Effect of Composition Changes on the Structural Relaxation of a Binary Mixture

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Within the mode-coupling theory for idealized glass transitions, we study the evolution of structural relaxation in binary mixtures of hard spheres with size ratios $\delta$ of the two components varying between 0.5 and 1.0. We find two scenarios for the glassy dynamics. For small size disparity, the mixing yields a slight extension of the glass regime. For larger size disparity, a plasticization effect is obtained, leading to a stabilization of the liquid due to mixing. For all $\delta$, a decrease of the elastic moduli at the transition due to mixing is predicted. A stiffening of the glass structure is found as is reflected by the increase of the Debye-Waller factors at the transition points. The critical amplitudes for density fluctuations at small and intermediate wave vectors decrease upon mixing, and thus the universal formulas for the relaxation near the plateau values describe a slowing down of the dynamics upon mixing for the first step of the two-step relaxation scenario. The results explain the qualitative features of mixing effects reported by Williams and van Megen [Phys. Rev. E 64, 041502 (2001)] for dynamical light-scattering measurements on binary mixtures of hard-sphere-like colloids with size ratio $\delta = 0.6$.

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I. INTRODUCTION

The study of glass-transition phenomena in dense colloidal suspensions has received much attention during the past years. Such systems are well suited for a test of theories since the particles’ properties can be tuned within a broad range. In particular, one can produce mixtures with particles of different sizes and observe effects of changing composition or size ratio. Recent experimental work of Williams and van Megen [1] has shown that even in the simplest such systems, namely binary hard-sphere mixtures (HSM), interesting mixing phenomena appear for the dynamics close to the glass transition. Three effects have been reported going over from a one-component to a binary system containing up to 20% by volume of smaller spheres: (i) a shift of the glass transition to higher packing fractions, (ii) an increase in the plateau values of the correlation functions at intermediate times, connected to an increase in the glass form factors, and (iii) a slowing down of the initial part of the relaxation towards this plateau.

In this paper, mixing effects in binary HSM are investigated in the framework of the mode-coupling theory of the idealized glass transition (MCT). The study of glass-transition phenomena in colloidal suspensions that are good realizations of one-component hard-sphere systems has revealed that MCT describes much of the experimental facts in these cases [2, 3]. MCT makes general predictions for all glass-forming systems, independent of their underlying microscopic properties, be they one- or multi-component systems. Thus, a universal glass-transition scenario has been established, involving scaling laws and power-law variations of time scales. These properties have been found in many, not only colloidal, systems, as reviewed in Refs. [4, 5]. But MCT is also able to derive detailed results depending on the specific interactions of a system. The aforementioned hard-sphere colloids are a paradigmatic example for which, among other things, the wave-vector dependence of the Debye-Waller factors in the glass state has been evaluated and compared with results from scattering experiments [6]. The quantitative study of model systems allows one to predict general, while nonuniversal, trends that arise in certain classes of glass formers. Such project has been carried out for molecular liquids, where the known differences of reorientational relaxation for angular momentum $\ell = 1$ and $\ell = 2$ could be explained [7, 8]. The work presented here in a similar way aims to explain the general trends occurring in a mixture when changing its composition or the size disparity of its constituents. Our discussion, motivated by the cited light-scattering experiments [1], focuses on binary HSM with not too large size disparity in the species, close to the glass-transition density.

For a derivation of the MCT for mixtures, the reader is referred to Ref. [9]. The theory has already been applied to analyze computer-simulation data for a binary soft-sphere mixture [10], a binary Lennard-Jones mixture [14, 15], a molecular-dynamics model of a silica melt [12], and of a two-component metallic melt [13]. Also, properties of binary HSM in the limit of large size disparity [14, 15, 17, 18] and of charged hard spheres, particularly in their low-density region [16, 20, 21], have been studied in the framework of MCT. Mixing effects in a binary HSM have been addressed recently using a standard liquid-state mode-coupling approximation, albeit for states of such low density that glassy dynamics does not occur [22, 23]. MCT equations for mixtures have been derived recently within a nonlinear-hydrodynamics theory [24]. The found equations are very different from the ones analyzed here, and a connection of their implications with the light-scattering data [1] was not discussed.

The paper is organized as follows. In Sec. I, we summarize the basic formulas specifying the model under study. Sections II and V discuss our results for the fluid-glass transition diagram and the glass-form factors,
respectively. We demonstrate in Sec. VI that these lead to two qualitatively different scenarios for the dynamics close to the glass transition. Section VII summarizes the results.

II. DEFINITION OF THE MODEL

A. General Equations of Motion

A classical $S$-component fluid of $N$ spherical particles shall be considered. The fluctuations of the partial number-densities shall be denoted as $\varrho_\alpha(q) = \sum_k \exp[i\vec{q}\vec{r}_k^{(\alpha)}]/\sqrt{N}$, $\alpha = 1, 2, \ldots, S$, where the sum runs over all $N_\alpha$ particle positions $\vec{r}_k^{(\alpha)}$ belonging to species $\alpha$. From this, the partial density correlators are constructed, written $\Phi_{\alpha\beta}(q,t) = \langle \varrho_\alpha(q)\varrho_\beta(q,t) \rangle$. Here, $\langle AB \rangle = \delta A^*\delta B$ with $\delta A = A - \langle A \rangle$ denotes a scalar product in the space of dynamical variables. Angle brackets indicate canonical averaging for temperature $T$. The time evolution is generated by a Liouvillian $\mathcal{L}$: $\varrho_\alpha(q,t) = \exp[\mathcal{L}t] \varrho_\alpha(q)$. Since the $\varrho_\alpha$ are spatial Fourier transforms of a real density variable in an isotropic, translational invariant system, $\Phi_{\alpha\beta}(q,t)$ is real, even in $t$, and it depends on the wave vector only through $q = |q|$. An evaluation of the density correlators $\Phi_{\alpha\beta}(q,t)$ is the major aim of this paper.

The starting point of the theory is the exact reformulation of the equations of motion using the Zwanzig-Mori technique. Considering the limit of a system of colloidal particles undergoing Brownian dynamics, this equation reads

$$\tau(q)\dot{\Phi}(q,t) + S(q)^{-1}\Phi(q,t) + \int_0^t M(q,t-t')\Phi(q,t')\,dt' = 0. \quad (1a)$$

It is to be understood as a matrix equation as is indicated by the bold symbols. $S(q)$ is the matrix of partial structure factors defined by $S_{\alpha\beta}(q) = \langle \varrho_\alpha(q)\varrho_\beta(q) \rangle$. The short-time behavior of the correlators is given by $\Phi(q,t) = S(q) - \tau(q)^{-1}t + \mathcal{O}(t^2)$, where $\tau(q)$ is a symmetric positive definite matrix of relaxation times. It shall be specified in terms of short-time diffusion coefficients $D_{\alpha\beta}(q)$ as $\tau_{\alpha\beta}(q) = 1/(q^2D_{\alpha\beta}(q))\delta_{\alpha\beta}$. The memory kernel $M(q,t)$ is given through the so-called fluctuating forces, $M_{\alpha\beta}(q,t) = (k_B T)^2(x_\alpha/m_\alpha)(x_\beta/m_\beta)(q\mathcal{L}_\alpha(q)|\mathcal{R}(t)\mathcal{L}_\beta(q))$. Here, $\mathcal{L}$ is the projector perpendicular to the number densities, $\varrho_\alpha(q)$, and the longitudinal parts of the number current densities, $\langle q_\alpha(q) = \mathcal{L}\varrho_\alpha(q)\rangle$. $\mathcal{R}(t) = \exp[i\mathcal{L}q t]$ is the reduced evolution operator. The $m_\alpha$ are the masses of the species labeled by $\alpha$, and $x_\alpha = N_\alpha/N$ are the number concentrations.

Equation (1a) is complemented by an approximate expression for the memory kernel. The MCT approximation for this quantity follows from a straightforward generalization of the one-component case [8] and gives the polar form

$$M(q,t) = \mathcal{F}[\Phi(t),\dot{\Phi}(t)](q) \quad (1b)$$

of a symmetric bilinear form of the density correlators

$$\mathcal{F}_{\alpha\beta}[\Phi^{(1)},\Phi^{(2)}](q) = \frac{1}{2q^2} \frac{\rho}{x_\alpha x_\beta} \sum_{\alpha'\alpha''\beta'\beta''} \sum_\vec{k} V_{\alpha\alpha'\alpha''}(q,\vec{k},\vec{p})\Phi_{\alpha'\beta'}^{(1)}(k)\Phi_{\beta'\beta''}^{(2)}(p)V_{\beta\beta''}\delta\Phi_{\alpha\beta}(q,\vec{k},\vec{p}). \quad (1c)$$

Here, $\rho$ is the total number density, $\vec{p} = \vec{q} - \vec{k}$, and $V_{\alpha\beta}(\vec{k},\vec{p})$ are vertices quantifying the coupling of a force fluctuation of wave vector $\vec{q}$ to density-fluctuation pairs with wave vectors $\vec{k}$ and $\vec{p}$, respectively. The vertices are given by the equilibrium structure of the system in terms of the Ornstein-Zernike direct correlation function $c_{\alpha\beta}(q)$ and static three-particle correlations. The latter shall be expressed in terms of the $S_{\alpha\beta}(q)$ using the convolution approximation. One thus arrives at

$$V_{\alpha\alpha'\alpha''}(q,\vec{k},\vec{p}) = (q\vec{k}/q)c_{\alpha\alpha'}(k)\delta_{\alpha\alpha''} + (q\vec{p}/q)c_{\alpha\alpha''}(p)\delta_{\alpha\alpha'}. \quad (1d)$$

A few remarks to these equations might be in order. The solution to Eqs. (1) exists for all $t \geq 0$ and it is uniquely determined by the initial conditions. For a system with colloidal short-time dynamics, the correlation functions $\Phi(q,t)$ are completely monotone functions [23]. This property is preserved by the specified MCT approximation. In detail, it implies the following. The matrices $\Phi(q,t)$ are positive definite, written $\Phi(q,t) \succeq 0$, for all times $t$ and at all $q$; and for the time derivatives, there holds $(-1)^l\partial_l^l\Phi(q,t) \succeq 0$ for all $l = 1, 2, \ldots$. Furthermore, the solution depends smoothly on $S_{\alpha\beta}(q)$, $\tau_{\alpha\beta}(q)$ and
of critical points shall be denoted by a superscript \( c \). To understand the bifurcation scenario, one needs to discuss the critical eigenvector of the linearization of Eq. (2a), \( H(q) \), given through

\[
H(q) - 2(S^c(q) - F^c(q))F[|F|^c, H](S^c(q) - F^c(q)) = 0 .
\]

This eigenvector is nondegenerate, which implies that all MCT bifurcations belong to the type \( A_\ell \), \( \ell = 2, 3, \ldots \), introduced by Arnol’d [20].

At the bifurcation singularity, a nontrivial long-time transient relaxation. The latter, be it Brownian or Newtonian, merely shows a discontinuity \( \delta M_{\ell}^c \) at the glass transition.

Here, the MCT expression for the transverse fluctuating-force kernel \( F^T(q) \) is obtained from \( F(q) \) by replacing in Eq. (4) the vertices by \( \sqrt{T}V_{\alpha\alpha'}(\tilde{q}, \tilde{k}, \tilde{p}) = (\tilde{q}^T \tilde{k}/q)c_{\alpha\alpha'}(k)\delta_{\alpha\alpha'} + (\tilde{q}^T \tilde{p}/q)c_{\alpha\alpha''}(p)\delta_{\alpha\alpha'} \). In this formula, \( \tilde{q}^T \) is a vector of length \( q \) perpendicular to \( \tilde{q} \).

**B. The Binary Hard-Sphere Mixture**

The general theory shall be applied to binary hard-sphere mixtures (HSM), consisting of large (A) and small (B) particles. If \( d_\alpha, \alpha = A, B \), denote the particle diameters, the packing fractions of the species read \( \varphi_\alpha = (\pi/6)(x_\alpha q)d_\alpha^3 \), and the total packing fraction is given by \( \varphi = \varphi_A + \varphi_B \). The thermodynamic state is
characterized by three control parameters. Let us choose them to be the total packing fraction \( \varphi \), the size ratio \( \delta = d_B/d_A \leq 1 \), and the packing contribution of the smaller species \( \hat{x}_B = \varphi_B/\varphi \). Whenever composition changes are considered in the following, a variation of \( \hat{x}_B \) for fixed \( \varphi \) and \( \delta \) is to be understood. This in turn implies the number concentration of the small particles to vary as

\[
\hat{x}_B = \frac{\hat{x}_B/\delta^3}{1 + \hat{x}_B(1/\delta^3 - 1)}.
\]

The procedure is somewhat in between a true addition, which would increase both total density and total packing fraction, and a replacement of a certain amount of large spheres by the same amount of smaller ones, which would reduce the total packing fraction. For sufficiently small \( \delta \), there appears a percolation threshold for the motion of the small particles in the glass formed by the large ones. This transition and its precursor phenomena shall not be considered in this paper.

Static structure input for our model is taken from the Percus-Yevick (PY) approximation \([32, 33]\). More accurate solutions of the Ornstein-Zernike integral equations for hard-sphere mixtures are available. Yet, one knows for one-component MCT that improvements aiming at, for example, thermodynamic consistency have little influence on the glassy dynamics. Unfortunately, the quality of the PY approximation at the desired high packing fractions is unknown. It is known that large errors of the structure factor can occur if one goes over to large values of \( 1/\delta \) \([34]\), but this case is excluded from our discussion.

With the structure factor and the direct correlation functions given, the vertices in Eqs. \((1a)-(1c)\) are well defined functions of the wave vectors and matrix indices. Hence, also the mode-coupling functional \( F \) in Eq. \((1d)\) is defined as a triple integral over the components of \( \vec{k} \); and the same holds for the functional \( F^T \). After introduction of bipolar coordinates and using rotational symmetry, the \( k \) integrals are transformed to double integrals over \( k = |\vec{k}| \) and \( p = |\vec{q} - \vec{k}| \). After performing the \( \vec{q} \to 0 \) limit in the functionals, the zero-wave-vector limits entering Eqs. \((3d)\) and \((6)\) are reduced to one-dimensional integrals over \( k \). As a next step, the wave vectors are reduced to points on a grid of \( M \) values. The grid is chosen as \( qd_A = q_0 + q\Delta q \), with \( q_0 = 0.2 \), \( \Delta q = 0.4 \), and \( q = 0, 1, \ldots, M - 1 \), unless otherwise stated. The integrals are replaced by Riemann sums. The resulting formulas are the same as explained explicitly before for the one-component systems \([35]\), but additional sums over matrix indices occur. As a result, the cited equations refer to ones for sets of \( M \) matrix correlators, where \( q \) serves as a label for the correlators. To complete the specification of the equations, the short-time diffusion constants are taken according to Stokes’ law, \( D^0_A = C/d_A \). The unit of time is chosen so that a choice of \( M = 100 \) is sufficient to avoid cut-off and discretization effects for the results \([5]\). Our work was done mostly with \( M = 200 \), implying a cut-off wave vector \( q^*d_A = 79.8 \). This enables us to handle size ratios \( \delta \geq 0.5 \) with the accuracy used earlier for the simple system. Thus, Eqs. \((1a)-(1c)\) are 600 coupled integro-differential equations for 600 correlators, and Eq. \((2a)\) formulate 600 implicit equations for the 600 glass form factors. The latter equations are solved by the iteration mentioned above.

Cuts through the liquid-glass transition surface in the three-dimensional control-parameter space for the binary HSM are depicted in Fig. \([\text{I}]\). To assure that the results do not seriously depend on the discretization used, we show as well the glass transition points calculated for \( \delta = 0.6 \)
and 0.8 from the model with $M = 600$, $\Delta q = 0.4/3$, $q_0 = 0.2/3$. In addition, for $\delta = 0.6$ the dotted line exhibits the result calculated with cutoff $q^*d_A = 39.8$ and $M = 100$ which are the discretization parameters used in Ref. [15]. One infers that for $\hat{x}_B \lesssim 0.3$, this discretization would be sufficient to produce reasonable results.

For fixed size ratio $\delta \lesssim 0.65$, the critical packing fraction first increases upon increasing $\hat{x}_B$. Since $\hat{x}_B = 0$ and $\hat{x}_B = 1$ both represent monodisperse hard-sphere systems, one gets $\varphi^c(\hat{x}_B = 0) = \varphi^c(\hat{x}_B = 1)$. Thus, the liquid-glass transition lines for $\delta \lesssim 0.65$ exhibit a maximum at some intermediate values of $\hat{x}_B$. It is well understood that big particles moving in a liquid of much smaller ones experience an effective attraction [37] that is of purely entropic origin. Such a short-ranged attraction leads to a stabilization of the liquid phase, as was explained earlier [38,39,40]. Our result is a direct analogon of this depletion-attraction effect. Similarly, from the discussion of polymer melts it is known that the introduction of smaller components into the system typically decreases the viscosity, i.e., drives the system further into the liquid phase; an effect sometimes called “plasticizing”. Therefore, the effect found here is an entropically induced plasticization effect.

For less-disparate-sized mixtures, the theory predicts an inversion of the effect described above. An example is shown in Fig. 3 for $\delta = 0.8$, where a decrease of $\varphi^c$ with increasing $\hat{x}_B$ up to some minimum point is observed. This is in accordance with similar MCT results for a binary soft-sphere mixture [1]. It means that the introduction of disorder due to a small polydispersity of the particles stabilizes the glass state. The transition diagram is not symmetric with respect to $\hat{x}_B \rightarrow (1-\hat{x}_B)$; our theory predicts for $0.65 \lesssim \delta \lesssim 0.8$ “S”-shaped transition lines.

To get another view on the transition diagram, let us define the relative change of $\varphi^c$ with respect to the one-component case through

$$\Delta \varphi^c(\delta) = (\varphi^c(\delta, x^+_{B}) - \varphi^c_0)/\varphi^c_0.$$  \hspace{1cm} (9)

Here, $x^+_{B}$ are the points at which a maximum or a minimum occurs in $\varphi^c(x_B)$ for fixed $\delta$; $\varphi^c_0 \approx 0.5159$ is the critical packing fraction of the one-component system. The resulting values are plotted in Fig. 2 together with data taken from Ref. [41]. There, results for $\Delta \varphi^c(\delta)$ of several experiments for random-loose sphere packings in two-component steel-ball mixtures have been presented. These are operationally defined as the random packing fractions obtained when pouring spheres into a container without subsequent densification through shaking. One observes that both $\Delta \varphi^c(\delta)$ and the data follow the same trend. Note that we get negative values for $0.65 \lesssim \delta < 1$. In Ref. [41], no such effect is discussed, but it is reported that there seems to be no observable change in the data.

There is no precise theoretical definition of the concept of random loose packing. Nevertheless, the reported values can be taken as a quantization of a mixing effect, i.e. of modifications of the random cage structure. The fact that the variation in $\Delta \varphi^c$ with $\delta$ agrees with these experimental findings supports the conclusion that MCT is able to capture the change in the average cage structure induced by the presence of the second component.

FIG. 1: Liquid-glass transition diagram of a binary hard sphere mixture (HSM) for size ratios $\delta = 0.5$ (triangles), $\delta = 0.6$ (diamonds), $\delta = 0.7$ (squares), and $\delta = 0.8$ (circles), plotted as critical total packing fraction $\varphi^c$ versus packing contribution of the smaller species, $\hat{x}_B = \varphi_B/\varphi$. Full lines are guides to the eyes. The dashed lines indicate results obtained from tripling the number $M$ of grid points from $M = 200$ to $M = 600$, and the dotted line for $\delta = 0.6$ shows results obtained using $M = 100$; see text for details.

FIG. 2: Maximum relative increase and decrease of the critical packing fraction, $\Delta \varphi^c(\delta)$, according to Eq. (9), as a function of the size ratio $\delta$ (crosses), together with experimental data for random loose packing (triangles, reproduced from Ref. [41], cf. text). For the MCT critical packing fraction values, two symbols are noted for those $\delta$, where a maximum and a minimum different from the $\delta = 1$ value could be identified.
The results from above suggest that the change of the glass-transition point with composition can be understood by looking at the geometrical structure of the system. This information is reflected by the static structure factors, which comprise the relevant input for the MCT vertex in Eq. (1d). In particular, it is understood that the $q$-vector region around the first sharp peak in $S(q)$ is important for explaining the MCT glass transition. Fig. 3 shows this region for the total structure factor, $S(q) = \sum_{\alpha\beta} S_{\alpha\beta}(q)$, calculated in Percus-Yevick approximation for binary mixtures with $\varphi = 0.515$, $x_B = 0.2$ and three values of $\delta$.

![Figure 3: Total structure factor, $S(q) = \sum_{\alpha\beta} S_{\alpha\beta}(q)$, calculated in Percus-Yevick approximation for binary mixtures with $\varphi = 0.515$, $x_B = 0.2$ and three values of $\delta$.](image)

Another way of looking at the local structure of the HSM is provided by the partial pair distribution functions, $g_{\alpha\beta}(r)$. These have been obtained by numerically solving the Ornstein-Zernike equation in the $r$-domain using Baxter’s factor function for the PY closure. Results are shown in Fig. 4 for $g_{AA}(r)$ and $g_{AB}(r)$, again at fixed $\varphi$ and $x_B$ for various $\delta$. Here, both quantities vary more or less in phase for $\delta \gtrsim 0.7$, indicating that the local ordering of the one-component system is only slightly disturbed. One infers the B particles to be responsible for smaller average particle distances, thus favoring arrest of the structure. For smaller $\delta$, the one-component system’s structure is modified more severely, since $g_{AA}(r)$ and $g_{AB}(r)$ no longer vary in phase. Instead, “chemical ordering” effects can be seen, and they are responsible for the shift of the glass transition to higher packing fractions.

Let us stress that the variation of $\varphi^c$ with concentration, while being small in total, nevertheless has a large impact on the dynamics close to the glass transition. This holds since relaxation times of the liquid in this region depend strongly on the distance to the critical packing fraction. We shall return to this point in Sec. IIIA.

![Figure 4: Results within the Percus-Yevick approximation for the partial pair correlation functions $g_{\alpha\beta}(r)$ of binary HSM at $\varphi = 0.516$, $x_B = 0.2$, and $\delta = 0.9$ (solid lines), $\delta = 0.8$ (dot-dashed lines), and $\delta = 0.6$ (dashed lines). Curves for $g_{AA}(r)$ have been shifted up by 1.0 for clarity.](image)

### IV. GLASS FORM FACTORS

The spontaneous arrest of density fluctuations within the glass state is quantified by the glass form factors $F_{\alpha\beta}(q)$. In principle, these quantities can be measured in a scattering experiment via the intensity of the elastic line in the cross section. The diagonal elements $f_{\alpha\alpha}(q)$ of the normalized quantities

$$f_{\alpha\beta}(q) = F_{\alpha\beta}(q)/\sqrt{S_{\alpha\alpha}(q)S_{\beta\beta}(q)}$$

have the meaning of the Debye-Waller factor for the distribution of species $\alpha$. In the limit $x_B \to 0$, $\hat{F}_{BB}(q)$ is the spatial Fourier transform of the density distribution of a single localized B particle. It is the Lamb-Mössbauer factor $f_B^q(q)$ of a B particle in the hard-sphere system of A particles. A similar statement holds with the role of A and B particles interchanged, i.e., $f_A^q(q) = f_{AA}(q, x_B \to 1)$, but then the tagged particle is of the size $1/\delta$ in units of the surrounding hard spheres’ diameter. If the packing fraction $\varphi$ decreases towards the transition value $\varphi^c$, the $f_{\alpha\alpha}(q)$ decrease towards their critical values, $f_{\alpha\alpha}^c(q)$. These values are of particular relevance since they specify the so-called plateau values of the correlation functions of
reasonably by a Gaussian, $f_s(q) = \exp[-(qr_s)^2]$, where $r_s$ is the particle’s localization length \cite{13}. The localization length becomes the smaller the bigger the radius $d_s$ of the tagged particle is with respect to the radius $d$ of the surrounding spheres \cite{13}, in particular one gets for a tagged particle of diameter $d^*/d = 1/0.6$ (1/0.8, 0.8, 0.6) the value $r_s/d = 0.041$ (0.056, 0.095, 0.136). This implies the distribution of the $f_{s,c}^\alpha(q)$, given in the limit $x_B \rightarrow 1$ by $f_s(q)$ with $d^*/d = \delta$, to be broader than that in the limit $x_B \rightarrow 0$, given by $f'(q)$. Therefore the width of the distribution $f_{s,c}^\alpha(q)$ has to increase for $\delta < 1$ as $x_B$ increases from zero to unity. This is demonstrated in the upper panel by the dash-dotted line. It represents a simple interpolation, $f_{s,c}^\alpha(q) \approx f'(q) + (f_{s,c}^\alpha(q) - f'(q)) \delta_B$ for $\delta_B = 0.6$ and $q > 6/d_A$.

The change of $f_{s,c}^\alpha(q)$ can be understood along the same line of reasoning. But one has to notice that in this case the localization length of a smaller sphere in a surrounding of big ones matters. In particular, one has $f_{s,c}^\alpha(q, x_B \rightarrow 0) = f_{s,c}^\alpha(q/\delta)$. This yields a width of this distribution smaller than the one of the $f_{s,c}^\alpha(q, x_B \rightarrow 1)$, cf. Eq. (8). Such an effect can be seen in the lower panel of Fig. 5 for $\delta < 1$. Instead one notices that for all $x_B \leq 0.6$, the $f_{s,c}^\alpha(q)$ follow closely the result for $x_B = 0$, i.e. they are still close to unity at small $q$. This is a consequence of the normalization chosen here, since it is dominated by a change in $S_{AB}(q)$ at small $q$. It could be eliminated when discussing e.g. matrix-normalized quantities, $f(q) = S^{-1/2}(q) F(q) S^{-1/2}(q)$, where the normalization properly accounts for the overall change in $\langle S(q) \rangle$.

The above argument only depends on the fact that $\delta < 1$, but not on the precise ratio of localization lengths. Thus it is quite general in binary HSM. Fig. 6 shows the scenario for $\delta = 0.6$, i.e. for a larger size disparity, and indeed one recognizes the same trends as above. Here, the deviations of $f_{s,c}^\alpha(q)$ from the tagged particle’s $f_{s,c}^\alpha(q)$ set in faster with increasing $x_B$ than it was the case for $\delta = 0.8$. But one has to keep in mind that for smaller $\delta$, the changes in $x_B$ induce larger changes in the number concentration $x_B$, cf. Eq. (8). The description of $f_{s,c}^\alpha(q)$ as a simple interpolation between $f_{s,c}^\alpha(q)$ and $f'(q)$ as explained above is notably worse, indicating that this simple picture quantitatively only works for $\delta$ not too different from unity. Also more pronounced in this case are the changes in $f_{s,c}^\alpha(q)$ for small $q$, going back to the same reason as outlined above. Let us note in addition that for both $\delta$, the trend noticed for the diagonal elements is also found for $f_{AB}(q) = f_{AB}(q)/S_{AB}(q)$, provided one is sufficiently far away from those $q$ where a divergence due to vanishing $S_{AB}(q)$ occurs.

Macroscopic mechanic stability of the system is characterized by the elastic moduli. The liquid exhibits a longitudinal elastic modulus given by the structure factor through $M_L^{00} = g(k_B T) \sum_{\alpha \beta} x_\alpha S_{\alpha \beta}(q \rightarrow 0) x_\beta$ \cite{4}.
In the glass, the longitudinal modulus $M_L$ is larger, $M_L = M^0_L + \delta M_L$, due to the arrest of the structure, Eq. (5). Figure 7 shows the results for the binary HSM at the transition points for $\delta = 0.6, 0.7, \text{and} 0.8$, and also the critical shear modulus, Eq. (6). All quantities are shown in units of $(\rho k_B T)$ in order to more clearly reveal the effect of composition change. Note that the total density $\rho$ of the system increases and superimposes a rise in the moduli one could call an “ideal mixing” contribution. This ideal mixing value is given by the one-component values, $\delta M^0_L \approx 56.9$ and $M^0_T \approx 18.3$, shown through dashed lines in Fig. 7. At intermediate $\hat{x}_B$, strong deviations from ideal mixing occur. For all $\delta$ investigated here, the moduli decrease below their one-component values, indicating that the system becomes softer upon addition of smaller spheres. The effect increases with decreasing $\delta$ and it is of the order of 40% for $\delta = 0.6$. It is partly connected with a corresponding increase in compressibility, $\kappa = 1/M^0_T$. Indeed, one observes for given $\delta$ minima in all three quantities at roughly the same $\hat{x}_B$. Let us nevertheless point out that apart from this thermodynamic contribution to the softening of the glass, mode-coupling effects still are necessary to explain the moduli for $\delta = 0.6$. This can be inferred from the crossing of the $M^0_T$ and $\delta M^L_T$ versus-\hat{x}_B curves that is absent in $M^L_T$.

V. DYNAMICS

Close to an ideal glass transition, the essential aspects of the dynamics are described by a universal scenario. This scenario has been discussed comprehensively for one-component systems [35]. The results of Ref. [27] assure that these universal results are shared by the dynamics of the HSM. In particular, a two-step decay process arises, with plateau values given by the critical glass form factors, $\hat{f}_{\alpha \beta}(q)$, and power-law relaxations towards and from the plateau, governed by anomalous exponents. If the total packing fraction is increased towards the critical value $\phi_c$ with other parameters kept fixed, a drastic increase in the relaxation time $\tau_\alpha$ of the slowest decay process is obtained that is typical for glass-forming liquids.

In this section, we shall focus on the general, but non-universal features of the glassy relaxation in the binary HSM. To demonstrate the changes induced by different
compositions, let us investigate a horizontal intersection of the transition diagram of Fig. 1 and consider a change in the compositions, let us investigate a horizontal intersection of the composition of the smaller particles $x_B$ for fixed packing fraction $\varphi = 0.515$. The wave vector is $qd_A = 5.4$. The unit of time here and in the following figures is chosen so that the short time diffusivity is $D_A = 0.01/d_A$. Filled diamonds mark the intersection of the decay curves with the plateau value $\hat{f}_{c\alpha}(q)$. The open diamonds mark $\alpha$-relaxation-time scales $\tau_\alpha(q)$ defined by $\hat{\phi}_{\alpha\alpha}(q, \tau_\alpha(q)) = 0.1$.

A. General Features

The dynamics for $\hat{x}_B \leq 0.2$ is demonstrated by Figs. 8 and 9 for the AA and BB correlation functions. We chose the wave vector $q = 5.4/d_A$ below the peak in $\hat{f}_{AA}(q)$: it corresponds roughly to the one used in the light-scattering experiment of Ref. 1. The normalized correlators $\hat{\phi}_{\alpha\alpha}(q, t) = \phi_{\alpha\alpha}(q, t)/\hat{f}_{\alpha\alpha}(q)$ cross their plateau values $\hat{f}_{c\alpha}(q)$ at certain times, say $t_\alpha(q)$, $\hat{\phi}_{\alpha\alpha}(q, t_\alpha(q)) = \hat{f}_{c\alpha}(q)$, that are marked by filled diamonds in the figures. Close to the transition, the correlators are close to this plateau for a large time interval. This is a manifestation of the cage effect. In a leading order approximation for $\varphi_c - \varphi$ tending to zero, the time scale $t_\alpha(q)$ neither depends on $\alpha$ nor on $q$ 4. The independence of $\alpha$ is demonstrated to a good approximation in the figures. As explained in connection with Figs. 5 and 6, the plateau increases with increasing $\hat{x}_B$ and the increase is more pronounced for the larger majority particles A than for the smaller minority particles B.

The decay of the correlators below the plateau is referred to as the $\alpha$ process. A characteristic time scale, $\tau_\alpha(q)$, for this process shall be defined by specifying 90% of the decay: $\hat{\phi}_{\alpha\alpha}(q, \tau_\alpha(q)) = 0.1 \hat{f}_{c\alpha}(q)$. These times are marked by open diamonds in the figures. For $\delta = 0.8$, Fig. 8 demonstrates that the $\alpha$-relaxation scale increases with increasing $\hat{x}_B$. This reflects the fact that with increasing $\hat{x}_B$ the state corresponds to a smaller distance from the transition point (compare Fig. 4).

The scenario for $\delta = 0.6$, exhibited in Fig. 9, appears more subtle. In this case, the glass-transition diagram implies the distance to the transition to increase with increasing $\hat{x}_B$, thus leading to faster decay on the $\alpha$-time scale.
Thus, three independent measurements of \( \Phi_{\alpha\beta}(q, t) \) could be used to invert Eq. (11) and therefore to determine the three distinct functions \( \Phi_{\alpha\beta}(q, t) \). The latter are better suited for a comparison with the theory. But let us also demonstrate the dynamics for a typical example of the directly measured function \( \phi^{m}(q, t) \). If one assumes the colloidal particles to be uniform spheres, one gets \[ \phi^{m}(q, t) = \frac{1}{N_q} \sum_{\alpha\beta} b_{\alpha}(q)b_{\beta}(q)\Phi_{\alpha\beta}(q, t). \]  (11)

Here, \( N_q \) is some normalization constant chosen to satisfy \( \phi^{m}(q, t = 0) = 1 \). It was a crucial point in Ref. 1 to be able to vary the \( b_{\alpha}(q) \) without altering the dynamics. Thus, three independent measurements of \( \phi^{m}(q, t) \) could be used to invert Eq. (11) and therefore to determine the three distinct functions \( \Phi_{\alpha\beta}(q, t) \). The latter are better suited for a comparison with the theory. But let us also demonstrate the dynamics for a typical example of the directly measured function \( \phi^{m}(q, t) \). If one assumes the colloidal particles to be uniform spheres, one gets \[ b_{\alpha}(q) \propto \frac{\delta^{3}}{(qd_{\alpha})^{3}} \left( \sin(qd_{\alpha}/2) - \frac{qd_{\alpha}}{2} \cos(qd_{\alpha}/2) \right). \]  (12)

Figure 10 shows the results for \( \delta = 0.6 \) and \( \delta = 0.8 \) at \( qd_{\alpha} = 5.4 \). The same qualitative picture as discussed above for the \( \hat{\phi}_{AA}(q, t) \) correlator arises, yet the increase in plateau values is less pronounced. The reason is a destructive interference effect in Eq. (12) caused by \( \Phi_{AB}(q, t) \leq 0 \). This holds especially for \( \delta = 0.8 \), and also for smaller wave vectors. Nonetheless, some increase remains in all cases, and one should be able to see this in experiment. One could be tempted to analyze such data in terms of a one-component model. However, this would be misleading. For a one-component system, the observed increase of the plateau \( f^{m,c}(q) = \sum_{\alpha\beta} b_{\alpha}(q)b_{\beta}(q)\Phi_{\alpha\beta}(q) \) would imply that the system becomes stiffer upon increasing the contribution of smaller particles. But we have seen above from a discussion of the mechanical moduli that the opposite is the case.

Figure 11 exhibits \( \alpha \)-relaxation scales \( \tau_{A} \) for the larger particles as a function of mixing. It corroborates the picture suggested by the glass-transition diagram. Since the \( \alpha \) relaxation close to the glass transition varies as \( \tau_{A} \sim (\varphi^{c} - \varphi)^{-\gamma}, \gamma > 2.5 \), the variations of \( \tau_{A} \) are much more pronounced than those of \( \varphi^{c} \). Note that the values of \( \tau_{A} \) for different \( \delta \) do not necessarily coincide at \( x_{B} = 1 \). MCT predicts all \( \alpha \)-relaxation times \( \tau_{\alpha}(q) \) to be coupled. Thus, the qualitative picture demonstrated in Fig. 11 will also hold for the \( \alpha \)-relaxation scales of other experimental quantities such as the viscosities or inverse diffusivities. Nucleation rates are also affected by the diffusivities; thus Fig. 11 demonstrates a possible reason for nucleation in binary mixtures to vary strongly with changes of the composition.
B. Dynamics Close to the Plateau

One notices in Figs. 8 and 9 a trend for the relaxation onto the plateau value. This part of the curve, which deals with the onset of structural relaxation, displays a slowing down of the relaxation with increasing $\hat{x}_B$ for both cases considered for $\delta$. In principle, the relaxation in this time window is a result of both structural and transient relaxation. In a leading approximation the latter is given by

$$\Phi(q,t) = \exp\left[-q^2 D(q)t\right] S(q),$$

with the matrix $D(q)$ of short-time collective diffusion constants, $D(q) = (q^2\tau(q))^{-1}S(q)^{-1}$. In particular, for a binary mixture this yields

$$\hat{\phi}_{AA}(q,t) = 1 - q^2 D'(q)t + O(t^2),$$

where $D'(q) = x(q)D(q)$ with $x(q) = S(q)/S_{AA}(q)$, and $D(q)$ and $S(q)$ are the diffusion constant and the structure factor of the one-component system, respectively. It has already been noticed in Ref. [1] that a feature factor of the one-component system, respectively. $D$ persists also for large $q$. Thus, one expects a slowing down of the short-time diffusion due to mixing in the limit of small $q$. For the wave vector discussed here, however, the effect is small: with $\delta = 0.6$, $\varphi = 0.515$, and $q\rho_A = 5.4$, one gets $x \approx 0.82$ (0.76, 0.78) for $\hat{x}_B = 0.05$ (0.1, 0.2). The approximations resulting from Eq. (14) are shown for $\hat{x}_B = 0$ and 0.2 as dashed lines in Fig. 9. One infers that this describes the dynamics only for $\phi_{AA}(q,t) \geq 0.98$. Note that $x(q)$ is not monotonous in $\hat{x}_B$, but the mentioned increase in the stretching of the short-time relaxation with increasing $\hat{x}_B$ is. Furthermore, at still larger wave vectors, one has $x(q) > 1$ as $x(q \to \infty) = 1/x_A$, yielding faster short-time diffusion in the mixture. But the slowing down of the relaxation towards the plateau persists also for large $q$, as can be inferred from the numerical solutions. Thus we conclude that the change in the short-time diffusion coefficients is not sufficient to explain the observed effect.

Let us now focus on the structural relaxation as defined in Sec. IIA. Figure 12 presents solutions of Eqs. (9) for $\delta = 0.6$ and different $\hat{x}_B$ at fixed $\varphi$, together with the solutions reproduced from Fig. 8. The long-time parts of corresponding curves can be scaled on top of each other, as is demonstrated for the $\hat{x}_B = 0.2$ curve. For other $\hat{x}_B$, the same observation is valid. Nevertheless, we have applied the same rescaling as used for $\hat{x}_B = 0.2$ instead of matching $t_0$ and $t_*$ independently for different $\hat{x}_B$. This is done in order to also demonstrate the drift of the scaling time $t_0(\hat{x}_B)$ with $\hat{x}_B$. At short times, all structural relaxation curves follow the same asymptote $t^{-1/3}$, and one notices that they deviate from one another at roughly $t = 10t_*$. This demonstrates that the increase of the stretching in the initial decay with increasing $\hat{x}_B$, exhibited for $2.5 \lesssim \log_{10}(t/t_*) \lesssim 5.5$, is a result of structural relaxation rather than transient dynamics.

In order to achieve a deeper understanding of the conclusions concerning the initial part of the structural relaxation processes demonstrated above, recall that one can derive scaling laws for an analytical description of the correlators near their plateau values. This has been discussed comprehensively for the one-component system in Ref. [24]. The theory is based on the observation that the liquid-glass transition is described by a $A_2$ bifurcation of Eq. (2a) for the glass form factors. It is straightforward to generalize the theory for one-component systems to the case of interest here. Let us merely note the basic results necessary to understand the following figures.

For the asymptotic expansion, one identifies a small parameter $\sigma$ and, connected to it, a time scale $t_\sigma = t_0(\sigma / 2)^{1/(2a)}$. Here, the critical exponent $0 < a < 1/2$ is one of the nontrivial exponents of MCT that is calculated from the mode-coupling functional at the transition via the so-called exponent parameter $\lambda$, $\lambda = \Gamma(1-a)/\Gamma(1-2a)$. The separation parameter $\sigma$ is also calculated from the mode-coupling functional, and is a smooth function of the control parameters that vanishes at the transition. The conditions $\sigma > 0$ and $\sigma < 0$ characterize glass states and liquid states, respectively. Setting $\tilde{t} = t/t_\sigma$, one obtains an expansion in the small quantity $\sqrt{\sigma}$.

$$\Phi(q,t) - F^\sigma(q) = H(q)\sqrt{\sigma} g(\tilde{t})
+ H(q) [\sigma h(\tilde{t}) + \sigma \nu] + K(q) [\sigma g(\tilde{t})^2 - \sigma / (1-\lambda)]$$
$$+ K(q) \sigma / (1-\lambda) + O(\sigma^{3/2}).$$

Let us first explain the leading order contribution, which is given by the first line of Eq. (15). It demonstrates the so-called factorization theorem, in that it splits the wave-vector and control-parameter dependence off from
the time-dependence. It is the critical eigenvector $H(q)$ introduced above that governs the former. The latter is given by a master function $g(\hat{t})$ that is the solution of

$$\frac{d}{dt} \int_0^t g(\hat{t} - t') g(t') \, dt' = \lambda g(\hat{t}) + \text{sgn} \sigma ,$$

(16)

obeying $g(\hat{t} \rightarrow 0) \sim (t/t_0)^{-\sigma}$. The shape function $g(\hat{t})$ does not depend on the details of the mode-coupling vertices, but only on the exponent parameter $\lambda$. Thus, the factorization theorem predicts that all correlators for all models resulting in the same $\lambda$ can be rescaled to have the same shape, given by the master function $g(\hat{t})$.

The corrections to the specified scaling law are given by the terms of order $\sigma$ in Eq. (15). They consist of a part parallel to the critical amplitude $H(q)$, where a new correction-to-scaling shape function, $h(\hat{t})$, and a constant determined by the details of the mode-coupling vertices, $\nu$, appear. In addition, two correction amplitudes, $K(q)$ and $K'(q)$, to be evaluated from the mode-coupling functional, are introduced by the next-to-leading order. They explain that factorization holds with different quality for different correlators. One finds the $K_{AA}(q)$ and $K'_{AA}(q)$ to show the same qualitative variation with $q$ in the HSM considered here as in the one-component case discussed in Ref. [35]. The only parameter that cannot be calculated within this approach is the time scale $t_0$; it is fixed by matching the long-time limit of the asymptotic solution at the critical point, $\Phi^c(q,t) = F^c(q) + H(q)(t/t_0)^{-\alpha} + O(t^{-2\alpha})$, to the numerical solution at long times.

We first investigate the variation of $\lambda$ as a function of the composition, shown in Fig. [3]. The exponent parameter is larger than the value found for the pure hard-sphere system, $\lambda(\hat{x}_B = 0) = \lambda(\hat{x}_B = 1) = 0.736$. It exhibits a maximum smaller than 0.8 for $\delta \geq 0.6$. As a result, the critical exponent decreases relative to the value $a = 0.311$ for the hard-sphere system. In particular we get $\lambda = 0.752 (0.778)$, and from this $a = 0.304 (0.291)$ for $\hat{x}_B = 0.1 (0.2)$. As a consequence, the stretching of the decay towards the plateau increases somewhat with increasing $\hat{x}_B$ and decreasing $\delta$. But this effect is rather small and cannot explain the slowing down effect specified above.

Figure [4] shows the critical amplitudes $H(q)$ in the case $\delta = 0.6$ for the AA correlator. The normalized quantity $\hat{h}_{AA}(q) = \frac{H_{AA}(q)}{S_{AA}(q)}$ was chosen to match the representation of Figs. [8] and [9]. While there is no general trend valid for all $q$, we note that at the wave vector $q = 5.4/d_A$ shown above, $\hat{h}_{AA}(q)$ decreases significantly upon increasing $\hat{x}_B$. Let us emphasize that the region of $qd_A \lesssim 10$ is the one accessible in dynamical light-scattering experiments on colloidal systems. Furthermore, let us add that qualitatively the same change with $\hat{x}_B$, although less pronounced, is observed in the $\delta = 0.8$ case. The decrease of $\hat{h}_{AA}$ yields a flattening of the $\phi(t)$-versus-log$t$ curve within the time window that can be described by the leading-order contribution to Eq. (15). The identified effect is further increased since the time scale $t_0$ decreases with increasing $\hat{x}_B$. One gets $t_0 = 0.4408 (0.2026, 0.1385)$ for $\hat{x}_B = 0 (0.1, 0.2)$ and other microscopic parameters as given above.

Let us turn the preceding discussion into a quantitative demonstration by comparing in Fig. [14] the asymptotic formula with the complete solution for the $\phi_{AA}$ correlator. The case $\hat{x}_B = 0$ shows a typical scenario for the one-component system, where the first line of Eq. (15) describes over 3 decades in time of the solution, as indicated by the open diamonds. This window of the analytic description is expanded by the next-to-leading-order formula by about 1 decade both at short and at long times, as can be seen from the circle symbols. For $\hat{x}_B = 0.1$ and 0.2, the range of validity for both the leading and the next-to-leading order is seen to shrink; at $\hat{x}_B = 0.2$ it is, including corrections, only about 2 decades. But to un-
FIG. 15: Asymptotic description of the normalized correlation functions $\phi_{\alpha\alpha}(q, t)$ for $qd_\alpha = 5.4$, $\varphi = 0.515$, $\delta = 0.6$ and different $\hat{x}_B$ as indicated. Lines and symbols as in Fig. 15 for $\hat{x}_B = 0$. Therefore, the regions of validity of the asymptotic expansions are similar as well. Indeed, the relevant quantity specifying the range of validity of the asymptotic expansion is not the size of the logarithmic time interval, but the size of the decay interval $|\phi_{\alpha\alpha}(q, t) - f_{\alpha\alpha}(q)|$. Figures 15 and 16 demonstrate that the analytic formula, Eq. (15), describes the structural relaxation in $\phi_{\alpha\alpha}(q, t)$ towards the plateau $f_{\alpha\alpha}(q)$ below 0.70, 0.85, and 0.90 for $\hat{x}_B = 0$, 0.1, and 0.2, respectively. This is the regime where Eq. (15) exemplifies the slowing down of this decay with increasing $\hat{x}_B$ that was reported in Ref. [1].

VI. CONCLUSIONS

Within the mode-coupling theory (MCT) for a binary hard-sphere mixture, four mixing effects have been identified for states near the ideal liquid-glass transition. First, mixing suppresses intermediate-ranged ordering effects and this leads to an increase of the small-wavevector limit of the total structure factor, Fig. 1. Equivalently, the compression modulus of the liquid decreases. A similar softening of the elastic restoring forces is found for the moduli for compression and shear of the glass near the transition points, Fig. 1. Second, an apparently opposite phenomenon is exhibited by the increase of the Debye-Waller factors, i.e. a stiffening of the glass with respect to spontaneous density fluctuations, Figs. 2 and 3. This means primarily that mixing for fixed packing leads to better localization of the particles. The third effect is closely related to this, viz. a stiffening of the cages of the localized particles upon changes of composition. These changes are described by the critical amplitude, which decreases upon mixing, as shown in Fig. 1. The universal MCT formula for the initial part of the structural relaxation, Eq. (15), shows that this leads to a slowing down of the short-time part of the glassy dynamics, as demonstrated in Figs. 1 and 2 and discussed quantitatively in Figs. 3 and 4. The above described second and third mixing effects have been identified originally in experiments on colloids [1].

The fourth general effect concerns the scale for the long-time relaxation, i.e. the scale for hydrodynamic phenomena like diffusion, or, more generally, for the $\alpha$-relaxation processes of the liquid. Two scenarios are found as exhibited by the liquid-glass transition diagram, Fig. 2, or by Fig. 1. For small size disparity, mixing stabilizes the glass state. As described above for the initial part of the structural relaxation, also the final part of the decay is slowed down upon mixing. This is shown in Fig. 2 for the size ratio $\delta = 0.8$. However, for larger size disparities, an entropically induced plasticizing effect is found. Due to mixing, the glass state is destabilized and the $\alpha$-relaxation times decrease. As a result, the $\hat{\phi}(t)$-versus-log($t$) diagrams cross upon mixing as shown in Fig. 3 and observed for $\delta = 0.6$ in the experiments of Ref. [1].
In summary, our work demonstrates that MCT can explain qualitatively the mixing effects on the glassy dynamics of colloids observed for the size ratio $\delta = 0.6$. A quantitative comparison of the results of our theory with the data of Ref. [24] will be discussed in a subsequent publication. Our theory suggests to also carry out experiments for a size ratio near $\delta = 0.8$ since a different scenario is predicted for that case.

It can be expected that the results of our theory will also be of some relevance to experiments on glass-forming binary metal alloys. The formation of metallic glasses can to some extent be understood by treating the constituent atoms as hard spheres, which will then be all of similar size [47]. Even though in this paper we have dealt only with Brownian short-time dynamics relevant for colloidal suspensions, it is known that the long-time phenomena connected with the glass transition are the same for Newtonian dynamics [28, 29]. Recently, the concentration dependence of the critical temperature $T_c$ was discussed for a computer simulation of a Co$_{100}$–Zr$_x$ model [13]. This simulation used fine-tuned pair potentials to model the metallic glass former; but if one estimates the size ratio of a corresponding hard-sphere mixture from the atomic radii of Co and Zr [49], one gets $\delta \approx 0.8$ since a different factor $\delta = 0$ was found to have a maximum at intermediate $x$, i.e. the glass transition was found to occur at smaller coupling strengths. But this corresponds to a decrease of $\varphi^c$ in the HSM model. A similar reasoning holds for computer-simulated Ni-Zr melts [13].

Let us add some remarks on the results derived by Harbola and Das [24]. Their equations, as opposed to the ones studied in this paper, predict for the glass-form factors $f_{\alpha \beta}(q)$ and for the critical packing fraction of the glass transition $\varphi^c$ a dependence on the mass ratio $m_A/m_B$ of the two species. This result appears surprising because one should not expect the equilibrium results for a classical system to depend on the particles’ inertia parameters. It is obvious that the limit of vanishing concentration $x_B$ has to reproduce the bell-shaped Lamb-Mößbauer factor for the glass-form factor of the minority species, as discussed above in connection with Fig. 5. This result is not obtained in the theory of Ref. [24], which, as a consequence, does not reproduce the experimental finding of an increase in the correlator’s plateau values upon mixing [4]. Furthermore, the theory of Ref. [24] predicts a much larger increase of the critical packing fraction $\varphi^c$ upon mixing than measured [4]. Indeed, it predicts that the glass transition can disappear completely if the size ratio $\delta$ is smaller than a critical value. This result seems implausible, since there is no obvious mechanism which prevents the large particles from becoming a glass upon increasing the density.

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