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Slow Dynamics of Concentrated Hard-Sphere Suspensions: Spatial Heterogeneities and Density Fluctuations

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Abstract. The influence of heterogeneous structure on the colloidal glass transition is studied by numerically solving the coupled diffusion equations recently proposed by Tokuyama for concentrated hard-sphere suspensions of interacting Brownian particles with both hydrodynamic and direct interactions. Near glass transition, the long-lived, cluster-like glassy domains are shown to be formed by the dynamic anomaly of the self-diffusion coefficient with a power-law exponent γ , where $\gamma=2$ here. Those spatial heterogeneities are responsible for the slow relaxation of the density fluctuations. Thus, the self-intermediate scattering function is shown to obey a two-step relaxation for intermediate times, and also to be well approximated by a Kohlrausch-Williams-Watts function with an exponent β around the α -relaxation time with a power-law exponent $\eta = \gamma / \beta$. For longer times, it obeys an exponential decay with a long-time self-diffusion coefficient. For whole times, the non-Gaussian effects are shown to be negligible.

INTRODUCTION

Recent experimental works¹⁻³ show that as the volume fraction ϕ of the hard-sphere colloidal suspensions is increased beyond the melting volume fraction ϕ_m , the system also exhibits a transition at the glass transition volume fraction ϕ_g from a fluid phase to a glass phase, similar to that in supercooled liquids. In recent years, many experimental, computational and theoretical attempts have been made to study this important problem, but more works still seem to be needed to obtain a deeper understanding of the dynamics of glass forming colloidal liquids. With the recent development of the mode-coupling theory (MCT)^{4,5} for the dynamics of supercooled fluids, much of the recent experimental studies²⁻³ in colloidal fluids have been designed around the predictions of MCT. The most striking feature of MCT is the prediction of

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two different slow relaxations of density fluctuations, the so-called β and α relaxations, whose time scales, t_β and t_α , diverge as the separation parameter $\sigma = \phi / \phi_x - 1$ approaches zero; $t_\beta \sim |\sigma|^{-\delta}$ and $t_\alpha \sim |\sigma|^{-\eta}$, where δ and η are exponents to be determined. In concentrated colloidal suspensions,²⁻⁴ MCT predicts $\delta = 1.66$ and $\eta = 2.58$. Recently, a new theory based on the coupled diffusion equations has been proposed by Tokuyama⁶ to study the dynamics of self-diffusion processes in concentrated suspensions. The most important feature of this theory is that the self-diffusion coefficient $D_s(\Phi)$ contained in the coupled equations becomes dynamically anomalous at ϕ_g as $D_s \sim |1 - \Phi(\mathbf{x}, t) / \phi_g|^\gamma$, where $\gamma = 2$ here, and $\Phi(\mathbf{x}, t)$ denotes the local volume fraction given by $\Phi(\mathbf{x}, t) = 4\pi a^3 n(\mathbf{x}, t) / 3$. Here $n(\mathbf{x}, t)$ is the average number density of colloids. This dynamic anomaly results from the many-body correlations between particles due to the long-range hydrodynamic interactions⁷ and causes the formation of the long-lived, finite-sized, irregularly shaped glassy domains where $\Phi(\mathbf{x}, t) \geq \phi_g$.^{8,9} Those slowly-varying glassy domains do influence the relaxations of the density fluctuations. A divergence of relaxation times at ϕ_x with the exponents $\delta = 1.0$ and $\eta(z_0)$, a two-step relaxation around the crossover time t_β , including von Schweidler decay, and also the Kohlrausch-Williams-Watts formula (KWW) with the KWW exponent $\beta(z_0) = \gamma / \eta(z_0)$ around the α -relaxation time t_α were found, where z_0 measures how the initial state of the system is spatially nonuniform and $z_0 = 1$ in a uniform state. Although the characteristic features of the relaxations are in part similar to those obtained by MCT, the basic standpoints are quite different from those of MCT. First, MCT has been applied to a uniform equilibrium initial state where $n(\mathbf{x}, t)$ becomes constant $n_0 = N / V$ in space and time, that is, $\Phi(\mathbf{x}, t) = \phi$, where $\phi = 4\pi a^3 n_0 / 3$ denotes the particle volume fraction, N the total number of colloids, and V the total volume of the system. On the other hand, the present theory deals with a spatially inhomogeneous system, and starts with the nonlinear deterministic diffusion equation for $\Phi(\mathbf{x}, t)$,⁷ which describes the dynamics of spatial heterogeneities from a nonuniform initial state with $\Phi(\mathbf{x}, 0)$ to a final state with $\Phi(\mathbf{x}, \infty)$. This is because a supercooled liquid is in a metastable equilibrium state below and also above ϕ_x , and exhibits spatial heterogeneities of the dynamic state.¹⁰ Secondly, MCT assumes that the density fluctuations $\delta n(\mathbf{x}, t)$ around n_0 obey the nonlinear stochastic equations. On the other hand, the present theory starts with the linear stochastic diffusion equation for the density fluctuations $\delta n(\mathbf{x}, t)$ around $n(\mathbf{x}, t)$.⁶ This is because the density fluctuations would be small compared to the causal part $n(\mathbf{x}, t)$ since the glass transition seems not to be a critical phenomenon. In fact, there is no correlation length diverging at the glass transition point. Hence the glass transition

seems to be dynamic in origin in contrast to critical phenomena. Thirdly, MCT predicts the critical volume fraction $\phi_c = 0.52 \pm 0.01$,⁵ while the present theory predicts $\phi_c = (\frac{4}{3})^3 / (7\ln 3 - 8\ln 2 + 2) \approx 0.57184 \dots$. The light-scattering experiments¹⁻³ show that the hard-sphere suspensions undergo a glass transition at ϕ_c which is between 0.56 and 0.58. Finally, MCT contains two parameters, the volume fraction ϕ , and a microscopic time scale t_0 which is treated as a free fit parameter. On the other hand, the present theory contains two parameters, ϕ and the initial state parameter z_0 , both of which can be fixed by an experiment. In this paper, we present the numerical solutions of the above coupled diffusion equations near ϕ_c .

MODEL

The dynamics of spatial heterogeneities of colloidal suspensions is described by the local volume fraction $\Phi(\mathbf{x}, t)$. On the other hand, the dynamics of 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 $F(\mathbf{x}, t) = \langle \delta n(\mathbf{x}, t) \delta n(\mathbf{0}, 0) \rangle / N$, where the angular brackets denote the average over an appropriate initial ensemble. 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 $F_s(\mathbf{k}, 0) = 1$. Hence we start with the following coupled diffusion equations already described elsewhere:⁶

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

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

with the Fourier transform, $D_s(\mathbf{k}, t)$, of the self-diffusion coefficient

$$D_s(\Phi(\mathbf{x}, t)) = D_s^s(\Phi) \frac{(1 - 9\Phi(\mathbf{x}, t)/32)}{[1 + (\Phi(\mathbf{x}, t) D_s^s(\Phi) / \phi_g D_0)(1 - \Phi(\mathbf{x}, t) / \phi_g)^{-2}]}, \quad (3)$$

and the conservation law $(1/V) \int d\mathbf{x} \Phi(\mathbf{x}, t) = \phi$, where D_0 is the single-particle diffusion coefficient, and $D_s^s(\Phi)$ the short-time self-diffusion coefficient (see Ref. 7 for details).

Here the second singular term in the denominator of Eq.(3) results from the many-body correlations between particles due to the long-range hydrodynamic interactions, while the numerator of Eq.(3) results from the coupling between the direct and the short-range hydrodynamic interactions between particles. We note here that the short-time self-diffusion coefficient $D_s^s(\Phi)$ still depends on space and time through $\Phi(\mathbf{x}, t)$. This point is different from the previous calculation in Ref. 8 where $D_s^s(\Phi)$ was simply replaced by the constant value $D_s^s(\phi)$. In fact, for short times $t \ll t_L$, $D_s(\Phi)$ reduces to $D_s^s(\phi) \sim |\sigma|^0$ since the direct interactions and the correlations are negligible, while for long times $t \geq t_L$, it reduces to the long-time self-diffusion coefficient $D_s^L(\phi) = D_s(\phi) \sim |\sigma|^2$, where $t_L \sim a^2/D_s^L$ and $t_L \sim a^2/D_s^L$ are characteristic times of the short- and long-time self-diffusion processes, respectively. A good agreement is indeed seen between the theoretical results⁷ and the experimental data.^{12,13} Thus, there exists a crossover from the short-time process described by D_s^s to the long-time process described by D_s^L for intermediate times, where the dynamic anomaly of $D_s(\Phi)$ plays an important role.

RESULTS

In order to solve the coupled diffusion equations (1) and (2) self-consistently, we first fix the values of the two parameters, ϕ and z_0 , as the initial conditions, where $z_0 = 1 - (1/V) \int d\mathbf{x} |1 - \Phi(\mathbf{x}, 0)/\phi|$. To integrate those equations, we employ the forward Euler difference scheme with the time step $0.01a_0^2/D_0$ and the lattice spacing $0.2a$ in the volume $(128a)^3$ of the three dimensional simulation system with periodic boundary conditions. The initial value $\Phi(\mathbf{x}, 0)$ is chosen at each position \mathbf{x} from a random number with a Gaussian distribution, which is characterized by a mean value 1 and a standard deviation s , where s is adjusted so as to find a given value of z_0 .

We first discuss the numerical solutions of Eq.(1), starting in a completely random configuration with $\Phi(\mathbf{x}, 0)$ toward a final configuration with $\Phi(\mathbf{x}, \infty)$. Figure 1 shows the space-time dependence of $\Phi(\mathbf{x}, t)$ at $z_0 = 0.8$ in the supercooled region with $\phi = 0.571$ ($< \phi_x$). Figure 2 shows a sequence of snapshots projected onto a plane of a typical configuration of the glassy phase where $\Phi(\mathbf{x}, t) \geq \phi_x$. On the time scales of order t_β , the finite-sized, glassy domains are formed. After t_β , the spatial rearrangement of those domains occurs and continues up to t_α . After t_α , they are dissolved, disappearing very slowly in the supercooled region for $\phi_\beta \leq \phi < \phi_x$, while

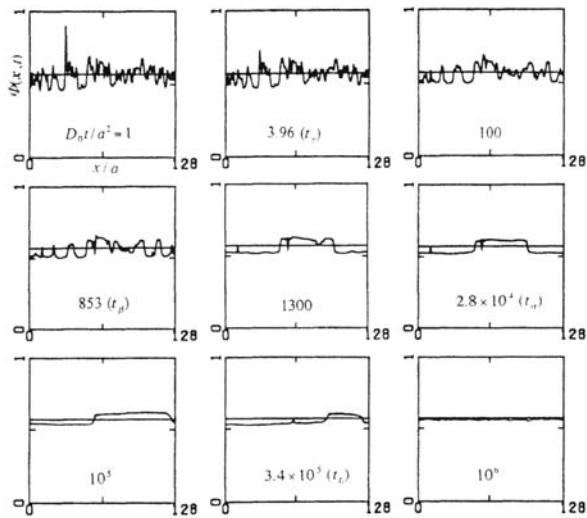


FIGURE 1. $\Phi(x,t)$ versus reduced distance x/a for $\phi=0.571$ at $z_0=0.8$.

they form clusters, covering a whole space very slowly in the glass region for $\phi \geq \phi_g$, where ϕ_g is a crossover volume fraction, over which the two-step relaxation appears.¹⁴ Hence one can assume that for times $t \gg t_\beta$, $\Phi(x,t)$ is scaled, near ϕ_g , as

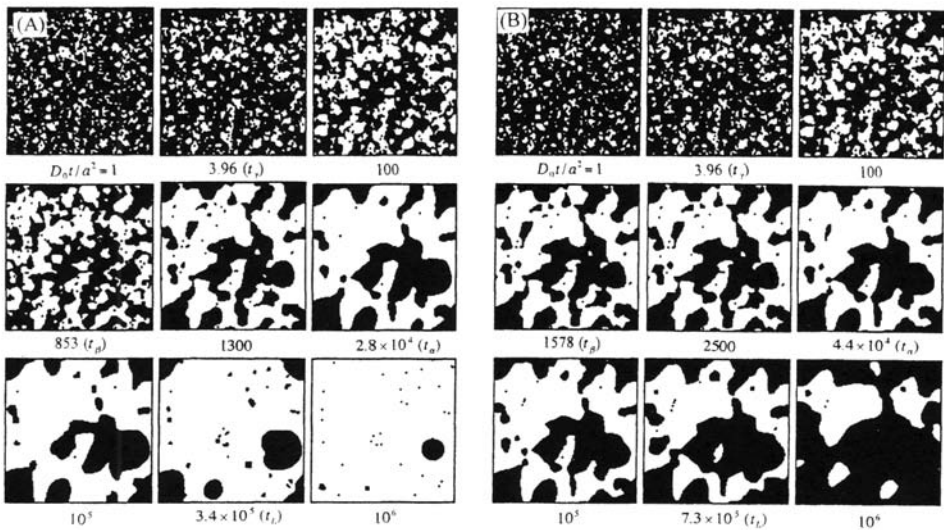


FIGURE 2. Typical configurations of glassy domains for (A) $\phi=0.571$ and (B) $\phi=0.573$ at $z_0=0.8$.

$$\Phi(\mathbf{x}, t) = \phi[1 + Z(t^\mu \mathbf{x})], \quad (4)$$

where $\mu(z_0)$ is a small exponent to be determined, and $\int d\mathbf{x} Z(\mathbf{x}) = 0$.

We next discuss the numerical solutions of Eq.(2). The numerical work shows that the self-intermediate scattering function $F_S(\mathbf{k}, t)$ can be written in the Gaussian approximation as

$$F_S(\mathbf{k}, t) = \exp\left[-\frac{k^2}{6} M_2(t)\right], \quad M_2(t) = \frac{6}{V} \int_0^t ds \int d\mathbf{x} D_S(\Phi(\mathbf{x}, s)), \quad (5)$$

where $M_2(t)$ indicates the mean-square displacement. As was shown in Ref. 8, at ϕ_x $F_S(\mathbf{k}, t)$ reaches the plateau with the height $F_S(\mathbf{k}, t \rightarrow \infty) = f_k^c(z_0, \sigma = 0)$. In the early stage on the time scale of order t_γ , the spatial inhomogeneities are described by the solution of Eq.(1) as $\Phi(\mathbf{x}, t) = \exp[-tD_S^S(\phi) \nabla^2] \Phi(\mathbf{x}, 0)$, and the density fluctuations obey the short-time exponential decay, $F_S(\mathbf{k}, t) = \exp[-k^2 D_S^S(\phi)t]$. After this stage, the dynamical behavior becomes complicated because of the anomalous property of $D_S(\Phi)$. In order to see the crossover behavior around t_β , it is convenient to calculate the logarithmic derivatives given by $\psi = \partial \log |f_k^c - F_S(\mathbf{k}, t)| / \partial \log t$ and $\psi_1 = \partial \psi / \partial \log t$.^{6, 8} Then, $\psi_1 = 0$ is shown to give two time roots, $t_{b_0}(\phi, z_0, ka)$ and $t_b(\phi, z_0, ka)$, which reveal two fairly flat regions; $\psi = b_0(\phi, z_0, ka)$ at $t = t_{b_0}$ where $t_\gamma \ll t_{b_0} \ll t_\beta$, and $\psi = b(\phi, z_0, ka)$ at $t = t_b$ where $t_\beta \ll t_b \ll t_\alpha$. Here the crossover time is given by $t_\beta \propto (D_S^S D_S^L)^{-1/2} \sim |\sigma|^{-1}$, where $\delta = 1$.⁶ The crossover volume fraction $\phi_\beta(z_0, k)$ is thus determined by the equal root $t_{b_0}(\phi_\beta, z_0, ka) = t_b(\phi_\beta, z_0, ka)$, or $b_0(\phi_\beta, z_0, ka) = b(\phi_\beta, z_0, ka)$ at fixed z_0 and k .¹⁴ With increasing volume fraction at a fixed z_0 , we thus observe a progression from normal colloidal fluid ($0 < \phi < \phi_\beta$), to supercooled colloidal fluid ($\phi_\beta \leq \phi < \phi_g$), and to glass ($\phi \geq \phi_g$). In the so-called β stage on the time scale of order t_β for $\phi \geq \phi_\beta$, therefore, $F_S(\mathbf{k}, t)$ obeys two kinds of power-law decays with exponents b_0 and b around t_β . In the early β -relaxation stage $t_\gamma \ll t \leq t_\beta$ the finite-sized, glassy domains are formed, and $F_S(\mathbf{k}, t)$ obeys

$$F_S(\mathbf{k}, t) = f_k^c(z_0, 0) - A_k(z_0)(t/t_\beta)^{b_0} \quad (6)$$

with a positive constant A_k , where $b_0(0.571, 0.95, 3) = 0.3$ and $b_0(0.573, 0.95, 3) = 0.33$. This power-law decay continues up to the crossover time t_β . In the late β -

relaxation stage $t_\beta \leq t < t_\alpha$, the glassy domains change very slowly, and $F_S(k, t)$ obeys the so-called von Schweidler decay

$$F_S(k, t) = f_k^c(z_0, 0) - B_k(z_0)(t/t_\alpha)^b \quad (7)$$

with a positive constant B_k , where $b(0.571, 0.95, 3) = 0.68$ and $b(0.573, 0.95, 3) = 0.71$. After this stage, the spatial rearrangement of the glassy domains occurs, and $\Phi(x, t)$ obeys the scaling given by Eq.(4). This is the so-called α -relaxation stage. Use of Eqs.(4) and (5) then leads to $M_2(t) \sim \sigma^2 t^\beta$, where $\beta(z_0) = 1 - 3\mu(z_0)$. Thus, we find the KWW function

$$F_S(k, t) = \exp[-(t/t_\alpha)^{\beta(z_0)}] \quad (8)$$

with the α -relaxation time $t_\alpha(\phi, z_0, k) \propto (k|\sigma|)^{-\eta(z_0)}$, where $\eta(z_0) = \gamma/\beta(z_0)$, and $\eta(0.95) = 2.69$ ($\beta = 0.744$, $\mu = 0.086$) and $\eta(0.8) = 3.65$ ($\beta = 0.548$, $\mu = 0.15$). The KWW formula can thus be explained by the existence of long-lived, glassy domains.

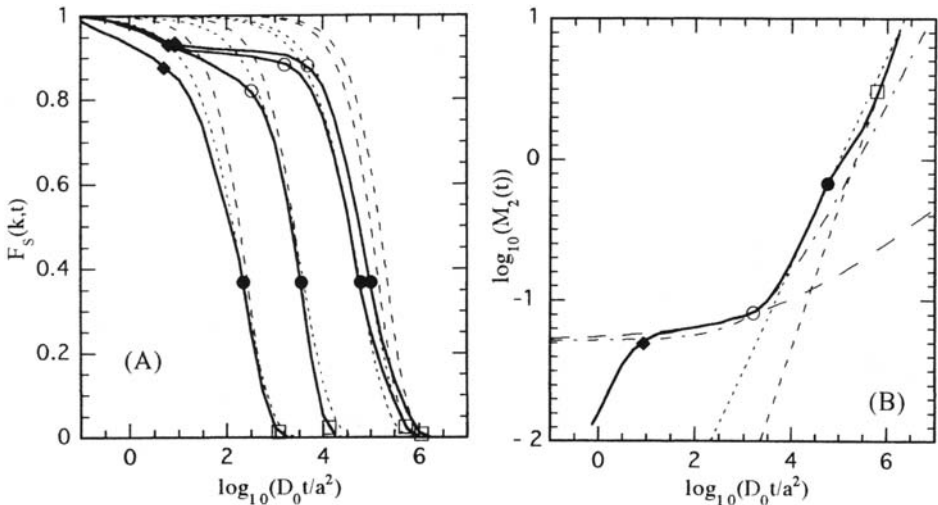


FIGURE 3. (A) the self-intermediate scattering function $F_S(k, t)$ for $\phi = 0.559$, 0.565 , 0.571 and 0.573 (from left to right), and (B) the mean-square displacement $M_2(t)$ for $\phi = 0.571$ at $z_0 = 0.95$ and $ka = 3$. The long-dashed, the dot-dashed, the dotted lines indicate Eqs.(6), (7) and (8), respectively, and the dashed lines the simple exponential. The symbols indicate the time scales: t_γ (\blacklozenge), t_β (\circ), t_α (\bullet), and t_L (\square).

This stretched behavior continues up to the time scale of order t_L . For the late stage of order t_L , we have $\Phi(\mathbf{x}, t) = \phi$, and the fluctuations obey $F_S(k, t) = \exp[-k^2 D_S^L(\phi)t]$. We show the time evolution of $F_S(\mathbf{k}, t)$ in Fig. 3(A) for different volume fractions; $\phi = 0.559$, 0.565 (ϕ_β), 0.571 ($<\phi_g$), and 0.573 ($>\phi_g$), and $M_2(t)$ in Fig. 3(B) for $\phi = 0.571$, where $z_0 = 0.95$ and $ka = 3$.

CONCLUSIONS

The main results reported here are as follows. (i) The existence of long-lived, irregularly shaped glassy domains in the supercooled region. (ii) The neglect of the non-Gaussian effects for whole times. (iii) Four characteristic stages in the supercooled region $\phi \geq \phi_\beta$ (see Fig. 3(B)). (iv) The two-step relaxation and the stretched behavior can be explained by the existence of long-lived, heterogeneous structure.

We finally note that long-lived heterogeneities are caused by the dynamic anomaly of the self-diffusion coefficient which results from the many-body correlations due to the long-range hydrodynamic interactions.⁷ The present formalism is also applicable for highly charged colloidal suspensions. In that case, the dynamic anomaly results from the pair correlation due to the long-range Coulomb attractive interactions between macroions and counterions.¹⁵

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