How Glassy Relaxation Slows Down by Increasing Mobility

Suvendu Mandal,1 Thomas Franosch,1 and Thomas Voigtmann2, 3

1 Institut für Theoretische Physik, Universität Innsbruck, Austria
2 Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR), 51170 Köln, Germany
3 Department of Physics, Heinrich-Heine Universität Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany

(Dated: May 7, 2018)

We investigate how structural relaxation in mixtures with strong dynamical asymmetry is affected by the microscopic dynamics. Brownian and Newtonian dynamics simulations of dense mixtures of fast and slow hard spheres reveal a striking trend reversal. Below a critical density, increasing the mobility of the fast particles fluidizes the system, yet, above that critical density, the same increase in mobility strongly hinders the relaxation of the slow particles. The critical density itself does not depend on the dynamical asymmetry and can be identified with the glass-transition density of the mode-coupling theory. The asymptotic dynamics close to the critical density is universal, but strong pre-asymptotic effects prevail in mixtures with additional size asymmetry. This observation reconciles earlier findings of a strong dependence on kinetic parameters of glassy dynamics in colloidal–polymer mixtures with the paradigm that the glass transition is determined by the properties of configuration space alone.

The microscopic description of classical many-particle systems has different starting points depending on whether one models a small-molecular system or a colloidal suspension. Molecular dynamics follows Newton’s equations of motion, while the coarse-grained description of the solvent in colloidal suspensions leads to stochastic Brownian dynamics of the colloids. Since in thermodynamic equilibrium of classical mechanics the kinetic degrees of freedom can be integrated out separately, the equilibrium phase behavior of colloids is the same as that of an atomic system, provided the effective interactions among the particles are the same [1, 2]. This has inspired the use of “colloids as big atoms” for all structural and not inherently kinetic features [3]. In essence, the description reduces from one in phase space to one in the much smaller configuration space.

The glass transition is a well-known kinetic phenomenon. The near-equilibrium long-time dynamics close to the glass transition shares many generic features among colloidal and molecular glass-formers [4–11], although this is not at all obvious and requires explanation. The dynamics of a tracer particle in a random heterogeneous medium (the Lorentz-gas model) close to the localization transition provides a counter-example: There, Newtonian and Brownian systems show different dynamical critical exponents and hence belong to different universality classes [12–14].

Mixtures of species with high “dynamical asymmetry” are a more realistic model system for cases where the heterogeneous environment is slowly evolving over time, e.g., in molecular crowding in cells [15–17]. Relaxation phenomena in such mixtures share features of both the glass transition and the localization transition [18–24]. A striking dependence on the mass ratio of the species was reported for a mixture of large and penetrable small particles (Asakura-Oosawa model) [25]: Upon addition of equally heavy small particles (mass ratio \( \alpha_m = m_{\text{large}}/m_{\text{small}} = 1 \)) structural relaxation slowed down, while the addition of lighter small particles (\( \alpha_m = 10000 \)) caused the dynamics to speed up.

If one accepts that such a mass-ratio dependence influences the glass transition point, this challenges fundamentally our understanding of the glass transition, because it would entail that in describing slow dynamics the reduction of phase space to configuration space is not admissible. The use, e.g., of colloidal model systems to understand molecular glasses, or the extrapolation of molecular-dynamics-simulation results to soft-matter systems would be questionable. One would also contest the validity of the mode-coupling theory of the glass transition (MCT), where any mass-ratio dependence explicitly drops out of the equations that determine the glass-transition point and the dynamics asymptotically close to it [8, 26–28]. Generally, the great success of classical configuration-space statistical physics approaches close to the glass transition [4, 29, 30] would then appear puzzling.

As we demonstrate here, the resolution lies in the fact that one has to carefully distinguish asymptotic from pre-asymptotic features in the dynamics. Regarding the glass-transition point itself, “kinetic universality” is found, i.e., the modes of short-time relaxation become irrelevant in determining the ultimate fate of the system (fluid or glassy). In the vicinity of this transition point, two qualitatively different trends emerge upon changing the kinetic parameters. The MCT glass transition separates a regime where mobile species cause the relaxation to speed up, from one where they slow down the overall dynamics. Studying carefully the influence of dynamical asymmetry thus provides a way to identify separate mechanisms of structural relaxation.

We start with a simple model, viz. a mixture of equal-sized Brownian hard spheres with different short-time diffusivities. A similar system with continuous interactions
has recently been studied \cite{31, 32} as a model for motility-induced phase separation of active particles. The use of true hard-sphere particles provides an important conceptual simplification. For Brownian hard spheres, interparticle forces vanish for all admissible configurations and only provide no-flux boundary conditions for the \(N\)-particle probability density in the case that two spheres touch. As a consequence, the uniform equilibrium distribution is still a stationary solution of the Smoluchowski equation, and, by virtue of the \(H\)-theorem, the only one. Thus, all equilibrium properties of the system remain unchanged by assigning fast and slow short-time diffusivities to the particles. (This is not necessarily the case if one includes non-equilibrium driving forces as in active Brownian particles \cite{33}.)

We compare our Brownian-dynamics (BD) simulations of mixtures of hard-sphere particles with different short-time diffusivities to Newtonian molecular-dynamics (MD) simulations with different mass ratios. Particles are slightly polydisperse (10%; \(N = 1000\) particles drawn from a Gaussian distribution). True hard-sphere interactions are guaranteed by an event-driven algorithm both for Newtonian and Brownian dynamics \cite{34, 35}. We study the dependence on the short-time kinetic parameters, i.e., the ratio of short-time diffusivities \(D_{\text{fast}}^0/D_{\text{slow}}^0 =: \alpha \geq 1\) for BD, and the mass ratio \(m_{\text{large}}/m_{\text{small}} =: \alpha_m \geq 1\) for MD. Both parameters are defined such that large \(\alpha\) or \(\alpha_m\) implies that the small and fast species is much more mobile than the other species, and for simplicity, we restrict to the case where small is fast. MCT calculations are performed based on the Percus-Yevick static structure factor, as outlined in Refs. \cite{26, 36}. Additional MD simulations of Asakura-Oosawa mixtures are performed to extend those of Ref. \cite{25} (with \(N_{\text{large}} = 500\) large particles of 10\% polydispersity, at size ratio \(\delta = 0.15\)).

As a simple quantity that highlights the dynamical behavior, we discuss the mean-squared displacements (MSD), \(\delta r^2_a(t) = \langle \| \mathbf{r}_a(t) - \mathbf{r}_a(0) \|^2 \rangle\), where \(a\) labels the species (fast or slow). For short times, the MSD in BD reflect the dynamical asymmetry as \(\delta r^2_f(t) \approx 6D^0_a t\) and thus \(\delta r^2_f(t) / \delta r^2_s(t) \sim \alpha\) for \(t \to 0\).

Figure 1 shows the MSD for a 50 : 50 mixture of equal-sized Brownian hard spheres with a short-time diffusivity ratio \(\alpha = 10\). All curves show the expected approach to the kinetic arrest transition with increasing packing fraction \(\varphi\); after the short-time diffusive regime, the MSD show subdiffusive behavior on a length scale comparable to the typical localization length of particles in the glass, known as the Lindemann length scale, \(r_{\text{loc}} \approx 0.1\sigma\). At larger length scales, \(\delta r^2(t) / \sigma^2 \gtrsim 1\), the MSD follow a long-time diffusive asymptote, \(\delta r^2(t) \approx 6D_{\text{loc}}^L t\) with long-time diffusion coefficient \(D_{\text{loc}}^L\), on a time scale that diverges upon approaching the glass transition.

For the BD simulation results (top panel of Fig. 1), the case \(\varphi = 0.20\) represents the low-density regime where particles interact only weakly, and \(D_{\text{loc}}^L \approx D^0_a\). Close inspection reveals that in comparison to the monodisperse case (all short-time diffusion coefficients equal), the long-time dynamics of the slow particles is slightly enhanced while that of the fast particles is slowed down. In essence, the slow particles play the role of obstacles that hinder the motion of the fast particles, and the fast particles serve to increase the effective thermal noise that gives rise to the mobility of the slow particles at long times.

This trend prevails for densities close to the glass transition, as exemplified for \(\varphi = 0.58\) for the BD simulations. There, however, the fast particles are slowed down much more strongly. While initially, fast-particle diffusion is faster than that of the slow particles by a factor \(\alpha = 10\), their long-time diffusivity is faster only by less than 20\%.

Numerical results from MCT (bottom panel of Fig. 1) are in qualitative agreement with the simulation. As anticipated in the theory, at high densities the transient
nearest-neighbor cageing of particles is the dominant mechanism of structural relaxation that slows down the dynamics. Cageing corresponds to an intermediate-time plateau in the MSD, $\delta r_{\text{loc}}^2 \approx 6 \sigma_{\text{loc}}^2$. Since both species share the same excluded-volume interactions, $r_{\text{loc}} \approx 0.06 \sigma$ is independent of the species. Thus, in the intermediate-time window, the MSD of both fast and small species become identical.

To demonstrate that a change in $\alpha$ does not change the MCT glass-transition point, we show in Fig. 2 the structural relaxation times $\tau$, extracted from the BD simulations as the point where the tagged-particle density correlation function for a wave number close to the static-structure peak has decayed to $1/e$. The relaxation times are shown in natural units associated with the short-time motion of each of the species. This highlights the relative speeding up of slow particles by increasing the dynamical size asymmetry, and the associated slowing down of fast particles. For the fast particles, the effect is more drastic: for $\alpha = 100$, the relaxation time of the fast-particle density fluctuations increases by up to a factor of 50, while the slow-particle dynamics speeds up by less than a factor of 2.

Asymptotically close to the glass transition, MCT predicts a power-law divergence, $\tau \sim |\phi - \phi_c|^{-\gamma}$. Both the critical point $\phi_c$ and the non-universal exponent $\gamma$ are determined solely by the static structural quantities of the system [8] and thus do not depend on $\alpha$. In the window of packing fractions $\phi \in [0.53, 0.575]$, the $\tau(\phi)$ curves from BD are well described by such power laws. All data sets can be consistently rectified using $\phi_c = 0.583 \pm 0.002$ and $\gamma = 2.3 \pm 0.2$. These values of $\phi_c$ and $\gamma$ are consistent with those found for nearly-monodisperse hard-sphere systems [8]. Thus, both the thermodynamic equilibrium phase diagram and the kinetic MCT-glass transition in a mixture of hard spheres with different short-time kinetics are independent of the dynamical size asymmetry.

At densities close to and above $\phi_c$, deviations from the scenario described above set in. To see this more clearly, we turn to mixtures that include in addition to dynamical asymmetry also a strong size asymmetry $\delta = \sigma_{\text{fast}}/\sigma_{\text{slow}} \ll 1$ in the steric interactions. For packing fractions $\phi \lesssim \phi_c$, the effect of increasing the dynamical asymmetry is qualitatively as discussed above: increasing $\alpha$, the structural relaxation of the slow particles speeds up slightly, see Fig. 3. This also holds true in MD upon increasing $\alpha_{m}$. Power-law fits to the structural relaxation times work in the regime $\phi \lesssim 0.585$, as demonstrated in the lower panels of Fig. 3. They yield values $\phi_c \approx 0.594$ and $\gamma \approx 2.5$ that do not depend on $\alpha$ or $\alpha_{m}$: they confirm that the glass transition point and the asymptotic approach to it depend neither on the dynamical asymmetry nor on the fact whether the short-time motion is Brownian or Newtonian [6, 7].

A crucial observation is that the MCT transition point divides the state space into two regimes with different dependence on the kinetic parameters: Below $\phi_c$, the trend just described prevails, i.e., $\tau$ decreases with increasing $\alpha$ or $\alpha_{m}$. Yet, in the high-density regime $\phi \gtrsim \phi_c$, this trend is reversed: here, the structural relaxation of the large particles slows down upon increasing the dynamical

![FIG. 2. Structural relaxation times $\tau$ of the self-intermediate scattering function to wave number $q = 7.0$ of the slow (filled symbols) and fast (open symbols) particles of an equimolar Brownian hard-sphere mixture with dynamical asymmetries $\alpha = D_{\text{fast}}/D_{\text{slow}}$, as a function of packing fraction $\phi$ and in units of the respective short-time diffusion coefficients. Symbols are BD simulation results, lines are corresponding power-law fits $A(\phi - \phi_c)^{-\gamma}$ with $\phi_c = 0.583$ and $\gamma = 2.3$.](image)

![FIG. 3. Left: Self-intermediate scattering functions (wave number $q = 7.0$) of the slow particles in binary hard-sphere mixtures with size ratio $\delta = \sigma_{\text{fast}}/\sigma_{\text{slow}} = 0.2$ and relative packing contribution $x = \phi_{\text{small}}/\phi = 0.01$. Data are shown for total packing fractions $\phi = 0.57$ and 0.60, for BD simulations (top panel, $\hat{t}_0 = D_{\text{slow}}/D_0$) with short-time diffusivity ratios $\alpha = 5$ (solid lines) and $\alpha = 20$ (dashed), and for MD simulations (bottom panel, $\hat{t}_0 = \sqrt{\rho \sigma_{\text{slow}}/k_B T}$) with mass ratios $\alpha_{m} = 1$ (solid) and $\alpha_{m} = 100$ (dashed). Right: structural relaxation times for various $\alpha$ and $\alpha_{m}$ (symbols), and power-law fits (lines).](image)
and mass ratio \( \alpha \) spanned by \((\varphi_{\text{large}}, \varphi_{\text{small}})\), for various values of \( D_{\text{large}}^L \) as labeled.

This is also clearly seen by a shift of structural relaxation to longer times in the density correlation functions for \( \varphi = 0.60 \) (left panels of Fig. 3).

The trend reversal in the dependence on \( \alpha \) or \( \alpha_m \) separates the dynamical regime of MCT from a regime of relaxation within the glass, even without the need to precisely determine \( \varphi_c \). The dynamical window over which MCT provides an accurate description of the data increases with increasing dynamical asymmetry, as is evident from the right panels of Fig. 3. This implies that for \( \alpha \) or \( \alpha_m \) close to unity, a determination of the MCT transition point \( \varphi_c \) using only power-law fits to the relaxation times (or similar quantities) becomes more difficult.

In the limit \( \delta \to 0 \), one expects the fast (small) particles to remain mobile even at densities where the slow (big) particles approach kinetic arrest. The small particles may then be thought of as providing effective entropically mediated depletion interactions between the large particles. In colloid–polymer mixtures, small non-adsorbing polymers provide short-range depletion attractions for the big colloidal particles, and these cause a reentrant melting of the big-particle glass upon addition of small polymers [37–39].

The standard hard-sphere model for colloid–polymer mixtures is the Asakura–Oosawa (AO) model [1, 25]. The model assumes that the small particles do not interact among themselves, even though they keep excluded-volume interactions with the big particles. It was a striking finding reported from computer simulation [25] that the reentry emerges from the lines of constant diffusivity in the AO model only if the small particles are sufficiently light.

Figure 4 shows iso-diffusivity lines for values of \( D_{\text{large}}^L \) close to the glass transition of the AO mixture of Ref. [25]. For \( \varphi \lesssim 0.58 \), the addition of lighter small particles causes the structural-relaxation dynamics to speed up (iso-diffusivity lines bend to larger \( \varphi \)), while the addition of equally heavy small particles has the opposite effect. This is consistent with earlier observations [25]. However, extending these results to larger \( \varphi \) that are closer to the expected MCT glass transition (\( \varphi \approx 0.58 \)), one notices that also the addition of heavy particles (\( \alpha_m = 1 \)) leads to the reentrant enhancement of structural relaxation that was observed for the addition of light particles (\( \alpha_m = 10000 \)). Thus, although the pre-asymptotic approach to the MCT transition differs for different \( \alpha_m \) quite drastically, from extrapolation of our data to \( D_{\text{large}}^L = 0 \) one anticipates that the kinetic transition itself does not depend on the mass ratio.

In summary, we have shown that increasing the mobility of fast particles in dynamically asymmetric mixtures can induce a counter-intuitive slowing down of the relaxation of the slower particles. This regime is to be contrasted from the one asymptotically close to, but below the glass transition, where an increase in mobility leads to faster relaxation that is governed by universal behavior whose power laws are independent of the kinetic parameters.

This surprising trend reversal calls for an interpretation. The critical density \( \varphi_c \) marks a change in transport mechanism. Below \( \varphi_c \), motion is liquid-like, and the hallmark of the approach to the glass transition is a strong increase in viscosity, respectively, the friction, \( \zeta = (1/3k_B T) \int_0^\infty \langle f(t) \cdot f(0) \rangle \, dt \), where \( f(t) \) is a fluctuating reduced force. The diffusion then follows from the Einstein relation, \( D = k_B T/\zeta \). Since increasing the mobility of the fast particles causes the fluctuating forces to decay faster, this reduces the friction and speeds up the diffusion. Conversely, above \( \varphi_c \), motion is solid-like, i.e., viscous relaxation is ineffective. Here, residual currents determine the diffusivity via the Green-Kubo relation, \( D = (1/3) \int_0^\infty \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \, dt \), as an integral over the velocity-autocorrelation function (VACF). Consequently, an increase in mobility of the fast particles causes the VACF to decay faster, and therefore, diffusion slows down.

Our interpretation is compatible with mode-coupling theory, which considers the friction contribution to be dominant, but ignores residual-current relaxation. For this reason, MCT can capture only the regime below \( \varphi_c \), but not the one above. Studying systematically the influence of kinetic parameters therefore offers a clear way of identifying the transition in transport mechanism without relying on power-law fits over a limited range of relaxation times.

Both Brownian and Newtonian dynamics yield the same qualitative results for both regimes. This extends an earlier finding on the kinetic universality [7] to include size ratios and kinetic parameters. Therefore, it also encompasses the dynamics of mobile intruders in crowded environments [24, 25], with the caveat that one has to carefully separate the asymptotic behavior from pre-asymptotic effects on the dynamics.
We thank A. Meyer for discussions and helpful comments on the manuscript. We gratefully acknowledge support by the DFG research unit FOR1394 “Nonlinear Response to Probe Vitrification”, and by the Austrian Science Fund (FWF) under grant I 2887-N27 (TF).

[1] E. M. Terentjev and D. A. Weitz, eds., The Oxford Handbook of Soft Condensed Matter (Oxford University Press, Oxford, UK, 2015).
[2] J. K. G. Dhont, An introduction to dynamics of colloids, 2nd ed. (Elsevier, Amsterdam, 2003).
[3] W. C. K. Poon, J. Phys. A 49, 401001 (2016).
[4] G. L. Hunter and E. R. Weeks, Rep. Prog. Phys. 75, 066501 (2012).
[5] E. Bouchbinder and J. S. Langer, Phys. Rev. Lett. 106, 148301 (2011).
[6] T. Gleim, W. Kob, and K. Binder, Phys. Rev. Lett. 81, 4404 (1998).
[7] G. Szamel and E. Flenner, EPL 67, 779 (2004).
[8] W. Götze, Complex Dynamics of Glass-Forming Liquids (Oxford University Press, Oxford, 2009).
[9] E. R. Weeks and D. A. Weitz, Phys. Rev. Lett. 89, 095704 (2002).
[10] P. N. Pusey and W. van Megen, Phys. Rev. Lett. 59, 2083 (1987).
[11] G. Szamel and H. Löwen, Phys. Rev. A 44, 8215 (1991).
[12] B. I. Halperin, S. Feng, and P. N. Sen, Phys. Rev. Lett. 54, 2391 (1985).
[13] J. Machta, R. A. Guer, and S. M. Moore, Phys. Rev. B 33, 4818 (1986).
[14] M. Spanner, F. Höfing, S. C. Kapfer, K. R. Mecke, G. E. Schröder-Turk, and T. Franosch, Phys. Rev. Lett. 116, 060601 (2016).
[15] F. Höfing and T. Franosch, Rep. Prog. Phys. 76, 046602 (2013).
[16] D. Truzzolillo, D. Marzi, J. Marakis, B. Capone, M. Camargo, A. Munam, F. Moingeon, M. Gauthier, C. N. Likos, and D. Vlassopoulos, Phys. Rev. Lett. 111, 208301 (2013).
[17] D. Marzi, B. Capone, J. Marakis, M. C. Merola, D. Truzzolillo, L. Cipelletti, F. Moingeon, M. Gauthier, D. Vlassopoulos, C. N. Likos, and M. Camargo, Soft Matter 11, 8296 (2015).
[18] V. Krakoviack, Phys. Rev. Lett. 94, 065703 (2005).
[19] A. J. Moreno and J. Colmenero, J. Chem. Phys. 125, 164507 (2006).
[20] J. Kurzidim, D. Coslovich, and G. Kahl, Phys. Rev. Lett. 103, 138303 (2009).
[21] K. Kim, K. Miyazaki, and S. Saito, EPL 88, 36002 (2009).
[22] Th. Voigtmann and J. Horbach, Phys. Rev. Lett. 103, 205901 (2009).
[23] T. O. E. Skinner, S. K. Schneyder, D. G. A. L. Aarts, J. Horbach, and R. P. A. Dullens, Phys. Rev. Lett. 111, 128301 (2013).
[24] T. Sentjabrskaja, E. Zaccarelli, C. De Michele, F. Sciortino, P. Tartaglia, Th. Voigtmann, S. U. Egelhaaf, and M. Laurati, Nature Commun. 7, 11133 (2016).
[25] E. Zaccarelli, H. Löwen, P. F. Wessels, F. Sciortino, P. Tartaglia, and C. N. Likos, Phys. Rev. Lett. 92, 225703 (2004).
[26] W. Götze and Th. Voigtmann, Phys. Rev. E 67, 021502 (2003).
[27] G. Foffi, W. Götze, F. Sciortino, P. Tartaglia, and Th. Voigtmann, Phys. Rev. Lett. 91, 085701 (2003).
[28] W. Götze, in Amorphous and Liquid Materials, edited by E. Lüscher, G. Frisch, and G. Jacucci (Nijhoff Publishers, Dordrecht, 1987) pp. 34–81.
[29] L. Berthier and G. Biroli, Rev. Mod. Phys. 83, 587 (2011).
[30] M. Ediger and P. Harrowell, J. Chem. Phys. 137, 080901 (2012).
[31] A. Y. Grosberg and J.-F. Joanny, Phys. Rev. E 92, 032118 (2015).
[32] S. N. Weber, C. A. Weber, and E. Frey, Phys. Rev. Lett. 116, 058301 (2016).
[33] H. Tanaka, A. A. Lee, and M. P. Brenner, Phys. Rev. Fluids 2, 043103 (2017).
[34] A. Scala, Th. Voigtmann, and C. De Michele, J. Chem. Phys. 126, 134109 (2007).
[35] D. C. Rapaport, The Art of Molecular Dynamics Simulations, 2nd ed. (Cambridge University Press, Cambridge, 2004).
[36] Th. Voigtmann, EPL 96, 36006 (2011).
[37] K. Dawson, G. Foffi, M. Fuchs, W. Götze, F. Sciortino, M. Sperl, P. Tartaglia, Th. Voigtmann, and E. Zaccarelli, Phys. Rev. E 63, 011401 (2001).
[38] K. N. Pham, A. M. Puertas, J. Bergenholtz, S. U. Egelhaaf, A. Mössaid, P. N. Pusey, A. B. Schofield, M. E. Cates, M. Fuchs, and W. C. K. Poon, Science 296, 104 (2002).
[39] E. Zaccarelli, I. Saika-Voivod, A. Moreno, E. La Nave, S. Buldyrev, F. Sciortino, and P. Tartaglia, J. Phys. Condens. Matter 18, S2373 (2006).