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# Slow Dynamics of Structure and Fluctuations in Supercooled Colloidal Fluids

# Slow dynamics of structure and fluctuations in supercooled colloidal fluids

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The importance of the dynamic singularity of the self-diffusion coefficient $D_S \sim [1 - \Phi(\mathbf{x},t)/\phi_g]^2$ in the coupled diffusion equations recently proposed, the nonlinear deterministic diffusion equation for the average local volume fraction $\Phi(\mathbf{x},t)$ and the linear stochastic diffusion equation for the density fluctuations $\delta n(\mathbf{x},t)$, is emphasized for understanding the slow dynamical behavior of concentrated hard-sphere suspensions, where $\phi_g = (4/3)^3/(7 \ln 3 - 8 \ln 2 + 2)$ is the colloidal glass transition volume fraction. It is shown that there exists a crossover volume fraction $\phi_\beta$, over which $\Phi(\mathbf{x},t)$ describes the formation of long-lived, irregularly shaped domains with $\Phi(\mathbf{x},t) \gtrsim \phi_g$, and $\delta n(\mathbf{x},t)$ describes two-step relaxations with time scales, $t_\beta \sim (1 - \phi/\phi_g)^{-1}$, and $t_\alpha \sim (1 - \phi/\phi_g)^{-2}$, where $\phi$ is the volume fraction of spheres. Thus the slow dynamics of a supercooled hard-sphere colloidal fluid ($\phi_\beta \lesssim \phi < \phi_g$) is explored from a unified viewpoint. [S1063-651X(97)15208-4]

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There has been growing interest in the dynamics of colloidal suspensions over the past two decades [1]. Especially, of great interest is the experimental discovery of a liquid-glass transition in concentrated hard-sphere suspensions [1–3], similar to that in supercooled liquids. Mode coupling theory (MCT) [4,5] has been applied to understand the dynamics of suspensions approaching the glass transition and has stimulated much of the recent theoretical, numerical, and experimental work on concentrated suspensions. Recently, a theoretical approach different from MCT has been proposed by Tokuyama [6] and has been investigated asymptotically [6], analytically [7], and numerically [8]. Results similar to those obtained by MCT have been found, although the basic standpoints in the two theories are quite different [8]. Our previous work has focused mainly on the dynamical behavior of the density fluctuations, such as two-step slow relaxations. In this paper, we discuss not only the slow dynamics of the density fluctuations, but also the clusterlike formation of a glassy phase with $\Phi(\mathbf{x},t) \gtrsim \phi_g$ in the supercooled hard-sphere fluid from a unified viewpoint.

The present paper deals with two kinds of diffusion equations; the nonlinear deterministic diffusion equation for the average number density $n(\mathbf{x},t)$ [9] and the linear stochastic diffusion equation for the density fluctuations $\delta n(\mathbf{x},t)$ around the causal motion $n(\mathbf{x},t)$ [6]. Instead of $n(\mathbf{x},t)$, it is convenient to introduce the average local volume fraction by $\Phi(\mathbf{x},t) = 4\pi a_0^3 n(\mathbf{x},t)/3$, where $a_0$ is a particle radius. On the other hand, the dynamics of density fluctuations can be measured by dynamic light scattering through the self-intermediate scattering function $F_S(\mathbf{k},t)$ [8,10], which is given by the Fourier transform of the autocorrelation function of the density fluctuations $\delta n(\mathbf{x},t)$, where $F_S(\mathbf{k},0) = 1$. Hence we here start with the coupled diffusion equations for $\Phi(\mathbf{x},t)$ and $F_S(\mathbf{k},t)$ [7,8]:

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

$$\frac{\partial}{\partial t} F_S(\mathbf{k},t) = -k^2 \sum_q D_S(\mathbf{k}-\mathbf{q},t) F_S(\mathbf{q},t), \qquad (2)$$

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

$$D_S(\Phi(\mathbf{x},t)) = \frac{D_S^S(\phi)[1 - 9\Phi(\mathbf{x},t)/32]}{1 + [\Phi(\mathbf{x},t)D_S^S(\phi)/\phi_g D_0][1 - \Phi(\mathbf{x},t)/\phi_g]^{-2}} \qquad (3)$$

and the conservation law $(1/V) \int d\mathbf{x}\, \Phi(\mathbf{x},t) = \phi$, were $D_0$ is the single-particle diffusion coefficient, $D_S^S(\phi)$ the short-time self-diffusion coefficient (see Ref. [6] for details), and $V$ the total volume of the system. Here the factor $(9/32)$ in the numerator of Eq. (3) results from the coupling between the direct and short-range hydrodynamic interactions among particles, while the second term in the denominator originates from the many-body correlations of long-range hydrodynamic interactions [9]. The most important feature of the above coupled equations is that the self-diffusion coefficient $D_S(\Phi(\mathbf{x},t))$ becomes zero as $D_S(\Phi) \sim [1 - \Phi(\mathbf{x},t)/\phi_g]^2$ near the transition point $\phi_g$. As was shown in Refs. [6–8], this singular behavior plays an important role in the dynamics of supercooled colloidal fluids for intermediate times, leading to two-step relaxations.

In order to solve the coupled diffusion equations (1) and (2) self-consistently, we first fix the values of the following two parameters as the initial conditions: the particle volume fraction $\phi$ and the initial local volume fraction $\Phi(\mathbf{x},0)$. To integrate those equations, we employ the forward Euler difference scheme with time step $0.01 a_0^2/D_0$ and lattice spacing $0.2 a_0$ in the volume $(128 a_0)^3$ of a three-dimensional simulation system with periodic boundary conditions. In order to
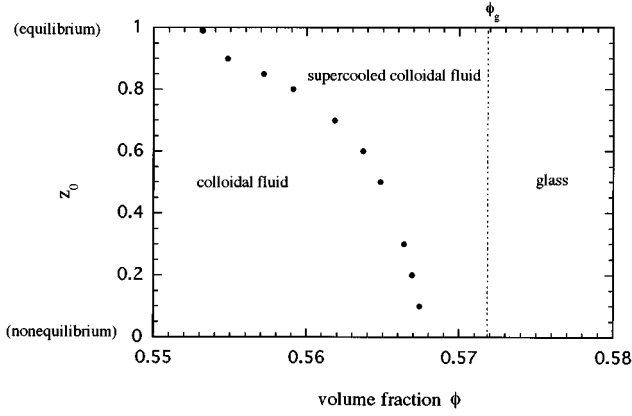
FIG. 1. Schematic phase diagram in the $z_0$-$\phi$ plane for hard-sphere suspensions. The solid circles indicate the crossover volume fraction $\phi_\beta$ and the dotted line the glass transition volume fraction $\phi_g$.

distinguish the initial states from each other qualitatively, we introduce a state parameter $z_0$ by [8]

$$z_0 = 1 - (1/V) \int d\mathbf{x} |1 - \Phi(\mathbf{x},0)/\phi|, \qquad (4)$$

where $0 \le z_0 \le 1$ and $z_0 = 1$ in equilibrium. This measures how close the initial state of the system is to the equilibrium state. 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 satisfy Eq. (4) for a given value $z_0$.

As was shown in Refs. [6–8], there are three kinds of characteristic times: the short time $t_\gamma = 2\pi/[k^2 D_S^S]$, the crossover time $t_\beta \approx 2\pi/[k^2(D_S^S D_S^L)^{1/2}]$ [11], and the long time $t_\alpha = 2\pi/[k^2 D_S^L]$, where $D_S^L = D_S(\phi)$ is the long-time self-diffusion coefficient and $t_\gamma \ll t_\beta \ll t_\alpha$. For short times $t_B \ll t \ll t_\gamma$, the self-diffusion coefficient $D_S(\Phi)$ reduces to the short-time self-diffusion coefficient $D_S^S(\phi)$ since the direct interactions and correlations are negligible, where $t_B$ is the Brownian relaxation time. For long times $t \ge t_\alpha$, on the other hand, $D_S(\Phi)$ reduces to the long-time self-diffusion coefficient $D_S^L(\phi)$ since $\Phi(\mathbf{x},t)$ reaches the equilibrium value $\phi$, following the nonlinear diffusion equation (1). Thus there are in general three characteristic stages for the colloidal fluid ($0 < \phi < \phi_g$). The first is an early stage ($E$) for $t_B \ll t \ll t_\gamma$, where the spatial inhomogeneities are described by $\Phi(\mathbf{x},t) \simeq \exp(-t D_S^S \nabla^2) \Phi(\mathbf{x},0)$, and the relaxation of the density fluctuations obeys the short-time exponential decay $F_S^S(\mathbf{k},t) = \exp(-k^2 D_S^S t)$. The second is an intermediate stage ($I$) for $t_\gamma \ll t \ll t_\alpha$, where the dynamical behavior is complicated because of the singularity of $D_S(\Phi)$. The last is a late stage ($L$) for $t \ge t_\alpha$, where $\Phi(\mathbf{x},t) \simeq \phi$, and $F_S(\mathbf{k},t)$ obeys the long-time exponential decay $F_S^L(\mathbf{k},t) = \exp(-k^2 D_S^L t)$.

In order to investigate the dynamical behavior in stage ($I$), we next calculate the logarithmic derivatives given by $\varphi = \partial \ln|f_k^c - F_S(\mathbf{k},t)|/\partial \ln t$ and $\varphi' = \partial \varphi/\partial \ln t$, where $f_k^c$ is the plateau height given by $f_k^c(z_0) = \lim_{l \to \infty} F_S(\mathbf{k},t;\phi = \phi_g)$

[6–8]. Then $\varphi' = 0$ gives two time roots $t_{b_0}$ and $t_b$, which reveal two fairly flat regions $\varphi = b_0(\phi,z_0,k)$ at $t = t_{b_0}(\phi,z_0,k)$ where $t_\gamma \ll t_{b_0} \ll t_\beta$ and $\varphi = b(\phi,z_0,k)$ at $t = t_b(\phi,z_0,k)$ where $t_\beta \ll t_b \ll t_\alpha$. Hence $F_S(\mathbf{k},t)$ obeys two kinds of power-law decays with exponents $b_0$ and $b$ around $t_\beta$ [6–8]. Thus the intermediate stage further separates into two stages: a formation stage ($F$) for $t_\gamma \ll t \ll t_\beta$ and a shrinkage stage (Sh) for $t_\beta \ll t \ll t_\alpha$. However, this separation occurs only for the range $\phi_\beta \le \phi < \phi_g$, where the crossover volume fraction $\phi_\beta(z_0,k)$ is determined by the equal root $t_{b_0}(\phi_\beta,z_0,k) = t_b(\phi_\beta,z_0,k)$ or $b_0(\phi_\beta,z_0,k) = b(\phi_\beta,z_0,k)$, at fixed values of $z_0$ and $k$ [12]. A schematic phase diagram of nonequilibrium hard-sphere suspensions is shown in Fig. 1, where $\phi_\beta(z_0,k)$ is numerically calculated at $ka_0 = 2.8$ for different values of $z_0$. With increasing volume fraction at a fixed $z_0$, therefore, we observe a progression from colloidal fluid ($0 < \phi < \phi_\beta$) to supercooled colloidal fluid ($\phi_\beta \le \phi < \phi_g$) to glass ($\phi \ge \phi_g$). We expect that in equilibrium ($z_0 = 1$) the crossover volume fraction $\phi_\beta$ may coincide with the melting volume fraction $\phi_m$ ($\sim 0.545$) of hard spheres, while in nonequilibrium ($z_0 = 0$) it reduces to $\phi_g$. In Fig. 2 we show the time evolution of $F_S(\mathbf{k},t)$ at $z_0 = 0.5$ and 0.8 for $\phi = 0.543$, $\phi_\beta(z_0,ka_0)$, and 0.571, where $\phi_\beta(0.5,2.8) = 0.565$ and $\phi_\beta(0.8,2.8) = 0.559$. Below $\phi_\beta$, the scattering function $F_S(\mathbf{k},t)$ decays quickly to zero, while above $\phi_\beta$ the shape of $F_S(\mathbf{k},t)$ becomes very sensitive to the value of $\phi$, forming a shoulder, which becomes a plateau with the height $f_k^c(z_0)$ at $\phi_g$. Thus the dynamical behavior of the supercooled region ($\phi_\beta \le \phi < \phi_g$) in stage ($I$) is quite different from that of the normal region ($0 < \phi < \phi_\beta$). We discuss this next.

In stage ($F$) the glassy regions where the local volume fraction $\Phi(\mathbf{x},t)$ is larger than $\phi_g$ form finite-sized, long-lived, irregularly shaped domains (see Fig. 3). Because of these domains, the smoothing process of the spatial inhomogeneities to the uniform state is slowing down, leading to a structural arrest. Thus the density fluctuations undergo a slow relaxation and obey the power-law decay

$$F_S^F(\mathbf{k},t) = f_k^c(z_0) - A_k(z_0)(t/t_\beta)^{b_0}, \qquad (5)$$

where $A_k = [f_k^c - F_S(\mathbf{k},t_{b_0})](t_\beta/t_{b_0})^{b_0}$. This power-law decay continues up to the crossover time $t_\beta$. For $t \ge t_\beta$, the shrinkage stage (Sh) starts. As is seen in Fig. 3, the glassy domains start to shrink, disappearing very slowly. Because of the glassy domains, the relaxation of the density fluctuations still becomes slow and obeys the so-called von Schweidler decay

$$F_S^{\text{Sh}}(\mathbf{k},t) = f_k^c(z_0) - B_k(z_0)(t/t_\alpha)^b, \qquad (6)$$

where $B_k = [f_k^c - F_S(\mathbf{k},t_b)](t_\alpha/t_b)^b$. The shrinkage and power-law decay continue up to the long time $t_\alpha$, over which the glassy domains disappear. On the other hand, in
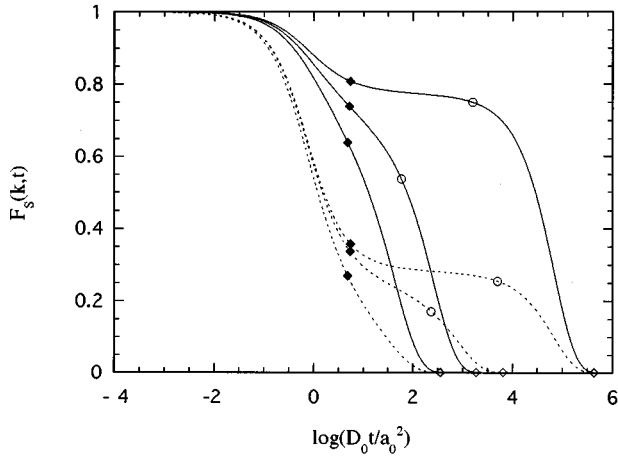
FIG. 2. Self-intermediate scattering function $F_S(k,t)$ versus dimensionless time $D_0 t/a_0^2$ for different volume fractions (from left to right): 0.543, $\phi_\beta$ and 0.571 at $z_0=0.8$ (solid lines) and 0.5 (dotted lines), where $\phi_\beta=0.559$ ($z_0=0.8$) and 0.565 (0.5), and $ka_0=2.8$. The symbols indicate the time scales: $t_\gamma$ ($\blacklozenge$), $t_\beta$ ($\bigcirc$), and $t_\alpha$ ($\diamondsuit$).

stage ($I$) of the normal region there is neither a formation of domains nor a power-law decay (see Figs. 2 and 4). Hence the spatial inhomogeneities become smooth monotonically, obeying Eq. (1), while the relaxation gradually changes from the short-time exponential decay $F_S^S(\mathbf{k},t)$ to the long-time exponential decay $F_S^L(\mathbf{k},t)$.

Figure 5 shows schematically the dynamic behavior of phases in the supercooled region at $z_0=0.8$ and $ka_0=2.8$. With increasing time, the system thus undergoes the four characteristic stages: the early stage ($E$) where the system is
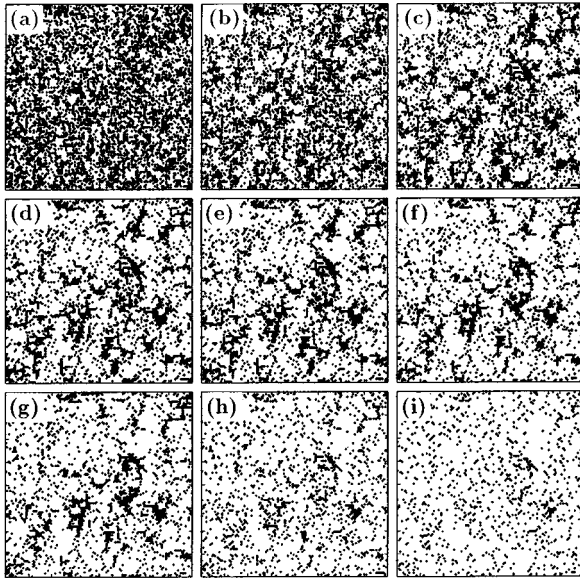


FIG. 3. Typical configurations, projected onto a plane, of pattern-evolution processes at $\phi=0.571$ in the supercooled region $\phi_\beta \lesssim \phi < \phi_g$ for dimensionless times (a) 1, (b) 6.35($t_\gamma$), (c) $10^2$, (d) $10^3$, (e) 1279($t_\beta$), (f) $10^4$, (g) $10^5$, (h) $4.4\times 10^5$($t_\alpha$), and (i) $10^6$, where $z_0=0.8$. The system size is $(128a_0)^2$, and the glassy regions are colored black.
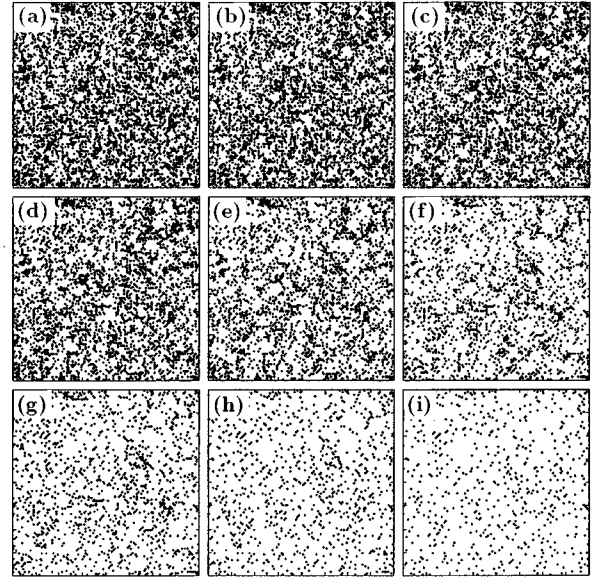


FIG. 4. Typical configurations, projected onto a plane, of pattern-evolution processes at $\phi=0.543$ in the normal region $0 \leqslant \phi < \phi_\beta$ for dimensionless times (a) 1, (b) 4.87($t_\gamma$), (c) 10, (d) 20, (e) 42, (f) $10^2$, (g) 200, (h) 359($t_\alpha$), and (i) $10^3$, where $z_0=0.8$. The system size is $(128a_0)^2$, and the glassy regions are colored black.

occupied by the colloidal fluid with $D_S^S$, the formation stage ($F$), the shrinkage stage (Sh), and the late stage ($L$) where the system is occupied by the colloidal fluid with $D_S^L$.

In conclusion, we have shown that there exists a crossover volume fraction $\phi_\beta(z_0,k)$, over which the fluid and glass phases coexist on the time scale of order $t_\beta(\phi,k)$. Finally, in order to test our results, we encourage experimentalists to measure the self-intermediate scattering function $F_S(\mathbf{k},t)$ for different values of the separation parameter $\sigma$ and also its plateau height $f_k^c$. Then, one can calculate the state param-
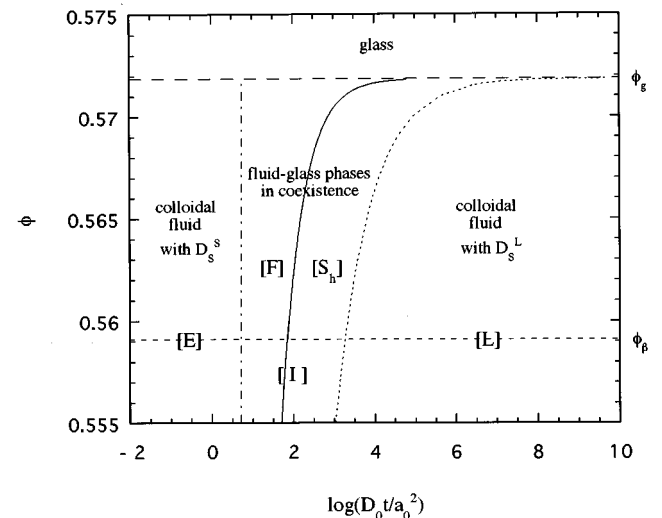


FIG. 5. Characteristic stages in the supercooled region $\phi_\beta \lesssim \phi < \phi_g$ at $z_0=0.8$ and $ka_0=2.8$. The dot-dashed line indicates the characteristic time $t_\gamma$, the solid line $t_\beta$, and the dotted line $t_\alpha$.

eter $z_0$ by fitting the theoretical plateau height $f_k^c(z_0)$ with experimental ones at a given value of $k$. Hence one can guess how much in nonequilibrium the experimental system is initially. Once the value of $z_0$ is found, one can thus ana-lyze experimental results in terms of the present theory. This will be discussed elsewhere.

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