Mixing effects for the structural relaxation in binary hard-sphere liquids

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(Dated: March 22, 2022)

We report extensive molecular-dynamics simulation results for binary mixtures of hard spheres for different size disparities and different mixing percentages, for packing fractions up to 0.605 and over a characteristic time interval spanning up to five orders in magnitude. We explore the changes in the evolution of glassy dynamics due to mixing and discover two opposite scenarios: for large size disparity, increasing the mixing percentage of small particles leads to a speed-up of long-time dynamics, while small disparity leads to a slowing down. These results agree with predictions based on the mode coupling theory for ideal glass transitions.

PACS numbers: 64.70.Pf, 82.70.Dd

This paper deals with structural relaxation in liquids, i.e. the dynamical phenomena which are precursors of the glass transition. These processes are characterized by rather complex dependencies of correlation functions on time and parameters like the density and the temperature. The introduction of several new experimental techniques and great progress in molecular dynamics simulation studies has unfolded a wealth of facts about the evolution of structural relaxation upon cooling or compressing glass-forming liquids [1,2].

To establish an understanding of structural relaxation and the glass transition, one should focus on systems as simple as possible. Atomic one-component systems with conventional interaction potentials cannot be used since they crystallize before structural relaxation is fully developed. Beginning with the work of Hansen and collaborators [3], binary mixtures of simple particles were used for molecular dynamics studies of the glass transition. A binary Lennard-Jones system has been used extensively in recent years to analyze structural relaxation [4].

In previous work, mixing was introduced merely as a means of suppressing crystallization [5]. In the following we analyze systematically the effect of mixing on structural relaxation to identify the influence of composition changes and variation of the particle size disparity on the glassy dynamics. We focus on binary hard-sphere mixtures (HSM), i.e. particles interacting via an hard-core potential, which we study via extensive molecular dynamics simulations.

A specific motivation for our studies comes from the light-scattering data by Williams and van Megen for a HSM of colloidal particles [6]. The system was prepared to approximate a binary HSM for the ratio \( \delta = 0.60 \) of the particle diameters. Three mixing effects have been reported. If the percentage of the smaller particles increases from 10% to 20% of the relative packing fraction, then (i) the time scale for the final decay of the density correlators decreases; (ii) the plateau value for intermediate times increases; (iii) the initial part of the structural relaxation slows down. The first effects means that mixing has stabilized the liquid as if the smaller particles provide some lubrification. This effect has some analog in the plasticization observed in dense polymeric liquids due to mixing with polymers of shorter lengths. However, the effects (ii) and (iii) indicate a stiffening of the dynamics upon mixing. These effects have never been reported for conventional systems, and one might wonder whether these are structural relaxation phenomena rather than colloid-specific features caused by, e.g., hydrodynamic interactions or polydispersity. Since our simulation studies are done implementing a Newtonian microscopic dynamics, this question will be answered by our results.

Another motivation of our work is provided by recent predictions for binary HSM based on mode-coupling theory (MCT) [7] calculations. This theory, which allows first principle evaluations of density-fluctuation correlators within a regime where structural relaxation dominates the dynamics, explains the light-scattering data for slightly polydisperse hard-sphere colloidal suspensions [8]. Extending MCT to binary HSM, the three mentioned mixing effects have been identified as structural relaxation properties [9]. The light scattering data for the \( \delta = 0.60 \) mixture could be described quantitatively to a certain extent [10]. However, surprisingly, the theory predicts two different scenarios. The speed-up of the dynamics reported in Ref. [6] was found only for sufficiently large size disparity, say a size ratio \( \delta \lesssim 0.65 \). For \( \delta \gtrsim 0.8 \), the opposite effect was predicted, i.e., mixing slows down the dynamics and the ideal-glass critical packing fractions decreases. The data reported in this letter confirms these astonishing predictions.

We perform standard constant-energy molecular dynamics [11] simulation for a binary mixture of 1237 hard-sphere particles. The two species (A and B) have diameters \( d_A \) and \( d_B \) respectively, with \( d_A \geq d_B \). The masses of the two species are taken as equal, thus all particles have the same thermal velocity, denoted as \( v_{th} \). Units of length and time are chosen such that \( d_A = 1 \) and \( v_{th} = 1 \). We use the size ratio \( \delta = d_B/d_A \) as a control parameter specifying the size disparity. To model a large size dispar-
ity, we choose $\delta = 0.60$. To model systems of small size disparity we study the value $\delta = 0.83$. For each of the two $\delta$ values, we study two different values of the relative packing fraction of the small species, $x = \varphi_B/\varphi_A$, where $\varphi_A = (\pi/6)d_\alpha^3$. For the $\delta = 0.60$ system, we have studied $x = 0.10$ and $x = 0.20$, corresponding to a fraction of B particles equal to 34% and 54%. For the $\delta = 0.83$ system, we have studied the cases $x = 0.276$ and $x = 0.37$, corresponding to having 40% and 50% of B particles. For each $\delta$ and $x$ values, we study several values of the total packing fraction $\varphi = \varphi_A + \varphi_B$, covering a region where dynamics slows down by 4 decades. During the long simulation runs, we check for crystallization by monitoring the time evolution of the pressure and by visual inspection of the configurations. We also evaluate the structure factor to make sure that no crystalline peaks have developed.

The $\varphi$ dependence of the diffusion coefficient, evaluated from the long time limit of the mean square displacement (MMSD), is shown in Fig. 1. Note that the variation of the diffusivities extends over more than four decades.

It is important to separate mixing effects already observed in normal liquid states from mixing effects which are peculiar of the structural relaxation dynamics. In hard-spheres, mixing effects for the normal-liquid dynamics are qualitatively explained within Enskog’s kinetic theory. The diffusion constant $D$ of the hard-sphere system (HSS) is expressed in terms of Enskog’s collision rate $\nu$, $D^E = 3v^2_{th}/(2\nu)$. This rate modifies Boltzmann’s collision rate for dilute gases by the contact value $g_{AA}$ of the pair-distribution function: $\nu = 4\sqrt{\pi}v^2_{th}g_{AA}d_\alpha^2$. Enskog’s formula is readily generalized to mixtures with equal constituents’ masses, giving $D_\alpha^E = 3v^2_{th}/(2\nu_\alpha)$, with $\nu_\alpha = 4\sqrt{\pi}v^2_{th}\sum g_{\alpha\beta}d_{\alpha\beta}^2$. Here $g_{\alpha\beta}$ denotes the pair-distribution function of the colliding pair $\alpha$ and $\beta$ for the distance at contact, $d_{\alpha\beta} = (d_\alpha + d_\beta)/2$. Results for $D_\alpha^E$ are included in Fig. 1 as lines for $\varphi < 0.39$, using values from Percus-Yevick theory for $g_{\alpha\beta}$. The relevant normal-liquid mixing effects for the HSM, as given by the Enskog theory, can be summarized in the following: (i) $D_A$ decreases and $D_B$ increases upon decreasing $\delta$; (ii) both $D_A$ and $D_B$ decrease upon increasing $x$; (iii) all $D_A$ values are smaller than all the $D_B$ values. A detailed discussion of normal mixing effects for an approximation to HSM has been published in Ref. 13.

In agreement with the pioneer work of Alder et al. for the HSS 14, the data for $D_\alpha$ are described correctly on a 30% accuracy level by the Enskog theory for $\varphi < 0.40$. Upon increasing $\varphi$ beyond 0.40, the cage effect starts dominating and leads to a suppression of $D$ and $D_\alpha$ below the corresponding Enskog values. Still we find that up to the large value $\varphi = 0.48$ there are only normal-liquid mixing effects since the log $D_\alpha$-versus-$\varphi$ curves do not exhibit crossings.

Increasing $\varphi$ further, the curves in Fig. 1 get a stronger bending, i.e., the cage-effect enhances. If $\varphi$ reaches 0.56, the diffusivities are about one order of magnitude smaller than in a conventional liquid. Within the interval $0.48 < \varphi < 0.56$, there occur crossings of the curves, i.e. the mixing properties change qualitatively. The crossing observed in Fig. 1 demonstrates a first remarkable feature of structural relaxation, viz., differently from Enskog predictions, diffusion of B particles for $\delta = 0.83$ becomes smaller than $D_A$ for the $\delta = 0.60$ case. For $\varphi > 0.56$, a new pattern evolves, showing the mixing effects for the fully developed structural relaxation. To support the association of the slowing down of the dynamics to the approach towards a glass transition, the

![FIG. 1: Diffusivities $D_\alpha$, $\alpha = A, B$, for binary hard-sphere mixtures with size ratios $\delta = d_B/d_A = 0.60$ (open symbols) and $\delta = 0.83$ (filled symbols); packing contributions of the smaller species $x = \varphi_B/\varphi$ as in the legend.](image)
hibits a single critical packing fraction agreement with MCT predictions, that each mixture ex-
more than 0.

for the particles A.

B have been shifted down by 0.

power-law fit can account well for the diffusivity changes. D have been fitted by a power-law function, D = A(δ, x |δ, x)−γ(δ, x). As shown in Fig. 4, the power-law fit can account well for the diffusivity changes over more than two orders of magnitude. For the four mixtures studied, we find that the critical packing fraction of species A deviates from that of species B by not more than 0.0007, so that we can confidently conclude, in agreement with MCT predictions, that each mixture exhibits a single critical packing fraction ϕc(δ, x). In the asymptotic limit ϕ → ϕc(δ, x), the MCT exponent γ should be the same for DA and DB. This is not the case for our fit results, as also found in previous studies [17], possibly because of preasymptotic correction effects.

The presence of crossings in the diffusivity curves on entering the region where structural relaxation becomes relevant clearly shows that dynamics for δ = 0.83 is significantly slower than the one for δ = 0.60. Moreover—

differently from the regime of normal-liquid dynamics where the diffusivities D(δ, x) exhibit the same trend with changes of x for δ = 0.83 and δ = 0.60—there is a qualitatively different x-dependence of the long-time dynamics for small and large size disparity, as recently predicted by MCT [4]. As shown in Fig. 1b, while at δ = 0.83 dynamics becomes slower on increasing x, the opposite behavior is observed at δ = 0.60. This second remarkable feature—the plasticization phenomenon alluded to before and exhibited by the δ = 0.60 simulation data—is clearly shown in Fig. 1b. Consistently with these findings, at δ = 0.60, the critical packing fraction increases on going from x = 0.10 (ϕc(x = 0.10) = 0.6139 ± 0.0004) to x = 0.20 (ϕc(x = 0.20) = 0.6169 ± 0.0004). The critical packing fractions for the system with δ = 0.83 show the opposite trend: they decrease on increasing x from x = 0.276 (ϕc(x = 0.276) = 0.5881 ± 0.0004) to x = 0.37 (ϕc(x = 0.37) = 0.5877 ± 0.0004). This third remarkable finding means that mixing stabilizes the glass for the system with small size disparity and destabilizes it for large size disparities. Different from the plasticization effect discovered by Williams and van Megen for δ = 0.60, for δ = 0.83 an increase of the concentration of the smaller minority particles leads to a slowing down of the long-time density-fluctuation dynamics. The different scenarios for the long-time relaxation scales are demonstrated also in Figures 2 and 3. They show the x dependence of the density auto-correlation functions φA(q, t) for α = A and B at two different wave vectors, below (qdA = 5) and above (qdA = 10) the first peak of the structure factor (qdA = 7), respectively.

Within MCT, the ideal glass states are characterized by arrest of the density fluctuations. Within the liquid state, for T below but close to Tc, the φA(q, t)-versus-log t curves exhibit a plateau at fαT(q), the so-called critical Debye-Waller factor. The curves are the flatter the smaller ϕc − ϕ, and the length of the plateau increases. This plateau, an outstanding feature of structural relaxation, is clearly exhibited in Figs. 2 and 3. The whole structural-relaxation process consists of two steps. The first step deals with the relaxation towards the plateau fαT(q). The second step is the long-time process dealing with the decay of φA(q, t) from the plateau to zero. The three mixing features discussed above concern the time scale of the second relaxation step.

The results for φA(q, t) shown in Figs. 2 and 3 for qdA = 5 exhibit a fourth remarkable mixing effect: upon increasing x, the plateaus of the correlators increase. Accompanied with this is a flattening of the φA(q, t)-versus-log t curve in the plateau region. An indication of the same effect is also shown by the φB(q, t). These findings are in accord with the two mixing anomalies discovered in the experimental study of the colloidal δ = 0.60 system [8]. Our results show that they are structural-relaxation phenomena that occur also in systems with Newtonian dynamics, and that they occur for small as well as for

FIG. 2: Normalized density-correlation functions for binary hard-sphere mixtures at a total packing fraction ϕ = 0.600 for particles with diameter ratio δ = 0.60. The full and dashed lines present mixtures with relative packing contributions of the smaller particles B of x = 0.20 and x = 0.10, respectively. Upper and lower panel exhibit the results for wave vectors qdA = 5 and qdA = 10, respectively. The results for the particles B have been shifted down by 0.3 relative to the ones for the particles A.
large size disparity of the particles. We also note that on increasing $x$ at $\delta = 0.6$, the increase of the height of the plateau value, associated with the speed-up of the dynamics, forces the relaxation curves for the same $\varphi$ but for different $x$ to cross at the beginning of the second relaxation step. For $\delta = 0.83$, an increase of $x$ at fixed $\varphi$ generates a slower dynamics and hence there is no crossing of the curves in the time interval for the second relaxation step.

To conclude, we have studied structural relaxation of four binary hard-sphere mixtures via molecular dynamics simulations over dynamic ranges extending over about five orders of magnitude. Surprising mixing effects for the slow dynamics have been identified. In particular, we have shown that increasing the mixing percentage of the smaller minority particles can lead to a speeding up as well as to a slowing down of the long-time decay processes, depending on whether the size disparity is large or small, respectively. There is also an increase of the plateau of the density-autocorrelation functions for small and intermediate wave vectors reflecting a stiffening of the nearly arrested glass structure. These findings, which pose a challenge to theories of the glass transition, show in particular, that the description of a glass-forming mixture by an effective one-component liquid cannot be possible for all properties of interest. The reported results also confirm the conclusions arrived at in a light-scattering study of a quasi-binary colloidal suspension [6], and predictions within mode-coupling theory [9]. Finally, our work suggests that mode-coupling theory can contribute to an understanding of qualitative trends for the microscopic details in the dynamics of glass-forming liquids.

W.G. and Th.V. thank their colleagues from the University of Rome for their kind hospitality during the time this work was performed. Our collaboration was supported by DYGLAGEMEM and the Deutsche Forschungsgemeinschaft through DFG grant Go 154/12-1. G.F., F.S. and P.T. acknowledge support from MIUR Prin and Firb and INFM Pra-Genf&l. We thank S. Buldyrev for providing us the MD code for HSM.

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