Glass Transition in Colloidal Hard Spheres: Mode-Coupling Theory Analysis

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Coherent intermediate scattering functions are measured by dynamic light scattering for several wave vectors around the structure factor peak on metastable colloidal fluids and glasses of hard spherical particles. The results are quantitatively described by a combination of the α and β processes. The scaling laws and factorization property predicted by mode-coupling theory are verified.

Much of the recent work on the liquid-glass transition (GT) has been stimulated by the predictions of mode-coupling theory (MCT) [1]. This theory predicts a dynamical singularity during supercooling of a liquid where its structure is arrested [2,3]. Suspensions of identical colloidal spheres stabilized by thin macromolecular surface coatings offer several advantages over other materials for both fundamental studies of the GT and assessment of the detailed dynamics predicted by MCT. First, they appear to be the simplest experimental system to show a GT since the interparticle forces are like those of hard spheres [4-6]. Second, the motion of the particles is heavily damped by the suspending liquid so that phonon-activated hopping motions, which may restore ergodicity in molecular glasses, should be strongly reduced and, consequently, the GT in suspensions should be close to the ideal GT prediction by the basic version of MCT. Third, the dynamics of suspensions can be studied by dynamic light scattering (DLS). This gives access to correlations in time over a range of more than nine decades and, through varying the wave vector q, a range of correlations in space.

MCT predicts that beyond the time scale t_0 of microscopic motions the relaxation of the intermediate scattering function (ISF or number density autocorrelator), $f(q,\tau)$, proceeds in two stages. These are connected by two time scales, τ_α and τ_β, which diverge as the separation parameter $\sigma = c_0(\phi - \phi_c)/\phi_c$ approaches zero; $\tau_\alpha = t_0|\sigma|^{-\gamma}$ and $\tau_\beta = t_0|\sigma|^{-\delta}$, with $\gamma = (1/2a) + (1/2b)$ and $\delta = (1/2a)$ [2,3]. Here ϕ is the particle volume fraction and ϕ_c its critical value for the GT. The dynamics in the regime $t_0 \ll \tau \ll \tau_\alpha$ is governed by the β process where

$$f(q,\tau) = f_c(q) + |\sigma|^{1/2}h(q)g_\pm(\tau/\tau_\beta). \tag{1}$$

Neither the universal master functions $g_\pm(\tau/\tau_\beta)$ (the subscript "$\pm$" denoting the sign of σ), the nonergodicity parameter $f_c(q)$, nor the critical amplitude $h(q)$ depend on concentration. The above factorization of spatial and temporal variables suggests that localized dynamics of caged particle clusters promote relaxation of density fluctuations to $f_c(q)$. On the fluid side of the transition ($\sigma < 0$) τ_β marks the crossover to the second relaxation stage, the α process, describing cage breakdown and allowing large-scale diffusion, for which a second scaling law holds,

$$f(q,\tau) = f_c(q)G(q,\tau/\tau_\alpha). \tag{2}$$

In the glass ($\sigma > 0$) the α process is arrested but the β process persists and saturates at long times to the value $g_+(\tau \to \infty) = (1-\lambda)^{-1/2}$. The quantities a and b are specified by the exponent parameter λ, in turn determined by the static structure factor $S(q)$. In comparing the dynamics of molecular glass formers with MCT, λ is generally treated as a free parameter [3]. For the hard sphere system approximations for $S(q)$ are available and the exponents and the functions appearing in Eqs. (1) and (2) have been evaluated (in particular, $a = 0.301$, $b = 0.545$, $\lambda = 0.758$, and $c_0 \cong 1.2$) [7,8].

As in previous work [4-6], we use suspensions of polymer particles (radius $R = 205$ nm) made nearly transparent, and therefore suitable for light scattering studies, by matching the refractive index of the suspending liquid to that of the particles. Thin steric barriers chemically grafted to the particle surfaces provide steeply repulsive interparticle forces. Identification of freezing and melting volume fractions, $\phi_f = 0.494$ and $\phi_m = 0.543$ (± 0.002), in accord with computer results for the perfect hard spheres, confirms the viability of these suspensions as model hard sphere systems [4,6,9].

Where previous MCT analyses of $f(q,\tau)$ measured on concentrated metastable colloidal fluids could be explained by the β process only [5,7], the more extensive measurements reported here show that *both* α and β processes are necessary for the description of the slow relaxation of the ISF's in a simple hard sphere system on the fluid side of the GT. In addition to verification of the scaling properties of these processes, the analysis provides the first comprehensive confirmation of the factorization property of the β relaxation.

Measurements of duration $T = 1000$ s were made of the intensity autocorrelation function $g^{(2)}(q,\tau) = \langle I(q,0) \times I(q,\tau)\rangle_T / \langle I(q)\rangle_T^2$ on eight metastable fluid samples in the concentration range 0.494–0.587. In the ergodic case all spatial configurations are accessible in the course of the measurement, so that the time average $\langle \cdots \rangle_T$ constitutes an ensemble average and the ISF is calculated in the usual way from $sf^2(q,\tau) = g^{(2)}(q,\tau) - 1$ [10] ($s \cong 0.2$ is the spatial coherence factor). The transition to noner-

godicity (fluid to glass) is indicated by a strong variation in $\langle I \rangle_T$ for different scattering volumes in the sample as well as a significant reduction in the mean square amplitude, $g^{(2)}(q,0)$, of intensity fluctuations. In the nonergodic glass phase, calculation of the (ensemble-averaged) ISF from $g^{(2)}(q,\tau)$ must then take into account both the fluctuating and nonfluctuating components of the scattered radiation associated with fluctuating and arrested structure, respectively. The derivation of a procedure for achieving this and its experimental verification have been described previously [6,10,11].

Figure 1 shows a representative set of ISF's, made at wave vectors below, near, and above the position q_m of the main peak in $S(q)$. Increasing the concentration from freezing ($\phi_f = 0.494$) to $\phi = 0.574$ lengthens the overall decay time of $f(q,\tau)$ by nearly four decades, from about 10^5 to 10^9 μs, and significantly three relaxation stages become increasingly apparent; the crossover times between these stages are indicated by points of inflection which, for $\phi = 0.574$, occur at around 10^4 and 10^7 μs. The fastest of these processes [indicated by the dashed curve in Fig. 1(b)] is associated with the microscopic diffusive motions of particles within their instantaneous neighbor cages and accounts for the initial few percent of the decay of $f(q,\tau)$. This is followed by two slower processes whose time scales lengthen and separate with increasing concentration. When the concentration is increased further by only 1%, from 0.574 to 0.581, $f(q,\tau)$ saturates to an almost constant value indicating the presence of concentration fluctuations whose duration significantly exceeds 1000 s. Thus, the occurrence of the kinetic GT is indicated at a concentration ϕ_c (0.574 $< \phi_c < 0.581$) by the cessation of large-scale diffusion and arrest of the fluid structure on the experimental time scale.

A significant feature of these colloidal systems is that the kinetic GT coincides with the suppression of homogeneously nucleated crystallization [5,6]. Below ϕ_c roughly isometric crystals are nucleated homogeneously throughout the sample. However, just above ϕ_c much larger crystals grow slowly on highly asymmetric nuclei. We have suggested elsewhere [12] that these asymmetric nuclei are shear-induced structures, resulting from the tumbling process used to randomize the particle positions prior to DLS measurements, which remain frozen in the structurally arrested glass. We speculate that infrequent small-scale collective particle rearrangements are responsible not only for the slow growth of these asymmetric crystals but also for the small remnant decay in $f(q,\tau)$ at long times when $\phi > \phi_c$ (see Fig. 1).

On the fluid side of the GT ($\sigma < 0$) MCT has been fitted to the data, shown in Fig. 1, by combining the α and β processes of Eqs. (1) and (2) using the master functions $g_\pm(\tau/\tau_\beta)$ and $G(q,\tau/\tau_\alpha)$ calculated for the hard sphere system [7,8]. In this procedure the amplitudes $h(q)$ and $f_c(q)$, the separation parameter σ, and the time scale τ_α are treated as adjustable parameters,
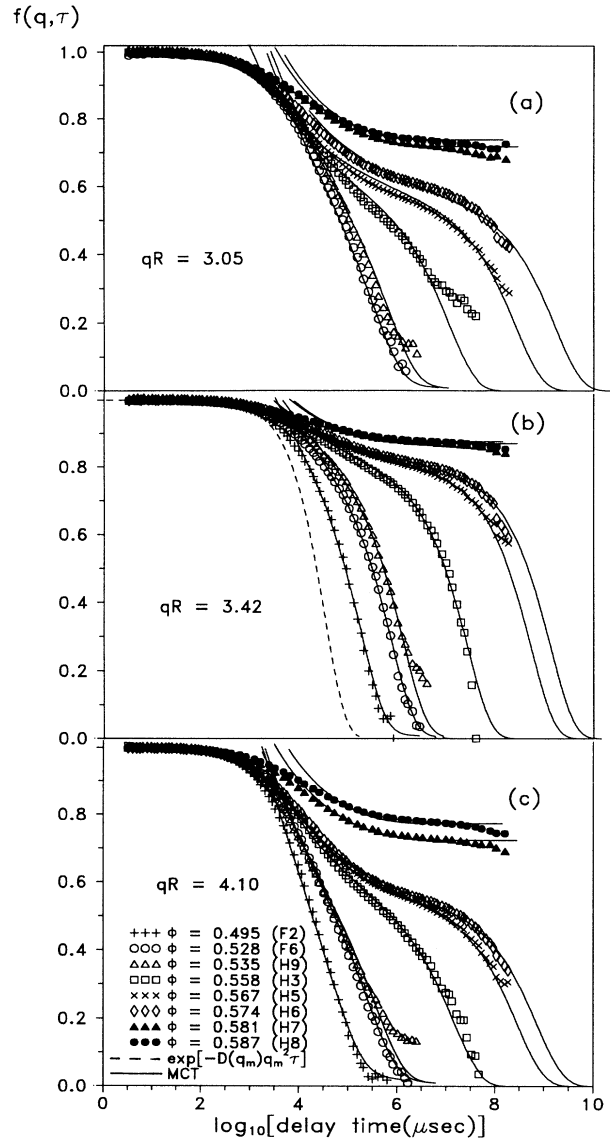

FIG. 1. Intermediate scattering functions for indicated values qR, the product of the scattering vector and the particle radius; the main maximum in $S(q)$ for the hard sphere fluid at freezing is located at $q_m R = 3.46$. The symbols refer to the experimental data for volume fractions indicated. The solid curves are the MCT fits. The dashed curve in (b) is the quantity $\exp[-q^2 D(q)\tau]$ representative of the microscopic dynamics, where $D(q)$ is the short-time q-dependent collective diffusion coefficient.

subject to the constraints of MCT that $h(q)$ and $f_c(q)$ are independent of concentration and that σ is independent of the scattering vector. Thus the only global parameter is the scaling time τ_α and it therefore absorbs most of the random and systematic errors in the data.

We reiterate that the MCT predictions apply only to the slow structural relaxation processes that emerge at high concentration and whose time scales lie beyond that
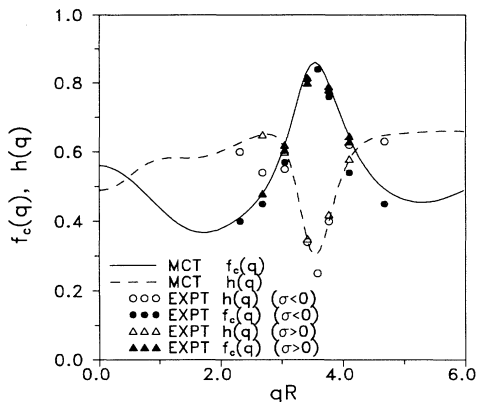
FIG. 2. Nonergodicity parameters $f_c(q)$ and critical amplitudes $h(q)$.

of the microscopic motions. It is evident from Fig. 1 that beyond the influence ($\simeq 10^4$ μs) of the microscopic diffusive motions MCT fits are possible over a matrix of scattering vectors and suspension concentrations. At $q = 3.05$ small systematic differences between MCT and experiment are evident. Here the amplitude $S(q)$ of the (un-normalized) coherent ISF, $S(q)f(q,\tau)$, is roughly one-tenth its peak value at $q = q_m$ and, as suggested elsewhere [11], both incoherent scattering associated with the small ($\simeq 5\%$) spread in particle size and multiple scattering may influence the experimental results.

A detailed MCT analysis of colloidal glasses is contained in a previous publication [6] but, for completeness, we include some results here. We assume, for $\phi > \phi_c$, that the α process is arrested and we accordingly analyze the data in terms of the β process only [Eq. (1)]. Because of the statistical errors in the experimental data, small variations in $f_c(q)$ and $h(q)$ from those found for $\sigma < 0$ have to be tolerated to obtain the theoretical results
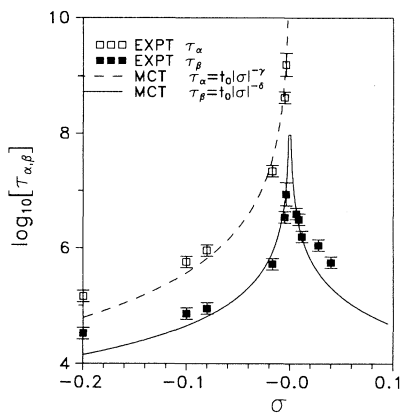

FIG. 3. Scaling times τ_α and τ_β vs the separation parameter σ. The MCT results are given by $\tau_\alpha = t_0|\sigma|^{-\gamma}$ and $\tau_\beta = t_0|\sigma|^{-\delta}$ and t_0 was calculated from τ_α and σ.
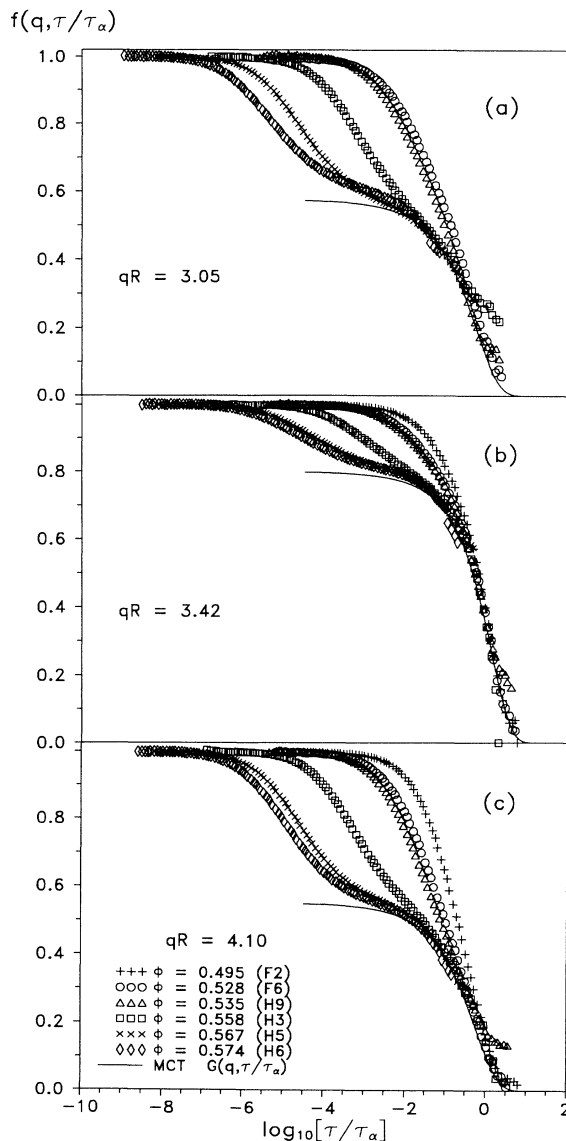

FIG. 4. Intermediate scattering functions expressed in terms of the scaled time τ/τ_α. The solid curves are the q-dependent master functions, $f_c(q)G(q,\tau/\tau_\alpha)$, of the α process.

in Fig. 1.

Figures 2 and 3 show the amplitudes and scaling times required for the MCT fits to the data; both are in good agreement with predictions. The predicted universality of the scaling times is confirmed by our finding that, apart from a few percent random variation, τ_α and by implication τ_β are independent of scattering vectors. τ_α and τ_β also show the predicted divergence and separation; for $\sigma = -0.1$, $\tau_\alpha/\tau_\beta \simeq 8$ while for $\sigma = -0.0035$, the smallest negative separation from the GT, $\tau_\alpha/\tau_\beta \simeq 180$. The characteristic times of the β process are consistent with the predicted symmetry about the GT. However, as one
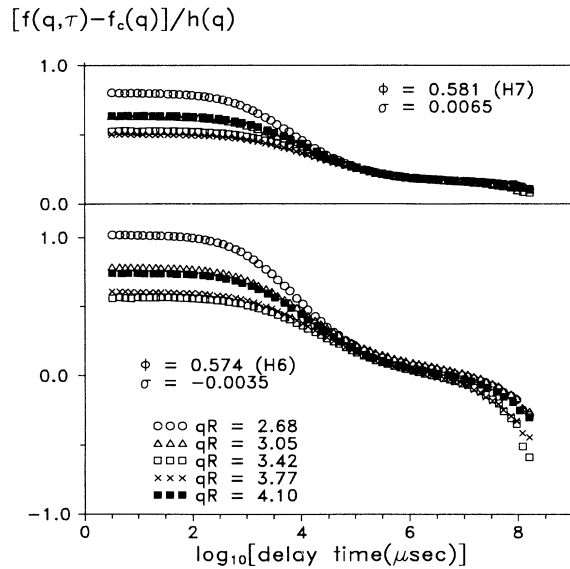
$[f(q,\tau)-f_c(q)]/h(q)$

FIG. 5. Intermediate scattering functions scaled according to Eq. (1). The top and bottom figures represent results for samples just above $(\sigma=0.0065)$ and below $(\sigma=-0.0035)$ the GT.

goes deeper into the hard sphere glass $(\sigma>0.03)$ deviations from the theory possibly due to the failure of the asymptotic results of MCT are apparent. Note that no parameters are involved in the consistency checks illustrated in Figs. 2 and 3.

A conventional test of the superposition principle for the α process is to plot the ISF's in terms of the rescaled time τ/τ_α, as shown in Fig. 4. The sections of the ISF's which obey the principle also follow the predicted master functions. However, there is a significant fraction of the ISF's, amounting to about 15% at the structure factor peak and 40% at the other wave vectors, which does not scale. This departure from scaling corresponds to the β process and spans a time window from about 10^4 μs (the time scale of the microscopic motion) to the crossover time τ_β which, for $\phi=0.574$ $(\sigma=-0.0035)$, is about 10^7 μs. As shown in Fig. 5 (lower figure), this is precisely the temporal range over which the factorization property

of the β process is satisfied, i.e., where the quantity $[f(q,\tau)-f_c(q)]/h(q)$ is independent of q. The small but systematic deviations from this factorization seen at long times on the fluid side of the GT can be attributed to the α process. These deviations are not apparent in the glass phase (shown for $\phi=0.581$, $\sigma=0.0065$ in the top part of Fig. 5), where the α process is arrested.

We conclude that the GT observed in these suspensions approximates the ideal GT predicted by the basic version of MCT. On the fluid side of the GT, Figs. 4 and 5, respectively, show that neither the α process alone nor the β process alone can account for the slow relaxation of concentration fluctuations. At a concentration ϕ_c the α process is arrested but the β process persists.

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