Mixing Effects for the Structural Relaxation in Binary Hard-Sphere Liquids

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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 5 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.

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This Letter 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 such as 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 a 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 effect means that mixing has promoted the liquid as if the smaller particles provide some lubrication. 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] and, hence, independent on the microscopic dynamics. 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 decrease. The data reported in this Letter confirms these unexpected predictions.

We perform standard constant-energy Newtonian dynamics [11] simulations for a binary mixture of $N = 1237$ hard-sphere particles. The different microscopic dynamics probed in the simulations (Newtonian) and in the experiments [6] (Brownian) offer us the possibility to distinguish between short time and structural relaxation phenomena . The two species (A and B) have diameters d_{A}

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and d_{B} respectively, with $d_{\mathrm{A}} \geq d_{\mathrm{B}}$. 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 $d_{\mathrm{A}} = 1$ and $v_{\mathrm{th}} = 1$. We use the size ratio $\delta = d_{\mathrm{B}}/d_{\mathrm{A}}$ as a control parameter specifying the size disparity. To model a large size disparity, we choose $\delta = 0.60$. To model systems of small size disparity, we study the value $\delta = 0.83$. For each of the two δ values, we study two different values of the relative packing fraction of the small species, $x = \varphi_{\mathrm{B}}/(\varphi_{\mathrm{A}} + \varphi_{\mathrm{B}})$, where $\varphi_\alpha = (\pi/6)\varrho_\alpha d_\alpha^3$. 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 δ and x value, we study several values of the total packing fraction $\varphi = \varphi_{\mathrm{A}} + \varphi_{\mathrm{B}}$, covering a region where dynamics slows down by four decades. During the long simulation runs, we check for crystallization not to occur.

Figure 1 shows the φ dependence of the diffusion coefficient over more than four decades, evaluated from the long-time limit of the mean square displacement [12]. In interpreting the data, 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 ν, $D^{\mathrm{E}} = 3v_{\mathrm{th}}^2/(2\nu)$. This rate modifies Boltzmann's collision rate for dilute gases by the contact value g_{AA} of the pair-distribution function: $\nu = 4\sqrt{\pi} v_{\mathrm{th}}^2 \varrho_{\mathrm{A}} g_{\mathrm{AA}} d_{\mathrm{A}}^2$ [12]. Enskog's formula is readily generalized to mixtures with equal constituent masses, giving $D_\alpha^{\mathrm{E}} = 3v_{\mathrm{th}}^2/(2\nu_\alpha)$, with $\nu_\alpha = 4\sqrt{\pi} v_{\mathrm{th}}^2 \sum_\beta \varrho_\beta g_{\alpha\beta} d_{\alpha\beta}^2$. Here $g_{\alpha\beta}$ denotes the pair-distribution function of the colliding pair α and β for the distance at contact, $d_{\alpha\beta} = (d_\alpha + d_\beta)/2$. Results for D_α^{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 δ; (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 pioneering work of Alder *et al.* for the HSS [14], the data for D_α are described correctly on a 30% accuracy level by the Enskog theory for $\varphi < 0.40$. Upon increasing φ beyond 0.40, the cage effect starts dominating and leads to a reduction of D and D_α 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-φ curves do not exhibit crossings.

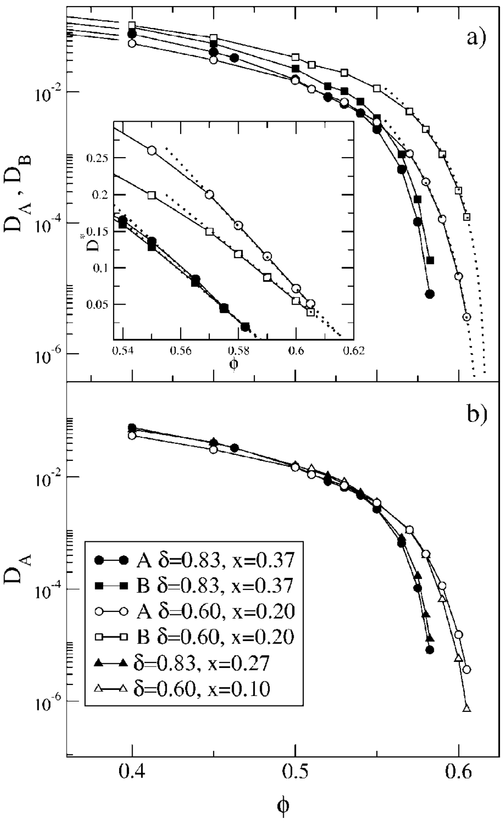

FIG. 1. Diffusivities D_α, $\alpha = \mathrm{A}, \mathrm{B}$, for binary hard-sphere mixtures with size ratios $\delta = d_{\mathrm{B}}/d_{\mathrm{A}} = 0.60$ (open symbols) and $\delta = 0.83$ (filled symbols). The legend in panel (b) reports the values of δ and $x = \varphi_{\mathrm{B}}/\varphi$ for the data shown in panels (a) and (b). (a) Results for the two different δ with $\alpha = \mathrm{A}$ (circles) and $\alpha = \mathrm{B}$ (squares). The solid lines for $\varphi < 0.39$ are the Enskog results for $D_{\mathrm{B}}(\delta = 0.6)$, $D_{\mathrm{B}}(\delta = 0.83)$, $D_{\mathrm{A}}(\delta = 0.83)$, and $D_{\mathrm{A}}(\delta = 0.6)$, from top to bottom. The dotted lines demonstrate power-law fits with exponents $\gamma_\alpha(\delta, x)$. The inset shows $D_\alpha^* = D_\alpha^{1/\gamma_\alpha}$ to demonstrate the extrapolation to zero diffusivity. (b) Variation of D_{A} upon changes of x for both δ values; circles (triangles) refer to the higher (lower) x value studied. The $\gamma_\alpha(\delta, x)$ values are $\gamma_{\mathrm{A}}(\delta = 0.6, x = 0.20) = 4.21$, $\gamma_{\mathrm{B}}(\delta = 0.6, x = 0.20) = 2.75$, $\gamma_{\mathrm{A}}(\delta = 0.83, x = 0.37) = 2.80$, $\gamma_{\mathrm{B}}(\delta = 0.83, x = 0.37) = 2.62$ [17].

Increasing φ further, curves in Fig. 1 get a stronger bending, i.e., the cage effect enhances. When φ reaches 0.56, the diffusivities are about 1 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, D_{B} 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 diffusivities have been fitted by a power-law function, $D_\alpha = \Gamma_\alpha(\delta, x)[\varphi_\alpha^c(\delta, x) - \varphi]^{\gamma_\alpha(\delta, x)}$. As shown in Fig. 1, the power-law fit can account well for the diffusivity changes over more than 2 orders of magnitude. For the four mixtures studied, we find that the A and B critical packing fractions differ by not more than 0.0008, so that we can confidently conclude, in agreement with MCT predictions, that each mixture exhibits a single critical packing fraction $\varphi^c(\delta, x)$. In the asymptotic limit $\varphi \to \varphi^c(\delta, x)$, the MCT exponent γ should be the same for D_A and D_B. This is not the case for our fit results, as also found in previous studies [15], possibly because for this quantity the correction to the asymptotic predictions are significant [4].

The presence of crossings in the diffusivity curves on entering the region where structural relaxation becomes relevant clearly shows that dynamics for $\delta = 0.83$ is significantly slower than the one for $\delta = 0.60$. Moreover—differently from the regime of normal-liquid dynamics where the diffusivities $D_\alpha(\delta, x)$ exhibit the same trend with changes of x for $\delta = 0.83$ and $\delta = 0.60$—there is a qualitatively different x dependence of the long-time dynamics for small and large size disparity, as recently predicted by MCT [9]. As shown in Fig. 1(b), while at $\delta = 0.83$ dynamics becomes slower on increasing x [16], the opposite behavior is observed at $\delta = 0.60$. This second feature—the plasticization phenomenon alluded to before and exhibited by the $\delta = 0.60$ simulation data—is clearly shown in Fig. 1(b). Consistently with these findings, at $\delta = 0.60$, the critical packing fraction increases on going from $x = 0.10$ [$\varphi^c(x = 0.10) = 0.6139 \pm 0.0004$] to $x = 0.20$ [$\varphi^c(x = 0.20) = 0.6169 \pm 0.0004$]. The critical packing fractions for the system with $\delta = 0.83$ instead do not increase when x goes from 0.276 [$\varphi^c(x = 0.276) = 0.5881 \pm 0.0004$] to 0.37 [$\varphi^c(x = 0.37) = 0.5877 \pm 0.0004$]. This third finding means that mixing does not change the glass transition seriously for the system with small size disparity and discourages it for large size disparities.

To better grasp the role of mixing on the particles dynamics, we study the density-autocorrelation functions $\phi_\alpha(q, t)$, defined as $\langle \rho_\alpha^*(\mathbf{q}, t)\rho_\alpha(\mathbf{q}, 0)\rangle / \langle |\rho_\alpha(\mathbf{q}, 0)|^2\rangle$, where $\rho_\alpha(\mathbf{q}, t) = (1/\sqrt{N})\sum_i e^{i\mathbf{q}\cdot\mathbf{r}_\alpha^i(t)}$ and $\mathbf{r}_\alpha^i(t)$ are the coordinates of particle i of type α at time t. Figures 2 and 3 show the x dependence of the $\phi_A(q, t)$ and $\phi_B(q, t)$ at two representative q values, below ($qd_A = 5$) and above ($qd_A = 10$) the first peak of the structure factor ($qd_A = 7$), respectively. Light-scattering experiments are able to probe the relaxation of density fluctuations in this range of q values. We note that in the case $\delta = 0.60$ (Fig. 2) both $\phi_A(q, t)$ and $\phi_B(q, t)$ decay faster on increasing x, independently from q. Instead, the opposite behavior is observed in the case $\delta = 0.83$ (Fig. 3). Such a speed up for $\delta = 0.60$ and slowing down for $\delta = 0.83$ on increasing x—in agreement with the previous discussion on the x dependence of D—confirms that the plasticization effect discovered by Williams and van Megen for $\delta = 0.60$ does not constitute the general case. For $\delta = 0.83$, an increase of the concentration of the smaller minority particles leads to a slowing down of the long-time density-fluctuation dynamics.

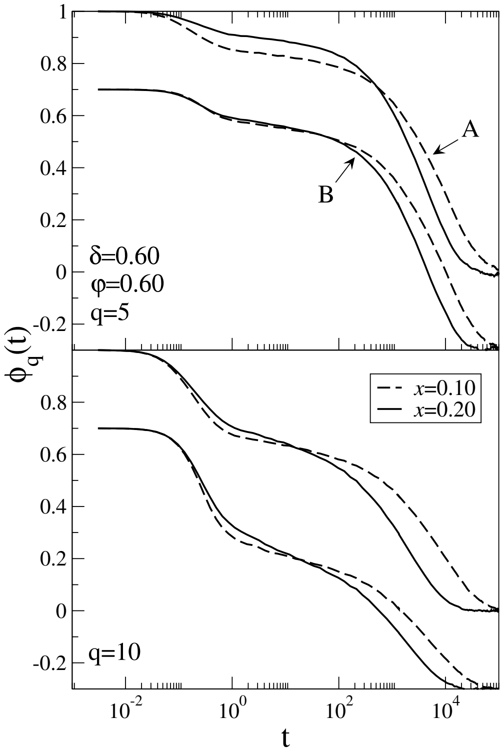

FIG. 2. Normalized density-correlation functions for binary HSM for $\delta = 0.60$. Here $\varphi = 0.60$. The full and dashed lines present mixtures with $x = 0.20$ and $x = 0.10$, respectively. Upper and lower panels exhibit the results for $qd_A = 5$ and $qd_A = 10$, respectively. The results for B particles have been shifted down by 0.3.

Within MCT, the ideal-glass states are characterized by arrest of the density fluctuations. Within the liquid state, for φ below but close to φ^c, the $\phi_\alpha(q, t)$-versus-log$t$ curves exhibit a two-step relaxation process with a plateau at $f_\alpha^c(q)$, the so-called critical Debye-Waller factor. The length of the plateau increases on decreasing $\varphi^c - \varphi$. The first relaxation step deals with the relaxation towards the plateau $f_\alpha^c(q)$. The second step is the long-time process dealing with the decay of $\phi_\alpha(q, t)$ from the plateau to zero. This plateau, a characteristic feature of structural relaxation, is clearly exhibited in Figs. 2 and 3. The three mixing features discussed above concerned the time scale of the second relaxation step. Figures 2 and 3 for $qd_A = 5$ exhibit a fourth important mixing effect, already reported in [6] for $\delta = 0.60$: Upon increasing x, the height of the plateaus of $\phi_A(q, t)$ increases. This is accompanied by a flattening of the $\phi_A(q, t)$-versus-log$t$ curve in the plateau region. An indication of the same effect is also shown by $\phi_B(q, t)$. Our results show that these mixing effects are structural relaxation phenomena that occur also in systems with Newtonian dynamics, and that they occur for small as well as for large particle size disparity. We also note that, on increasing x at $\delta = 0.6$, the increase of the height of the plateau value, together

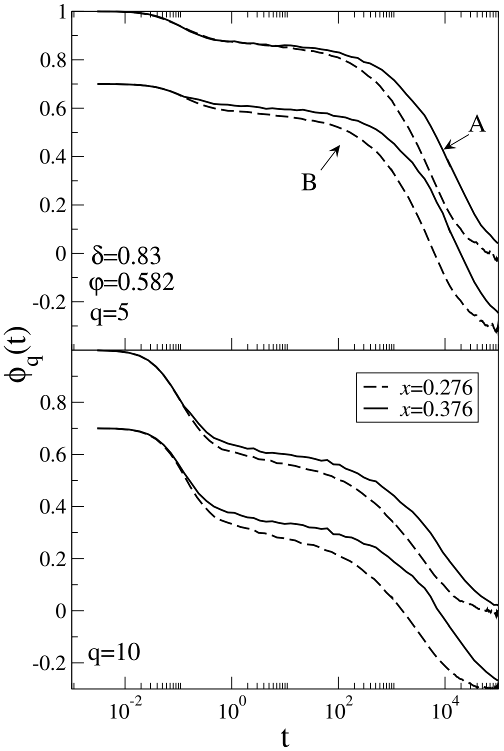

FIG. 3. As in Fig. 2, but for size ratio $\delta = 0.83$. The packing fraction is $\varphi = 0.582$.

with the speed up of the dynamics, forces the relaxation curves for the same φ but for different x to cross at the beginning of the second relaxation step. For $\delta = 0.83$, an increase of x at fixed φ generates a slower dynamics and, hence, no crossing of the curves in the time interval for the second relaxation step is observed.

In conclusion, we have studied structural relaxation of four binary hard-sphere mixtures via molecular-dynamics simulations over dynamic ranges extending over about 5 orders of magnitude. Several interesting 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 height 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 of a light-scattering study of a quasibinary colloidal suspension [6], and the predictions within MCT [9]. Finally, our work suggests that mode-coupling theory can help in predicting changes in the dynamics of glass-forming liquids produced by systematic changes of the model details.

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[1] Articles in J. Non-Cryst. Solids **307–310** (2002).
[2] Articles in J. Phys. Condens. Matter **15** (2003).
[3] J. N. Roux, J.-L. Barrat, and J.-P. Hansen, J. Phys. Condens. Matter **1**, 7171 (1989).
[4] W. Kob, in *Slow Relaxations and Nonequilibrium Dynamics in Condensed Matter*, edited by J.-L. Barrat, M. Feigelman, J. Kurchan, and J. Dalibard, Les Houches Summer School of Theoretical Physics (Springer, Berlin, 2003), pp. 201–269.
[5] S. I. Henderson, T. C. Mortensen, S. M. Underwood, and W. van Megen, Physica (Amsterdam) **233A**, 102 (1996).
[6] S. R. Williams and W. van Megen, Phys. Rev. E **64**, 041502 (2001).
[7] W. Götze, in *Liquids, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin, Les Houches Summer School of Theoretical Physics (North-Holland, Amsterdam, 1991), pp. 287–503.
[8] W. van Megen, Transp. Theory Stat. Phys. **24**, 1017 (1995).
[9] W. Götze and Th. Voigtmann, Phys. Rev. E **67**, 021502 (2003).
[10] Th. Voigtmann (to be published).
[11] D. C. Rapaport, *The Art of Molecular-Dynamics Simulation* (Cambridge University Press, Cambridge, England, 1997).
[12] J.-P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
[13] H. M. Schaink and C. Hoheisel, Phys. Rev. A **45**, 8559 (1992).
[14] B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. **53**, 3813 (1970).
[15] W. Kob and H. C. Andersen, Phys. Rev. Lett. **73**, 1376 (1994).
[16] It is interesting to observe that, for large δ values, increasing the relative φ of the small species x decreases the φ of both the glass and the crystallization (substitutional) line [e.g., J.-L. Barrat *et al.*, J. Phys. C **20**, 1413 (1987)].
[17] Note that, for the case of $\delta = 0.6$ and $x = 0.20$, the γ_A and γ_B values are very different. In particular, the value for the A particles is larger than one would expect on the basis of previous works. We also note that the γ values are sensitive to the range of density fitted. We report here the best fit values over the slowest five points. A fit with $\gamma_A = 3.0$ has also been tried. The fit interval is smaller but the conclusion $\varphi^c(x = 0.20) > \varphi^c(x = 0.10)$ remains valid.