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Glass Transition and Dynamical Heterogeneities in Charged Colloidal Suspensions under Pressure

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Constant-pressure Monte Carlo simulations have been performed to study the static and dynamical properties of a liquidlike ordered suspension of like-charged colloidal particles subjected to a sudden compression. We report for the first time a liquidlike ordered monodisperse suspension undergoing a glass transition at a very low volume fraction ($\phi = 0.003$) and existence of dynamical heterogeneities near the glass transition. Mobile particles have been identified using the non-Gaussian parameter for the self-part of the Van Hove correlation function, and they are found to form clusters. The pressure dependence of mean cluster size and the cluster-size distribution of the mobile particles are discussed.

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Glassy phase can be obtained by abruptly cooling (quenching) and/or compressing (pressure crush) a liquid [1]. Many liquids undergoing glass transition exhibit nonexponential decay of time correlation functions and non-Arrhenius temperature dependence of relaxation time with decreasing temperature [2]. In the recent past, researchers have focused their attention on nonexponential relaxation by performing computer simulations [3,4] and experiments [5,6] on atomic systems. These studies suggest that a superposition of different relaxation processes, or dynamical heterogeneity, underlies the nonexponential behavior. Simulations [3,4] on a Lennard-Jones (LJ) binary system have shown the existence of dynamical heterogeneities. There is also experimental evidence, though indirect, for the presence of dynamical heterogeneities [5,6]. The direct experimental evidence for the existence of dynamical heterogeneities has come only recently from studies on hard-sphere (HS) colloidal suspensions [7,8]. These provide support in favor of the Adams and Gibbs approach to the theories of glass transition. However, many more experiments and simulations are required for obtaining a complete understanding of the nature and the dynamics of the glass transition. This necessitates investigations on glass transition in systems which are amenable to experimental verification with ease. We show that a charged colloidal system is one among such systems which can be studied in real space as well as in Fourier space, and also in real time due to submicron length scales and convenient time scales (10^{-6} to 1 s). These colloidal systems exhibit structural ordering, similar to that observed in simple atomic systems, at volume fractions as low as 0.001 due to long-ranged screened Coulomb interactions.

The glass transition in atomic systems can be studied by varying temperature, T, and pressure, P. Temperature has been used extensively as a variable in the study of glass transition, whereas the investigations using pressure as a parameter are very limited. High-pressure studies are expected to advance the understanding of relaxation processes near the glass transition [1]. In the case of HS suspensions, volume fraction ϕ is the only relevant variable and has been varied to study glass transition [7,8]. HS suspensions exhibit crystallization for $\phi \geq 0.49$ and undergo glass transition for $\phi > \phi_g \sim 0.58$ [9]. Unlike atomic and HS systems, monodisperse charged colloidal suspensions offer several advantages to probe the glass transition: (i) One advantage is the easy tunability of interparticle interaction over a wide range by varying the inverse Debye screening length κ, which in turn can be varied by changing ϕ, charge Ze on the particle, and salt concentration C_s [10,11]. (ii) These suspensions exhibit structural ordering at much lower volume fractions ($\sim$0.001) as compared to HS suspensions [10,11]. (iii) The osmotic pressure (hereafter referred to as pressure) experienced by colloidal particles can be varied in experiments using a membrane that is permeable to salt ions but not to colloidal particles. (iv) The magnitude of the pressure that needs to be varied in such experiments is only of the order of 10 to 100 dyn/cm^2, which is 10 orders of magnitude lower than that in atomic systems. Such small values for the pressure arise due to the low particle concentration ($n_p \sim 10^{12}\ \text{cm}^{-3}$) [10,11].

Glass transition in binary [12] and polydisperse [11,13] charged colloids have been studied as a function of effective temperature T^*, which is achieved by varying the salt concentration in these suspensions. To our knowledge, no studies exist on glass transition in these systems as a function of pressure. Further, the existence of dynamical heterogeneities near the glass transition of atomic systems driven by pressure has not been established. This motivated us to carry out constant pressure Monte Carlo (MC) simulations on charged colloids as a function of P. We report here the phase behavior of a liquidlike ordered charged colloidal suspension subjected to sudden compression. The colloidal liquid showed crystallization under the application of sequential compression, whereas freezing into a colloidal glassy state has been observed under sudden compression. Surprisingly, the glass transition occurs at much lower volume fraction ($\phi = 0.003$) as compared to the experimental observations of glass transition ($\phi \geq 0.2$) in monodisperse charged colloidal suspensions [14]. We also report, for the first time, the existence of dynamical heterogeneities near glass transition driven by pressure.

We perform extensive constant pressure MC simulations of an aqueous colloidal suspension of N ($= 2000$) charged particles, having diameter $d = 109$ nm and charge $Ze = 600e$, placed in a cubic MC cell of volume V. The (N, P, T) MC procedure used in this study has been described elsewhere [15]. The particles are assumed to interact via screened Coulomb repulsive potential [10] given by $U(r) = [2Z^2e^2e^{(\kappa d)}/\epsilon(2 + \kappa d)^2][e^{-\kappa r}/r]$, where ϵ is the dielectric constant of water ($= 78$) at temperature T ($= 298$ K), and κ is given by $\kappa^2 = 4\pi e^2(n_p Z + C_s)/(\epsilon k_B T)$. Here k_B is the Boltzmann constant and ϕ is related to n_p by $\phi = \pi d^3 n_p/6$. The units of various quantities reported in this paper are as follows: P, dyn/cm^2; energy, $k_B T$; κ, $1/d$; length is expressed in units of average interparticle distance defined as $a_s = n_p^{-1/3}$; and the MC time t in units of MC steps (MCS), where one MCS is defined as a set of N configurations during which, on the average, each particle gets a chance to move.

The starting configuration corresponding to a well equilibrated liquid state for $\phi = 0.902 \times 10^{-3}$, $\kappa = 0.587$, $C_s = 2$ μM, and $P = 1.07$ is obtained by melting a body centered cubic lattice. The equilibrium state is characterized to be liquidlike from the behavior of the pair-correlation function $g(r)$ and the mean square displacement (MSD) $\langle r^2(t) \rangle$ [11]. The liquid is subjected to sudden compression by simply setting the pressure in the MC procedure to the desired higher value. We found it sufficient to use 5×10^6 configurations for equilibration for pressures away from the glass transition and about 2×10^7 configurations close to the transition. After reaching equilibrium, 10^5 independent configurations have been used to calculate $g(r)$, $\langle r^2(t) \rangle$, average number density $\langle n_p \rangle$, self-part of the Van Hove correlation function $G_s(r, t)$ [13], and the non-Gaussian parameter $\alpha_2(t)$ [3].

The knowledge of transition pressure P_c at which the colloidal liquid crystallizes is essential for identifying the supercooled liquid state and the glass transition. Hence, freezing of a colloidal liquid into a colloidal crystal under the application of pressure is studied by incrementing the pressure sequentially, and crystallization is found to occur at $P_c = 4.8$. However, the same colloidal liquid showed liquidlike behavior with a smooth second peak in $g(r)$ (see Fig. 1) when subjected to different amounts of pressure crush for pressure up to 20 and distortions in the second peak (see Fig. 1) with an increase in the magnitude of first peak height in $g(r)$ for $P > 20$. The latter behavior in $g(r)$ is often considered as a signal for the glasslike ordering in colloidal as well as atomic systems [12,16]. The disordered state occurring for $P > 20$ is confirmed to be glass, from the time independent shape of $h_s(r, t)$ [Fig. 1(b)] which is characteristic of a frozen structure. The quantity $h_s(r, t) = 4\pi r^2 G_s(r, t)$ gives the probability density for a particle to move a distance r in time t [12,13]. Since in a liquid particles undergo macroscopic diffusion, the corresponding $h_s(r, t)$ will show time dependence [Fig. 1(c)]. Further, it can be seen that at very long times the MSD [Fig. 2(a)] of particles in the glassy state is also very small ($\langle r^2(t) \rangle / a_s^2 < 0.1$). In the liquid state, for $P < 20$, the corresponding MSD of particles is larger than a_s^2 ($\langle r^2(t) \rangle / a_s^2 > 1$). The glass transition pressure P_g is identified using the well known Wendt-Abraham parameter [16] $R_g = g_{\min}/g_{\max}$, where $g_{\min}$ and $g_{\max}$ are, respectively, the values of $g(r)$ at its first minimum and its first maximum. The R_g derived from $g(r)$ for different values is shown in Fig. 3(a). The value of R_g at the intersection is about 0.14, which is the same as that found in atomic systems [16], and the corresponding value of the pressure defines the glass transition pressure $P_g = 27$. The plot of ϕ versus P also shows [Fig. 3(b)] the occurrence of glass transition at P_g.

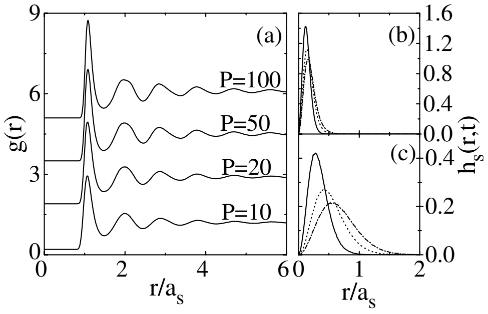

FIG. 1. (a) $g(r)$ vs reduced distance r/a_s for suspensions with $\kappa d = 0.587$ after subjecting the initial liquidlike ordered suspension with $\phi = 0.902 \times 10^{-3}$, $P = 1.07$ dyn/cm^2, and $C_s = 2$ μM to different amounts of pressure crush. The curves are shifted vertically by different amounts for the sake of clarity. Self-part of the Van Hove correlation function $h_s(r, t)$ at different MC times for (b) $P = 100$ dyn/cm^2 and (c) $P = 20$ dyn/cm^2. Continuous line is for $t = 500$ MCS; dotted line is for $t = 1500$ MCS; dash-dotted line is for $t = 2500$ MCS.

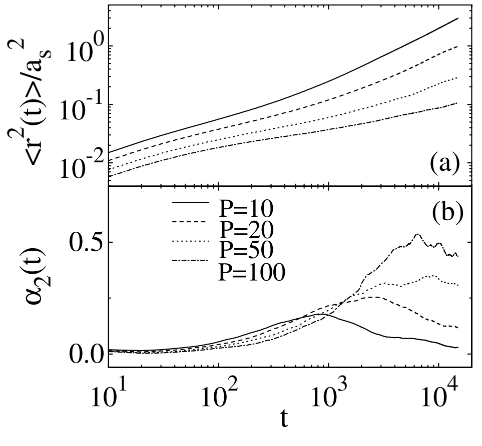

FIG. 2. (a) Mean square displacement $\langle r^2(t)/a_s^2 \rangle$ vs time (in MCS units) for several values of P. (b) Non-Gaussian parameter $\alpha_2(t)$ vs time for the same values of P as in (a).

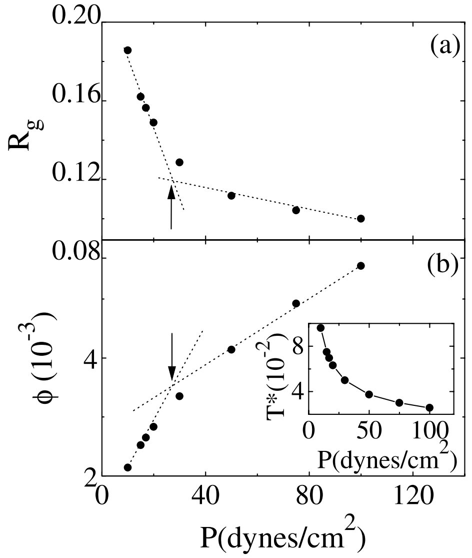

FIG. 3. (a) Wendt-Abraham structural parameter R_g as a function of P to which the initial liquidlike ordered suspension is pressure crushed. (b) Plot of ϕ versus P. The arrows indicate the glass transition pressure $P_g = 27$ dyn/cm^2. The values of R_g and ϕ at P_g are 0.136 and 0.0032, respectively. Inset shows T^* versus P.

In addition to the structure, we also study the dynamics of the particles as a function of pressure. Unlike in molecular dynamics simulations, we do not observe ballistic motion at short times because of the stochastic dynamics underlying the MC procedure. The motion of particles is found to be diffusive at all times, i.e., $\langle r^2(t)\rangle \propto t^m$, $m = 1$ for the liquidlike ordered state observed at $P = 1.07$. It is known that for short times particles diffuse freely in the liquid state. This fact has been used to estimate the physical time corresponding to one MCS to be about 18 μs via the relation $\langle r^2(t)\rangle = 6D_0 t$ and the knowledge of diffusion constant $D_0 = 4.82 \times 10^{-8}$ cm^2/s. In the supercooled state obtained by pressure crush, the MSD showed three stages in time [Fig. 2(a)]. The short time diffusive behavior becomes subdiffusive ($m < 1$) at intermediate time due to the "caging" experienced by particles, and the slow rise is due to the β relaxation. The span of the subdiffusive regime increases with P. At the end of subdiffusive regime, MSD once again rises which corresponds to cage rearrangement that occurs at longer times as the glass transition is approached. The rise in MSD at long times at lower pressures is due to the α relaxation. This is confirmed by monitoring the particle trajectories over a long period. The particles are found to spend most of their time confined in cages, formed by their neighbors, and move significant distances during cage rearrangements. Such a motion for particles has been observed in HS suspensions [8].

Dynamical heterogeneities near a glass transition can be detected by investigating time dependence of $G_s(r,t)$. To a first approximation $G_s(r,t)$ has a Gaussian form, referred to as $G_g(r,t)$, but deviation from this at intermediate times reflects the presence of dynamical heterogeneities [3,4]. Such deviations can be characterized by the non-Gaussian parameter $\alpha_2(t) = [3\langle r^4(t)\rangle/5\langle r^2(t)\rangle^2] - 1$ [3]. $\alpha_2(t) = 0$ if $G_s(r,t)$ is a Gaussian. Figure 2(b) shows the time dependence of α_2 at four different pressures. We find α_2 starts to increase for all the pressures on the time scale of the β relaxation. On the other hand, α_2 decreases to its lowest value in the supercooled liquid state (for $P < 27$) and continues to be high for the glassy state (for $P > 27$) in the α-relaxation regime. α_2 is found to decrease at longer times ($t > 10^4$ MCS) in the glassy state as compared to the supercooled state. The time t^* at which this maximum is attained is found to increase rapidly with the pressure up to P_g and slowly beyond P_g. The increase in α_2 is evidence that the dynamics of the colloidal liquid becomes more heterogeneous with increasing pressure. Studies on the supercooled liquid of LJ systems with decreasing temperature showed similar behavior in α_2 [3,4].

We further observe from Fig. 2(b) that α_2 for glass is more than that in the supercooled liquid in the α-relaxation regime. Observations on HS colloidal glass showed a drop in the value of α_2 as compared to that of the HS liquid [8] close to the glass transition. This difference in the behavior of α_2 between these two systems could be due to the following reasons. Even though there is no change in T across the glass transition in both systems, there is a change in the effective temperature T^*, of the charged colloidal system. For a charged colloidal system, T^* is defined as $k_B T/U(a_s)$ [11,12] and its variation with P is shown as an inset of Fig. 3(b). The effect of pressure crush in charged colloids is twofold. (i) It reduces the interparticle separation, and (ii) it also results in an effective temperature quench to the system. Thus the pressure crushed charged colloidal liquid is also a supercooled liquid.

To study structural relaxation and cooperative motion of particles in the supercooled liquid state of charged colloids, we examined mobile (fastest moving) particles by following the procedure of Glotzer's group [3,4]. We monitor the displacements of particles up to time t^*. We choose this time interval because t^* is the time at which the liquid is likely to be the most "dynamically heterogeneous" and also the distribution of particle displacements is the broadest. The particle displacements are calculated for all particles in this time interval. The distribution of particle displacements at any time t is given by the self-part of the Van Hove correlation function $G_s(r,t)$. The subset of mobile particles was defined by selecting all the particles which have traveled farther than the distance r^* in the time interval $[0,t^*]$. Note that $G_s(r,t^*) > G_g(r,t^*)$ for $r > r^*$ [Fig. 4(a)]. This definition implies that mobile particles are those that contribute to the long tail of $G_s(r,t^*)$; see Fig. 4(a). The total number of mobile particles thus defined is about 5% of the total number of particles at all the pressures studied here. The studies on the supercooled LJ liquid have shown the same percentage for the mobile particles [3,4].

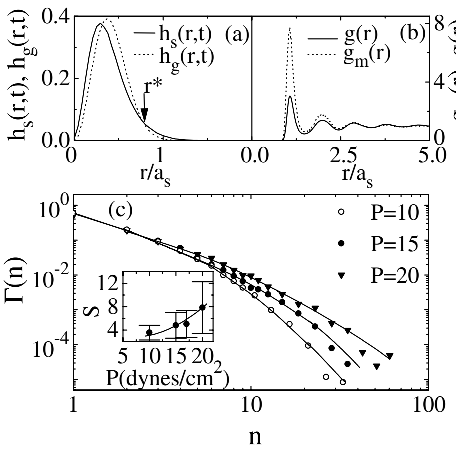

FIG. 4. (a) Solid line: $h_s(r,t)$ for particles at $t = t^*$ for $P = 20$ dyn/cm^2. Dashed line: Gaussian approximation $h_g(r,t) = 4\pi r^2 G_g(r,t)$ determined using the calculated $\langle r^2(t) \rangle$ for the same time. (b) Pair-correlation functions $g_m(r)$ and $g(r)$ for the mobile and bulk particles, respectively, for the value of P the same as in (a). (c) Probability distribution $\Gamma(n)$ of clusters of mobile particles of the size n for three values of P. Inset: Mean cluster size S vs P. Lines drawn through the simulation points are guides to the eye.

The spatial correlation between the mobile particles is investigated by calculating the pair-correlation function $g_m(r)$ for the mobile particles and comparing it with that of the bulk denoted by $g(r)$. It can be seen from Fig. 4(b) that the peak height of $g_m(r)$ is much larger than that of $g(r)$, suggesting that the mobile particles are spatially more correlated as compared to the rest of the particles in the bulk. The analysis of snapshots of the configurations of the mobile particles showed that these particles tend to form clusters. Figure 4(c) shows the probability distribution $\Gamma(n)$ of clusters of size n for the mobile particles. It can be seen that the clusters of larger size form with an increase in pressure; i.e., the cluster size grows as one approaches the glass transition. A significant fraction of the mobile particles is found to be part of the big clusters. For instance, at $P = 20$ there is typically at least one cluster in each configuration that contains ≈60 particles. The average cluster size $S = \sum n^2 \Gamma(n) / \sum n \Gamma(n)$ [4] (shown as an inset) is found to increase linearly with P. We found that for $P = 20$ the $\Gamma(n)$ decays as $n^{-\gamma}$ with $\gamma = 1.80$ except for the tail portion which is found to be system size dependent. For example, the largest cluster size for simulations with $N = 1024$ is found to be 51 in contrast to 60 for $N = 2000$. This value of γ is close to that observed in the LJ system [4] and in HS suspensions [8]. This suggests that the behavior of dynamical heterogeneities near the glass transition in charged colloids obtained by pressure crush is similar to that observed in LJ fluids and HS suspensions.

To conclude, the present simulations have shown that the charged colloidal suspensions can serve as an ideal condensed matter system to study the glass transition under pressure. We have established for the first time the existence of spatially correlated dynamical heterogeneities in the supercooled fluid state of charged colloidal suspensions. Another important result from these simulations is that the glassy state in deionized charged colloids can be obtained at very low volume fraction by subjecting them to small amounts of pressure crush. This reduction will greatly help experimentalists to probe the glass transition in these systems using microscopy and light scattering.

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