Is There a Reentrant Glass in Binary Mixtures?

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By employing computer simulations for a model binary mixture, we show that a reentrant glass transition upon adding a second component occurs only if the ratio α of the short-time mobilities between the glass-forming component and the additive is sufficiently small. For $\alpha \approx 1$, there is no reentrant glass, even if the size asymmetry between the two components is large, in accordance with the two-component mode-coupling theory. For $\alpha \ll 1$, on the other hand, the reentrant glass is observed and reproduced only by an effective one-component mode-coupling theory.

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The ability to manipulate the rheological behavior of physical systems by the addition of suitable smaller components is a task of high technological interest. At the same time, the glassification and melting of dynamically arrested states present the theorists with a challenging problem. Recent experiments [1,2] have revealed that the addition of nonadsorbing polymers to sterically stabilized colloidal dispersions induces a new glass transition scenario. Upon adding polymers to the pure colloidal glass, the dynamics of the colloids is first speeding up, until the glass is molten and a fluid state is reached. By further increasing the polymer concentration, the fluid vitrifies again and a reentrant glass transition materializes. This new kinetically arrested phase is called "attractive" glass (in contrast to the ordinary "repulsive" or hard-sphere-like colloidal glass), since it is generated by effective depletion attractions between the colloids, mediated by the polymers. The occurrence of an attractive glass seems to be generic for any system with a short-ranged attraction and was recently also found for colloids in a solvent of varying quality [3] and in micelle-polymer mixtures [4,5]. The reentrant scenario of the attractive glass had been predicted by mode-coupling theory of the colloids by treating *only* the colloids explicitly, and assuming that they interact via an effective, polymer-mediated depletion interaction [6–8]. It has also been observed in computer simulations of particles interacting via a short-ranged attraction [9,10], provided that its range is small enough with respect to the core size. Nevertheless, a general understanding about the circumstances under which additives affect the glass transition is still lacking. A similar situation occurs for asymmetric molecular mixtures, such as molten salts [11], but just on a different (microscopic) length scale.

In this Letter, we study systematically the question of whether and how the dynamical properties of the additives influence the occurrence of the glass transition, in the framework of a simple binary model mixture. We show thereby that the relative *short-time mobility* of the constituent components plays a crucial role in determining the occurrence of vitrification of a fluid or melting of a glass. Our central result is that a reentrant glass scenario requires not only a large size asymmetry but also that the short-time mobility of the added component be much higher than that of the glass-forming species. In the case of a very high additive mobility as compared to the mobility of the glass-forming component, one can think in terms of the adiabatic approximation: Then, for an instantaneous configuration of the glass-forming component, the additives are equilibrated, establishing thereby the static effective interaction potential between the former [12]. It is precisely in this limit that the concept of a *static*, effective, one-component description with a depletion attraction is expected to be applicable also in the *dynamical* sense. On the other hand, if the short-time mobilities of the two species are comparable, the depletion potential still *exactly* determines the partial static structure of the larger component [13], but not its dynamical behavior. It is therefore interesting to examine whether the lack of validity of the depletion picture in the dynamical sense has an influence on the glass transition scenario, which is a genuinely *kinetic* arrest.

From its basic formulation, the two-component mode-coupling theory (MCT) for the ideal glass transition [14] asserts that the latter depends only on the static partial structure factors of the mixture and, hence, it is independent on the individual short-time mobilities [15]. This assertion holds both for Brownian dynamics (relevant for colloid/polymer mixtures) and for Newtonian short-time dynamics (relevant for molecular glass formers). Our computer simulation studies reveal, however, that the scenario and the location of the glass transition in the mixture depends crucially on the ratio α between the short-time mobilities of the glass-forming component and of the additive. We also show that MCT correctly predicts the glassification scenarios for the two extreme limits: If $\alpha \approx 1$, the *two-component* MCT yields no reentrance, while for $\alpha \ll 1$ the effective *one-component* MCT predicts the occurrence of a reentrant glass. We first describe the model and the simulation techniques, and then compare the simulation results to two-component and one-component MCT. Finally, estimates for the crossover towards adiabaticity and experimental consequences are presented.

Our results are obtained for the Asakura-Oosawa (AO) binary model [16,17], which is a simple prototype for a colloid-polymer mixture, where the glass-forming particles (“colloids”) are hard spheres of diameter σ_c and the additives (“polymers”) do not interact with each other but only feel the colloids as hard spheres with an interaction radius $(\sigma_c + \sigma_p)/2$, where σ_p denotes the diameter of gyration of the polymer coils. The motivation to study such an asymmetric nonadditive mixture is twofold: First, the static structure and the equilibrium phase behavior are known, facilitating to a great extent the understanding of the dynamical behavior. Second, the AO mixture is a minimal model for depletion and fluid-fluid phase separation in mixtures, containing the basic physical mechanisms driving the occurrence of both repulsive and attractive glasses. Since there is no energy scale in the interactions, the thermal energy $k_B T$ scales out and is irrelevant. The remaining parameters for the AO model are the size asymmetry $q = \sigma_p/\sigma_c$, and the partial colloid and polymer packing fractions $\eta_c = \pi\rho_c\sigma_c^3/6$ and $\eta_p = \pi\rho_p\sigma_p^3/6$, where ρ_c, ρ_p are the partial number densities of colloids and polymers, respectively.

We carried out extensive molecular dynamics (MD) simulations of the AO mixture, introducing the two masses m_c and m_p for the colloids and the polymers. The latter determines the ratio of short-time mobilities (or thermal velocities) α between polymers and colloids as $\alpha = \sqrt{m_p/m_c}$. MD simulations were performed using an event-driven algorithm [18]. The relative numbers of particles and the volume of the simulation box were chosen in order to achieve equilibrium conditions for all studied values of q, α, and η_p, within reasonable computer time [19]. Thus, we fixed the number of colloidal particles to $N_c = 500$ for $q = 0.15$ and $q = 0.50$, and to $N_c = 40$ for $q = 0.04$ [20]. Partial mean squared displacements were used to determine, via the Einstein relation, the self-diffusion coefficients D_c and D_p of the colloids and polymers, respectively [21]. Units of mass, length, and energy are chosen as m_c, σ_c and $k_B T$.

Results for D_c as a function of α are shown in Fig. 1(a) for different q at a fixed state point. The diffusive motion of the colloids significantly depends on the short-time mobilities ratio and on q. For sufficiently small α, the added polymer accelerates the dynamics if q is small and slows it down if q is large. This behavior is in agreement with previous studies of the dependence on the range of the effective attraction of the colloidal glass transition [8,22]. However, by increasing α, the picture completely changes. The added polymer *always* slows down the dynamics of the colloids, irrespective of the attractive range. This is clear evidence that, although the *statics* is identical along each curve at fixed q, the *dynamics* is significantly affected by the relative mobilities.

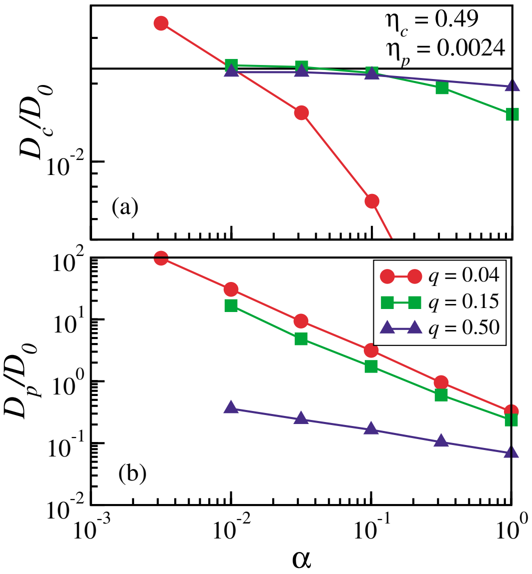

FIG. 1 (color online). Diffusion coefficients for (a) the colloidal particles and (b) the polymers in function of the ratio of the short-time mobilities α, at the state point $\eta_c = 0.49$, $\eta_p = 0.0024$ and for three different q values, normalized with $D_0 = \sqrt{k_B T \sigma_c^2/m_c}$. The horizontal line in (a) indicates the value of D_c when $\eta_p = 0$. Legends in (b) apply to both panels.

Data for D_p, at the same state point and varying q and α, are shown in Fig. 1(b). For small q, $D_p \propto \alpha^{-1}$, which pertains to the motion of an ideal gas inside the disordered medium formed by the colloids. For large q, the polymers are caged by the colloids. This causes a significant reduction of D_p for fixed α and a much weaker dependence of this quantity on α.

In order to obtain a broader picture of the dynamical behavior of the system on the entire (η_c, η_p) plane, we estimate the isodiffusivity lines from the MD simulations. These can be considered as precursors of the incipient glass transition line and provide an estimate of the shape of the latter [23]. Results for the isodiffusivity lines for $q = 0.15$ are shown in Fig. 2 and for $q = 0.50$ in Fig. 3. In each figure, results for two very different mass ratios, corresponding to $\alpha = 1$ and $\alpha = 0.01$, are shown. For $q = 0.15$, two different kinds of behavior result: For $\alpha = 0.01$, a clear reentrance is observed, while for $\alpha = 1$, the addition of polymers always slows down the dynamics. For a smaller size asymmetry, $q = 0.50$, there is always polymer-induced vitrification and no reentrance, but the impact of added polymer on the glass formation, embodied in the slope of the isodiffusivity curves on the (η_c, η_p) plane, depends strongly on α. For small mobility ratios, the isodiffusivity curves are almost vertical, pointing to an insensitivity of the diffusion coefficient on the amount of added polymer. For larger α, addition of polymer considerably slows down the dynamics.

In order to provide a criterion for the applicability of MCT to different regimes of mobility ratios, we calculated the location of the ideal glass transition within the framework of this theory. We solved the implicit

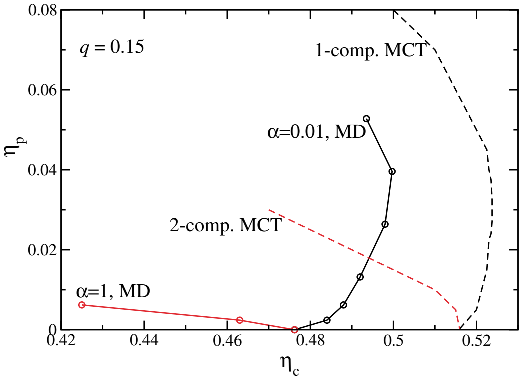

FIG. 2 (color online). Isodiffusivity lines ($D/D_0 = 0.03$) on the (η_c, η_p) plane for $\alpha = 0.01$ and $\alpha = 1$, accompanied by ideal glass transition lines from effective one-component and two-component MCT. The results refer to $q = 0.15$.

equations for the matrix of partial nonergodicity parameters $\mathbf{F}(q)$,

$$\mathbf{F}(q) = \mathbf{S}(q) - \{\mathbf{S}^{-1}(q) + \mathcal{F}[\mathbf{F}(q)]\}^{-1}, \tag{1}$$

where $\mathbf{S}(q)$ is the matrix of partial static structure factors, and $\mathcal{F}[\mathbf{F}(q)]$ is the long-time limit memory kernel within MCT approximation [14]. More specifically, it is a quadratic functional of $\mathbf{F}(q)$, coupling all different wave vectors, by means of coupling coefficients that depend only on partial static structure factors and partial concentrations of the system. A glass transition occurs when, upon changing the control parameters, the solution of Eq. (1) jumps from zero (ergodic state) to a finite value (glassy state). Note that, within MCT, inertia parameters drop out; hence, the location of the ideal glass line is independent of α. Equation (1) holds also for the one-component case, where $\mathbf{S}(q)$ and $\mathbf{F}(q)$ are 1×1 matrices.

The partial structure factors $S_{ij}(k)$ with $i, j = c, p$, needed as input for the two-component and one-component MCT, were obtained from the recently developed fundamental measure density functional theory [24]. This theory yields analytical expressions for $S_{ij}(k)$, which compare well with simulation data. For the effective one-component MCT, $\mathbf{S}(q) = S_{cc}(q)$.

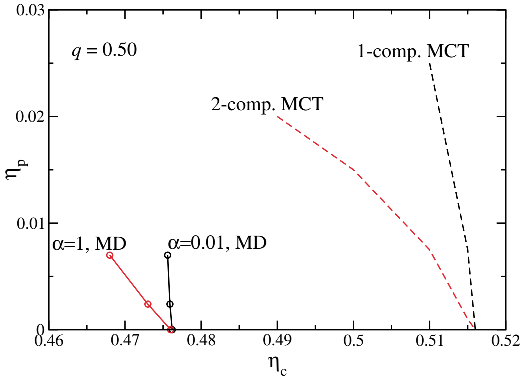

FIG. 3 (color online). Same as Fig. 2 but for $q = 0.50$.

Results from both effective one- and two-component MCT are shown in Figs. 2 and 3 for $q = 0.15$ and $q = 0.50$, respectively. In the first case, the two-component MCT predicts a vitrification of the fluid upon addition of polymers, while the effective one-component MCT predicts a reentrant scenario. In the second case, both the two-component and the effective one-component MCT predict a vitrification of the fluid upon addition of polymers. In this last case, the slope of the ideal glass line is almost vertical for the one-component calculation. The comparison between isodiffusivity lines and MCT calculations allows us to conclude that the MD results for small α are properly captured by the effective one-component MCT, while the MD results for large α are captured by the full two-component MCT calculation. Results in Fig. 3 are consistent with MCT calculations for binary hard-sphere mixtures for $q = 0.50$ (see Fig. 1 in [25]).

The ratio α needed to reach the adiabatic limit regime in which an effective one-component description applies dynamically can be estimated as follows. During the time necessary for a colloidal particle to move along a distance σ_p, there has to be a sufficiently large number of collisions, exceeding at least some typical threshold value $N_0 \approx 100$. This is necessary in order to provide enough statistics to feel the effective interaction dynamically [26]. The resulting adiabaticity condition reads $\alpha \lesssim 12\eta_p/(q^2 N_0)$.

For the two chosen cases, $\alpha = 0.01$ and $\alpha = 1$ in Figs. 2 and 3, we realize that, for a typical η_p, the above criterion is fulfilled in the former but not in the latter case. This in turn explains why the effective depletion potential is dynamically meaningful for the case $\alpha = 0.01$, so that the effective one-component MCT is applicable. On the other hand, for $\alpha = 1$ adiabaticity is not achieved and both the colloids and polymers are cage formers, so that the two-component MCT has to be employed in the study of the vitrification transition.

The same scaling arguments can be also carried out for short-time *Brownian* dynamics, for which $\alpha = D_c^{(0)}/D_p^{(0)}$, with $D_c^{(0)}$ and $D_p^{(0)}$ denoting the short-time diffusion coefficients of the colloids and the polymers, respectively, in their common solvent. In a mixture of uncharged colloids and polymers, these coefficients scale with the inverse radii of the particles, according to Stokes' expression; hence, they are coupled to q via $D_c^{(0)}/D_p^{(0)} = q$. Then the critical asymmetry q below which adiabaticity holds is given by $q_c = (12\eta_p/N_0)^{1/3}$, which is close to 0.1 for typical values of η_p and N_0. On the other hand, in mixtures of *charged* suspensions, the *physical* hard core diameters $\sigma_c^{(0)}$ and $\sigma_p^{(0)}$ are different and independent from the effective interaction diameters that enter in the q ratio. Indeed, effective interaction diameters σ_c and σ_p are dictated by the long-range Coulomb interactions; thus, they can greatly exceed the physical ones. The charge on the particles provides in this case the physical parameter that allows tuning of the physically relevant size ratio q. In this case, the adiabaticity criterion reads as $\sigma_p^{(0)}/\sigma_c^{(0)} \lesssim 12\eta_p/(q^2 N_0)$.

In conclusion, we have shown that a sufficient asymmetry in size *and* short-time mobilities is necessary for the reentrant glass scenario to materialize in binary mixtures. For glass-forming mixtures governed by molecular dynamics, the glass transition depends on the mass ratio between the two components [27], but huge mass asymmetries are needed to achieve the adiabatic limit. Vastly different mass ratios can be realized in binary mixtures of dusty plasmas [28], whose dynamics is almost Newtonian. On the basis of the scaling argument pertaining to Brownian dynamics, a reentrant glass transition in colloid-polymer mixtures would occur for size asymmetries that do not exceed the value $q_c = 0.1$. This helps to explain why a very small size asymmetry was indeed necessary to obtain an attractive glass in experimental studies [1,4]. The scaling condition is stronger than the one resulting from an *a priori* effective one-component picture in the framework of MCT [8,22]. Although our results have been obtained for the AO model, we expect that the weak interactions between real polymers do not cause any qualitative changes and that indeed our conclusions carry over to any asymmetric binary mixture. The most striking consequences are obtained for a mixture of charged colloids: A reentrant glass can be lost if the physical core of the high-charge particles is decreased, even if the charges are kept constant. By tuning the short-time mobility, the glass formation upon addition of a second repulsive component can be tailored, opening the way for external manipulation of the rheology of the mixture.

If the kinetic glass transition in a mixture is calculated within mode-coupling theory, it is not known *a priori* whether the two-component or the effective one-component version of the theory has to be employed. We have shown that it is an appropriate adiabaticity criterion that determines which theory must be applied. The impact of the α dependence of the glass transition should also have important consequences in asymmetric star polymer mixtures, where the lighter polymers have been used as rheology modifiers for the larger ones [29,30].

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