Probing the Equilibrium Dynamics of Colloidal Hard Spheres above the Mode-Coupling Glass Transition

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We use dynamic light scattering and computer simulations to study equilibrium dynamics and dynamic heterogeneity in concentrated suspensions of colloidal hard spheres. Our study covers an unprecedented density range and spans seven decades in structural relaxation time, τ_α, including equilibrium measurements above φ_c, the location of the glass transition deduced from fitting our data to mode-coupling theory. Instead of falling out of equilibrium, the system remains ergodic above φ_c and enters a new dynamical regime where τ_α increases with a functional form that was not anticipated by previous experiments, while the amplitude of dynamic heterogeneity grows slower than a power law with τ_α, as found in molecular glass formers close to the glass transition.

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Hard-sphere assemblies often constitute the simplest model to tackle a variety of fundamental questions in science, from phase transitions in condensed matter physics to the mathematics of packing or optimization problems in computer science. Experimentally, hard-sphere systems are obtained using colloidal particles [1], emulsions, or granular materials [2]. When crystallization is avoided, e.g., by introducing size polydispersity, hard spheres at thermal equilibrium become very viscous and eventually form an amorphous solid [3] at large volume fraction, φ, in analogy to the glass transition of molecular liquids [4] and the jamming transition of grains [2]. However, the nature of the colloidal glass transition, its precise location, the functional form of the structural relaxation time divergence, and the connection between slow dynamics and kinetic heterogeneities remain largely open issues [5,6].

For hard spheres at thermal equilibrium, several distinct glass transition scenarios have been described. In the first, the viscosity or, equivalently, the time scale for structural relaxation, $\tau_\alpha(\varphi)$, diverges algebraically:

$$\tau_\alpha(\varphi) \sim (\varphi_c - \varphi)^{-\gamma}. \tag{1}$$

This is predicted [7] by mode-coupling theory (MCT), and supported by the largest set of light scattering data to date [5]. Packing fractions $\varphi_c \approx 0.57$–0.59 are the most often quoted values for the location of the "colloidal glass transition." It is widely believed that a truly nonergodic state is obtained at larger φ [1,3,5]. Within MCT, the amplitude of dynamic heterogeneity quantified by multipoint correlation functions also diverges algebraically. In particular, the four-point dynamic susceptibility should

diverge as [8] $\chi_4 \sim (\varphi_c - \varphi)^{-2} \sim \tau_\alpha^{2/\gamma}$, a prediction that has not been tested experimentally.

Several alternative scenarios [9–11] suggest a stronger divergence:

$$\tau_\alpha(\varphi) = \tau_\infty \exp\left[\frac{A}{(\varphi_0 - \varphi)^\delta}\right]. \tag{2}$$

Equation (2) with $\delta = 1$ is frequently used to account for viscosity data [6] because it resembles the Vogel-Fulcher-Tammann (VFT) form used to fit the viscosity of molecular glass formers [4], with temperature replaced by φ. Moreover, it is theoretically expected on the basis of free volume arguments [9], which lead to the identification $\varphi_0 \equiv \varphi_{\rm rcp}$, the random close packing fraction where osmotic pressure diverges. Kinetic arrest must occur at $\varphi_{\rm rcp}$ (possibly with $\delta = 2$ [10]), because all particles block each other at that density [10,12,13]. Entropy-based theories and replica calculations [11] predict instead a divergence of τ_α at an ideal glass transition at $\varphi_0 < \varphi_{\rm rcp}$, where the configurational entropy vanishes but the pressure is still finite. Here, the connection to dynamical properties is made through nucleation arguments [14] yielding Eq. (2), with δ not necessarily equal to unity [15]. In this context, the amplitude of dynamic heterogeneity should increase only moderately, typically logarithmically slowly in τ_α [16].

In molecular glass formers where dynamical slowing down can be followed over as many as 15 decades, the transition from an MCT regime, Eq. (1), to an activated one, Eq. (2), has been experimentally demonstrated [4]. For colloidal hard spheres, the situation remains controversial, because dynamic data are available over a much

smaller range [1,5,6,17], typically five decades or less. Crucially, equilibrium measurements were reported only for $\varphi < \varphi_c$, leaving unknown the precise nature and location of the divergence. Theoretical claims exist that the cutoff mechanism suppressing the MCT divergence in molecular systems is inefficient in colloids due to the Brownian nature of the microscopic dynamics, suggesting that MCT could be virtually exact [18]. This viewpoint is challenged by more recent MCT calculations [19], and by computer studies of simple model systems where MCT transitions are avoided both for stochastic and Newtonian dynamics [20,21].

Here, we settle several of the above issues by studying the equilibrium dynamics of colloidal hard spheres using dynamic light scattering and computer simulations. By extending previous data by at least 2 orders of magnitude in τ_α, we establish that the volume fraction dependence of both τ_α and χ_4 follows MCT predictions only in a restricted density range below our fitted $\varphi_c \approx 0.59$. Unlike previous studies, we provide equilibrium measurements *above* φ_c, thereby proving unambiguously that in our sample the algebraic divergence at φ_c is absent. Instead, a new regime is entered at larger φ, where the dynamics is well described by Eq. (2) with $\delta \approx 2$ and φ_0 much larger than φ_c. The amplitude of kinetic heterogeneities then grows slower than a power law with τ_α, as in molecular glasses close to the glass transition.

Dynamic light scattering (DLS) experiments are performed in the range $0.01 < \varphi < 0.5981$. We use poly-(methyl methacrylate) (PMMA) particles of average diameter $\sigma = 260$ nm, stabilized by a thin layer of grafted poly-(12-hydroxy stearic acid) (PHSA). The size polydispersity, about 10%, is large enough to prevent crystallization on a time scale of at least several months. The particles are suspended in a mixture of cis-decalin and tetralin that almost perfectly matches their average refractive index, allowing the dynamics to be probed by DLS. Additionally, a careful analysis of the combined effects of optical and size polydispersity shows that we probe essentially the self-part of the intermediate scattering function [22]:

$$F_s(q, t) = \left\langle \frac{1}{N} \sum_{j=1}^{N} e^{i\mathbf{q}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]} \right\rangle. \quad (3)$$

Here, $\mathbf{r}_j(t)$ is the position of particle j at time t, $\mathbf{q}$ is the scattering vector ($q\sigma = 6.5$, close to the first peak of the static structure factor) and brackets indicate an ensemble average. A combination of traditional [23] and multi-speckle [24] DLS is used to measure the full decay of $F_s(q, t)$. We carefully check equilibration by following the evolution of the dynamics after initialization, until F_s stops changing over a time window of at least $10\tau_\alpha$. Samples are prepared by dilution, starting from a very concentrated batch obtained by centrifugation. All volume fractions relative to that of the initial batch are obtained with a relative accuracy of 10^{-4}, using an analytical bal-

ance and literature values for particle and solvent densities [17]. Relative volume fractions are converted to absolute ones by comparing the experimental φ dependence of the short-time self-diffusion coefficient measured by DLS to two sets of theoretical calculations [25] at low density, $\varphi \leq 0.2$. For less polydisperse samples, this calibration method yields φ values compatible with those obtained by mapping the experimental freezing fraction to $\varphi_f = 0.494$ [26]. The remaining uncertainty on the absolute φ is about 5%, because [25] contains two slightly different predictions. To ease the comparison with the simulations, we set the absolute φ, within this uncertainty range, so that our experimental and numerical τ_α closely overlap for $\varphi > 0.55$.

We use a standard Monte Carlo algorithm [21] to study numerically a 50:50 binary mixture of hard spheres of diameter σ and 1.4σ, known to efficiently prevent crystallization. We work in a three dimensional space with periodic boundary conditions, and mainly use $N = 10^3$ particles. No noticeable finite size effects were found in runs with $N = 8 \times 10^3$ particles performed for selected state points. In an elementary move, a particle is chosen at random and assigned a random displacement drawn within a cubic box of linear size 0.1σ centered around the origin. The move is accepted if the hard-sphere constraint remains satisfied. One Monte Carlo step corresponds to N such attempts. The dynamics is characterized by the self-intermediate scattering function, Eq. (3), measured for $q\sigma = 6.1$, close to the first diffraction peak.

Representative $F_s(q, t)$ obtained by DLS are plotted in Fig. 1, showing that the relaxation is fast and monoexponential at low φ, while a two-step decay is observed when increasing φ, reflecting the increasingly caged motion of particles in dense suspensions [3]. We measure the structural relaxation time by fitting the final decay of F_s to a stretched exponential, $F_s(q, t) = B \exp[-(t/\tau_\alpha)^\beta]$.

Figure 2(a) shows $\tau_\alpha(\varphi)$ for both experiments and simulations. Time units are adjusted to maximize the overlap
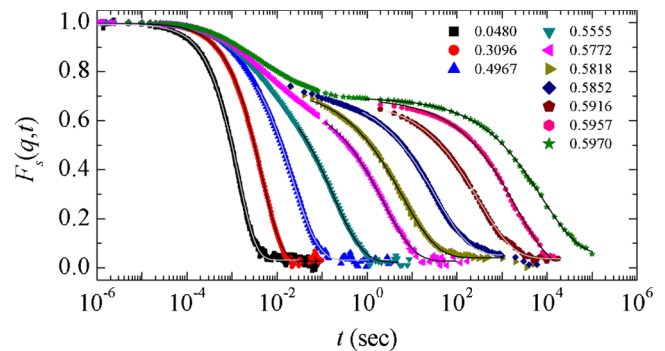

FIG. 1 (color online). Time dependence of the self-intermediate scattering function $F_s(q, t)$ in DLS experiments at $q\sigma = 6.5$ for representative volume fractions. Lines are stretched exponential fits to the final decay, yielding relaxation times spanning about 7 decades. Ergodicity is preserved above the (avoided) MCT glass transition at $\varphi_c \approx 0.59$.

(≈ 5.5 decades) of both data sets at high φ. Our experimental data are well fitted by Eq. (1) in the range $0.49 < \varphi \leq 0.585$, with $\varphi_c = 0.590 \pm 0.005$ and $\gamma = 2.5 \pm 0.1$. For the slightly less polydisperse sample of Ref. [5], a similar power law behavior with $\gamma \approx 2.7$ and $\varphi_c = 0.571–0.595$ was reported, the two quoted values of φ_c stemming from experimental uncertainty in the volume fraction determination. However, our measurements for the largest densities strongly deviate from the MCT fit. Attempts to include points at $\varphi > 0.59$ in the MCT fit yield unphysically large values of γ. Similar deviations are found in our simulations, showing that hydrodynamic interactions play little role in experiments performed at large φ, although they probably explain the discrepancy with simulations at low volume fraction; see Fig. 2(a). Therefore, our results unambiguously demonstrate that the mode-coupling singularity is absent in our hard-sphere colloidal system, as is also found in molecular glass formers [4].

What is the fate of the fluid phase above φ_c? Figures 2(a) and 2(c) show that the increase of τ_α at high φ is extremely well described by an exponential divergence, Eq. (2). We find that the data can be fitted well using the conventional form with $\delta = 1$, yielding $\varphi_0(\delta = 1) \approx 0.614 \pm 0.002$.
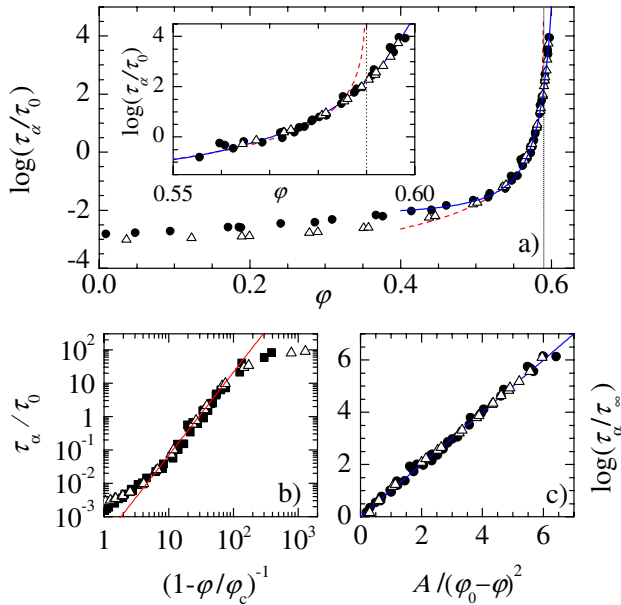

FIG. 2 (color online). (a) Relaxation time scale τ_α for hard spheres in experiments (black circles) and simulations (open triangles), respectively, in units of $\tau_0 = 1$ sec and $\tau_0 = 7 \times 10^4$ MC steps. The red dashed line is a power law fit, Eq. (1), with $\varphi_c = 0.590$ (vertical dotted line) and $\gamma = 2.5 \pm 0.1$. The continuous blue line is a fit to DLS data using Eq. (2), with $\varphi_0 = 0.637$ and $\delta = 2$. The zoom in the inset shows that the MCT singularity is absent. (b) Same data plotted against $1/(1 - \varphi/\varphi_c)$. A straight line with slope γ is obtained in an MCT regime covering almost 3 decades in τ_α. (c) Data for $\varphi > 0.41$ plotted using reduced variables with $\varphi_0 = 0.637$ and 0.641 for experiments and simulations, respectively.

This is consistent with previous analysis of viscosity data [6]. However, the quality of the fit improves when the exponent δ is allowed to depart from unity. The optimal value, robust for both experimental and numerical data, is $\delta = 2.0 \pm 0.2$, which yields our best estimate for the location of the dynamic glass transition: $\varphi_0 \approx 0.637 \pm 0.002$ (experiments) and $\varphi_0 \approx 0.641 \pm 0.002$ (simulations). Figure 2(c) shows the linear dependence of $\log \tau_\alpha$ on $(\varphi_0 - \varphi)^{-2}$, demonstrating the exponential nature of the dynamic singularity.

The behavior of dynamical heterogeneity provides additional evidence of a crossover from a restricted MCT regime to an "activated" type of dynamics. Using methods detailed in [27,28], we study the evolution of the three-point dynamic susceptibility defined by: $\chi_\varphi(q, t) \equiv \partial F_s(q, t)/\partial \varphi$. This linear response function is directly connected to a four-point dynamic susceptibility: $\chi_4(q, t) = N\langle \delta F_s(q, t)^2 \rangle$, where $\delta F_s(q, t)$ denotes the fluctuating part of the self-intermediate function; χ_4 is a powerful tool to quantify dynamic heterogeneity in glass formers [16], because it represents the average number of molecules whose dynamics are correlated. In hard spheres, the following relation holds [27]:

$$\chi_4(q, t) = \chi_4(q, t)|_\varphi + \rho k_B T \kappa_T [\varphi \chi_\varphi(q, t)]^2, \quad (4)$$

where ρ is the number density, κ_T the isothermal compressibility (measured in simulations, taken from the Carnahan-Starling equation of state in experiments), and $\chi_4(q, t)|_\varphi$ denotes the value taken by $\chi_4(q, t)$ in a system where density is strictly fixed. Only the second contribution to $\chi_4(q, t)$ in (4) can be accessed experimentally, but both terms can be determined in simulations. We obtain $\chi_\varphi(q, t)$ by applying the chain rule to the fitted F_s (B, τ_α, β) [28], where the φ dependence of B, τ_α, β is fitted by smooth polynomials. Our results are independent of the choice of fitting functions, and consistent with that obtained from finite differences between data at nearby φ, when available. Figure 3 shows the peak of dynamical susceptibilities as a function of φ. First, we numerically establish in Fig. 3(a) that the term comprising χ_φ is the main contribution to χ_4 when $\varphi > 0.52$, implying that a good estimate of χ_4 can be obtained using three-point functions in hard spheres, as surmised in [27], and established for molecular glass formers in [8]. For both simulations and experiments, the MCT prediction for the algebraic divergence of $\chi_4(q, t)$ only holds over a limited density range. Indeed, when plotted against τ_α, χ_4 eventually grows slower than a power law, as found for the size of dynamically correlated regions in molecular glasses close to the glass transition [28]—a hallmark of activated dynamics [16].

Our results establish the existence of a nontrivial, exponential divergence of $\tau_\alpha(\varphi)$ at a critical volume fraction $\varphi_0 \approx 0.637$ much above the putative "colloidal glass transition" at $\varphi_c \approx 0.59$. It is natural to ask whether φ_0 and φ_{rcp} coincide. This is a difficult question because φ_{rcp} can
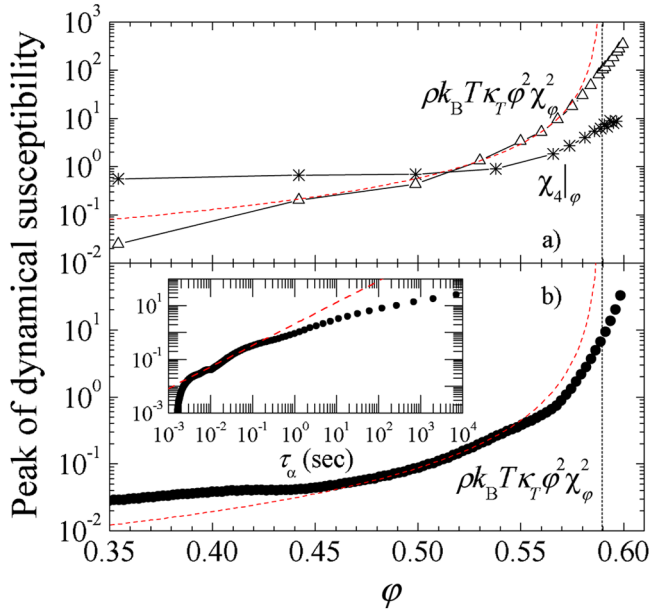
FIG. 3 (color online).   Peak of dynamic susceptibilites, Eq. (4), measured in (a) simulations and (b) experiments. In (a) both contributions to χ_4 are compared, validating χ_φ as a valuable tool to quantify dynamic heterogeneity in hard spheres. The predicted MCT algrebraic divergence (red dashed line) holds over a small density range. The inset shows that the size of dynamic heterogeneities grows slower than a power law at large τ_α, as found in molecular glass formers.

always be shifted to a larger value by trading order and packing [12]. For the binary mixture studied here, the on-set of jamming has been located at $\varphi_J = 0.648$ [13]. Furthermore, for 10% polydispersity, the estimate $\varphi_{rcp} \approx 0.67$ was obtained in numerical work [29], well above φ_0. Finally, we have employed Monte Carlo simulations to produce disordered hard-sphere configurations with finite pressure above φ_0 by a very fast compression of fluid configurations used to produce the equilibrium data in Fig. 1 (open symbols). These results support the possibility that $\varphi_0 < \varphi_{rcp}$, implying a fundamental difference [30] between the glass [11] and jamming [13] transitions in hard spheres.

In conclusion, we report a set of dynamic data for a well-known colloidal hard-sphere system covering an unprece-dented dynamic range of equilibrium relaxation time scale. While the onset of dynamical slowing can be described by an MCT divergence at a critical volume fraction φ_c, upon further compression a crossover from an algebraic to an exponential divergence at a much larger volume fraction φ_0 is observed, accompanied by a similar crossover for the growth of dynamical correlations. Our results show that the apparent singularity at φ_c does not correspond to a genuine "colloidal glass transition", suggesting that the MCT tran-sition is generally avoided in colloidal materials, just as in molecular glass formers.

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