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 only occurs 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 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 non-adsorbing polymers to stericallystabilized 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 micellepolymer mixtures [4]. 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 by means of their effective, polymer-mediated depletion interactions [5, 6, 7]. It has also been observed in computer simulations of particles interacting via a short-ranged attraction [8, 9], provided that the range of the attraction is small enough with respect to the core size. Nevertheless, a general understanding about the mechanisms and the circumstances under which additives affect the glass transition is still lacking. A similar situation occurs for asymmetric molecular mixtures (such as molten salts), 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 [10]. 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 [11], 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 [12] asserts that the latter only depends on the static partial structure factors of the mixture and hence it is independent on the individual short-time mobilities. 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. In what follows, we first describe the model and the simulation techniques. Our simulation results are then compared 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 [13, 14], which is a simple prototype for a colloid-polymer mixture but can also be used to model asymmetric non-additive hard-sphere mixture for molecular systems. In this model, 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 non-additive 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 Asakura-Oosawa is a minimal model for depletion and fluid-fluid phase separation in mixtures, thus it contains 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 $q = \sigma_p / \sigma_c$, which corresponds to the range of the attractive potential in the effective onecomponent picture [13], and the partial number densities ρ_c, ρ_p of the colloids and polymers, which are most conveniently expressed in terms of the partial colloid and polymer packing fractions $\eta_c = \pi \rho_c \sigma_c^3/6$ and $\eta_p = \pi \rho_p \sigma_p^3/6$, 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 determine 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 [15]. 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 [16]. 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 [17]. Partial mean squared displacements for colloids and polymers were calculated in order to estimate, via the Einstein relation, the selfdiffusion coefficients D_c and D_p of the colloids and polymers, respectively. To reduce statistical errors, averages were performed over 50 independent configurations for q = 0.50 and q = 0.15, and over 10 for q = 0.04. The units of mass, length, and energy are chosen as m_c , σ_c and $k_B T$.

Simulation data for D_c as a function of the mass ratio are presented in Fig. 1(a) for different q at a fixed state point. It can be seen that the diffusive motion of the colloids depends significantly on the mass ratio and on q. For sufficiently small mass ratios, 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 of the glass transition of the colloids on the range of the effective attractive poten-

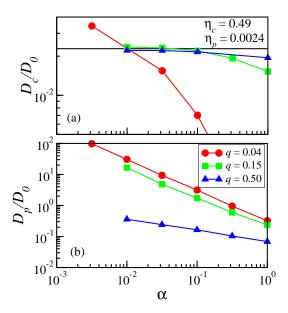


FIG. 1: The dependence of the diffusion coefficients on the ratio of the short-time mobilities for (a) the colloidal particles and (b) the polymers, at the state-point $\eta_c = 0.49$, $\eta_p = 0.0024$ and for three different *q*-values, normalized with $D_0 = \sqrt{k_B T \sigma_c^2/m_c}$. The horizontal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

tial [7, 18]. However, by increasing the mass ratio, the picture completely changes. The added polymer *always* slows down the dynamics of the colloids, irrespective of the range of the attractive potential. This is clear evidence that, despite of the fact that the *statics* is identical along each curve at fixed q, the *dynamics* is significantly affected by the relative mobilities of the two components.

Data for D_p , at the same state point and varying qand 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 $\eta_c - \eta_p$ -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 [19]. 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

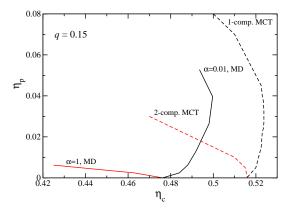


FIG. 2: Isodiffusivity lines on the $\eta_c - \eta_p$ -plane for $\alpha = 0.01$ and $\alpha = 1$, accompanied by ideal glass transition lines from the effective one-component and the two-component versions of MCT. The results refer to q = 0.15.

 $\eta_c - \eta_p$ -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 have calculated the location of the ideal glass transition within the framework of this theory. We have solved the implicit equations for the matrix of partial non-ergodicity parameters $\mathbf{F}(q)$,

$$\mathbf{F}(q) = \mathbf{S}(q) - \{\mathbf{S}^{-1}(q) + \mathcal{F}[\mathbf{F}(q)]\}^{-1}$$
(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 [12]. More specifically, it is a quadratic functional of $\mathbf{F}(q)$, coupling all different wave-vectors, by means of coupling coefficients that only depend 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 . Eq. (1) holds also for the onecomponent case, where $\mathbf{S}(q)$ and $\mathbf{F}(q)$ are 1×1 matrices.

The partial structure factors needed as input for the two-component and one-component mode coupling theory were obtained from the recently developed fundamental measure density functional theory [20]. This theory yields analytical expressions for the partial structure factors $S_{ij}(k)$ with i, j = c, p which compare well with simulation data. In the case of the effective one-component MCT, $\mathbf{S}(q) = S_{cc}(q)$.

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

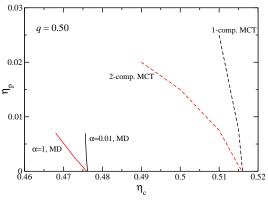


FIG. 3: Same as Fig. 2 but for q = 0.50.

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.

Since the isodiffusivity lines are precursors of the shape in the $\eta_c - \eta_p$ plane of the glass transition line, the comparison between these lines and the 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.

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 [21]. The resulting adiabaticity condition reads as

$$\alpha \lesssim 12\eta_p/(q^2 N_0). \tag{2}$$

For the two chosen two cases, $\alpha = 0.01$ and $\alpha = 1$ in Figs. 2 and 3, we realize that, for a typical η_p , the abiabaticity criterion (2) 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 employed for the derivation of criterion (2) can be 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 (2) reads as $\sigma_p^{(0)}/\sigma_c^{(0)} \leq 12\eta_p/(q^2N_0)$.

In concluding, we have shown that a sufficient asymmetry in the short-time mobilities is necessary for the reentrant glass-scenario to materialize in highly asymmetric binary mixtures. For glass-forming mixtures governed by molecular dynamics, the glass transition depends on the mass ratio between the two components [22], but huge mass asymmetries are needed to achieve the adiabatic limit. Vastly different mass ratios can be realized in binary mixtures of dusty plasmas [23], whose dynamics is almost Newtonian. On the basis of the considerations put forward in this Letter, the size asymmetry q for colloid-polymer mixtures has to be smaller than 0.1 in order to get a reentrant glass. This condition is stronger than the one obtained by using a priori an effective one-component picture. Indeed, in the present calculation one-component MCT would predict a reentrant glass for $q \leq 0.3$, while for previous studies of effective one-component pictures [7, 18] q up to at least 0.2 was

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found to have an attractive glass [24]. This finding helps to explain why in experimental studies [1, 4], a very small size asymmetry was indeed necessary in order to obtain an attractive glass. 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 a 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 onecomponent versions of the theory has to be employed. We have shown that it is the adiabaticity criterion (2) that determines which theory must be applied. The impact of the α -dependence of the glass transition should also have unexplored important consequences in polymer mixtures, such as, e.g., mixtures of star polymers of different arm numbers and radii, in which the lighter polymeric component has been used as a modifying agent of the flow-behavior of the heavier one [25, 26].

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