hence $D_s(\hat{\Phi})$ becomes dynamically anomalous when $\delta\phi(\mathbf{r}, t) / \phi_g = -\sigma$. Similarly to the nonequilibrium case, therefore, the glassy regions with $\delta\phi/\phi_g \geq -\sigma$ freeze for intermediate times, forming spatially heterogeneous structure. In contrast to the spatial heterogeneities in the nonequilibrium case, however, their size and magnitude are very small. Although it might be difficult to observe them experimentally, they are still important because they do influence the dynamics of the equilibrium density fluctuations. In fact, as long as the relative magnitude $|\delta\phi/\phi_g|$ is the same order as $|\sigma|$, the fluctuations $\delta\phi$ obey the nonlinear stochastic diffusion equation, up to order $|\delta\phi|^3$,

$$\frac{\partial}{\partial t} \delta\phi(\mathbf{r}, t) = \nabla^2 [D_s^L(\phi)\delta\phi + D_s^S(\phi)\{v(\phi)\delta\phi^2 + w(\phi)\delta\phi^3\}] + \xi(\mathbf{r}, t) \quad (20)$$

with $v = \alpha(1 - 9\phi/32) / [\phi_g(c + \sigma^2)^2]$ and $w = c(1 - 9\phi/32)(c - 3\sigma^2) / [3\phi_g^2(c + \sigma^2)^3]$, where $c(\phi) = D_s^S(\phi)\phi / (D_0\phi_g)$. Here the Gaussian random force $\xi(\mathbf{r}, t)$ satisfies

$$\begin{aligned} \langle \xi(\mathbf{r}, t) \rangle &= \langle \xi(\mathbf{r}, t) \delta\phi(\mathbf{r}', 0) \rangle = 0, \\ \langle \xi(\mathbf{r}, t) \xi(\mathbf{r}', t') \rangle &= -2\delta(t-t')(4\pi a^3 \phi/3) \nabla \cdot [D_s(\hat{\Phi}(\mathbf{r}, t)) \nabla \delta(\mathbf{r} - \mathbf{r}')], \end{aligned} \quad (21)$$

where the brackets denote the average over an equilibrium ensemble.

In order to calculate the self-intermediate scattering function $F_s(k, t) = \langle \delta n_{\mathbf{k}}(t) \delta n_{-\mathbf{k}}(0) \rangle$ from Eq. (20), we here simply use the following three steps. The first is to split up the variable $\delta\phi_q(t)$ into two parts, a linear part in $\delta\phi_q(0)$ and others; $\delta\phi_q(t) = F(q, t) \delta\phi_q(0) + I_q(t)$, where $I_q(t)$ describes nonlinear terms of order $|\delta\phi_q(0)|^2$ and fluctuations. The second consists of a factorization for the four-point correlation of $\delta n_{\mathbf{k}}(0)$, resulting in products of $S(k)$. The third is to use the convolution

approximation $\langle \delta n_k \delta n_p \delta n_{-q} \rangle \approx \delta_{q,k+p} S(k)S(p)S(q) / \sqrt{N}$. Thus, one can obtain, to lowest order in $|\delta\phi_k(0) / \phi|$,

$$\frac{\partial}{\partial t} F_s(k, t) = -k^2 [D_s^L(\phi) + D_s^S(\phi)m_s(t)] F_s(k, t) \quad (22)$$

with the memory term

$$m_s(t) = \frac{2}{3\pi} \int_0^{a/r_c} dq q^2 S(q) [v(\phi) + 3\phi w(\phi) F(q/a, t)] F(q/a, t), \quad (23)$$

where the spatial cutoff r_c is set so as to be $m_s(t=0) = 1$. We note here that the memory term (23) is determined by the intermediate scattering function $F(q, t)$. From Eq.(22), $F_s(k, t)$ obeys $F_s(k, t) = \exp(-k^2 D_s^S t)$ for short times since $D_s^S \gg D_s^L$, while it obeys $F_s(k, t) = \exp(-k^2 D_s^L t)$ for long times since $m_s(\infty) \approx 0$. In order to solve Eq.(22), therefore, one has to derive another equation for $F(q, t)$ from first principles. This can be done by employing a procedure similar to that in the derivation of Eqs. (1) and (2), except that the direct correlations are now taking into account. In the following, however, we just use the empirical relation for $F(q, t)$ proposed by Segrè and Pusey¹⁵ instead, which is given by $F(q, t) = \exp[-q^2 D^c(q) M_2(q, t) / (6D_s^S)]$, where $D^c(q, \phi)$ denotes the q -dependent, short-time collective-diffusion coefficient. In Fig. 4

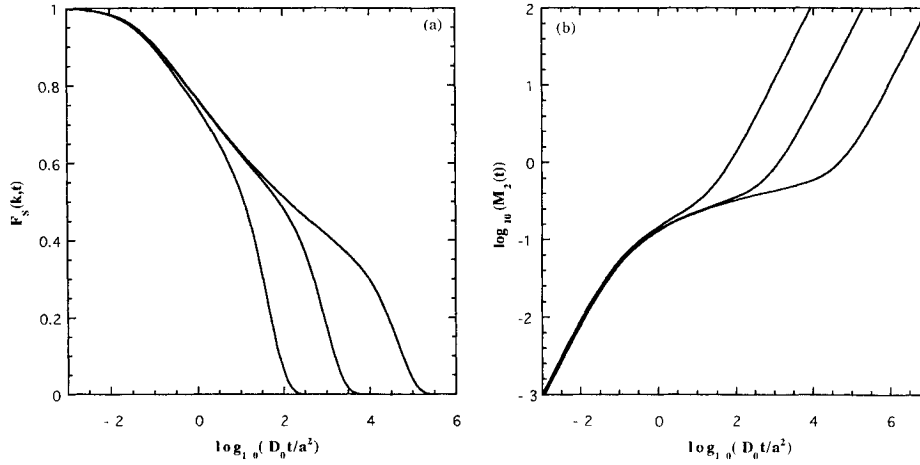


FIGURE 4. Time evolution of (a) $F_s(k, t)$ at $ka=3.5$ and (b) $M_2(t)$ for $\phi=0.545, 0.566$, and 0.571 (from left to right).

$F_S(k, t)$ and $M_2(t)$ are shown for different volume fractions at $ka = 3.5$, where we have just put $D^c(q, \phi) = D_S^S(\phi) / S(q)$ for simplicity since $D^c(q)$ is not known.

CONCLUSIONS

In summary, we conclude that the idea of the dynamic anomaly of the diffusion coefficient causes the long-lived spatial heterogeneities near ϕ_g in equilibrium and nonequilibrium suspensions. Since the spatial heterogeneities are enhanced in the nonequilibrium suspensions, the α and β relaxation processes can be seen even for low volume fractions near ϕ_g in case (CS). On the other hand, since their size and magnitude are small in the equilibrium suspensions, it might be difficult to observe them experimentally. However, they are still important since they do influence the dynamics of equilibrium density fluctuations. In both cases (HS) and (CS), the dynamic anomaly has been shown to result from the many-body correlations due to the long-range interactions, such as the hydrodynamic interactions between particles in case (HS)¹² and the Coulomb attractive interactions between macroions and counterions in case (CS)¹⁴. Hence we emphasize that in order to discuss the dynamics of colloidal suspensions near ϕ_g , those long-range interactions are indispensable in addition to the repulsive short-range interactions.

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