A Double-Transition Scenario for Anomalous Diffusion in Glass-Forming Mixtures

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We study by molecular dynamics computer simulation a binary soft-sphere mixture that shows a pronounced decoupling of the species’ long-time dynamics. Anomalous, power-law-like diffusion of small particles arises, that can be understood as a precursor of a double-transition scenario, combining a glass transition and a separate small-particle localization transition. Switching off small-particle excluded-volume constraints slows down, rather than enhances, small-particle transport. The data are contrasted with results from the mode-coupling theory of the glass transition.

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Transport properties in disordered media are important in a wide range of applications from biophysics to geosciences. Intriguing behavior arises from ‘fast’ species moving through a dense host system, such as power-law-like dynamical conductivities of ion-conducting melts [1]. Likewise, ‘anomalous diffusion’ appears in many amorphous media: mean-squared displacements (MSD) that grow like $\delta t^2 \sim t^\mu$ (with some positive $\mu < 1$) over large time windows, instead of obeying Einstein’s law for ordinary diffusion ($\mu = 1$), are seen in biophysical tracer experiments investigating cellular environments [2–4], in zeolites [5, 6], gels [7, 8], amorphous semiconductors and photoconductors [9], or specially confined colloidal suspensions [10–12].

These systems can be thought of as mixtures composed of a small (fast) species and slow (big) host particles providing a highly complex confining structure (called ‘molecular crowding’ in biophysical literature). One way to deal with this, is to simplify the discussion to stochastic lattice gases and single tracers moving in a random environment [13–15], invoking as a reference point the single-file diffusion of non-overtaking particles, $\delta t^2 \sim t^{1/2}$ [16–18]. Such modeling obviously leaves out two aspects: the dynamics leading to a time-scale separation in the first place, and interactions among the carrier particles.

In order to highlight the remarkable features arising from dynamical many-body effects in anomalous diffusion, we investigate a binary, disparate-size soft-sphere mixture. We show how anomalous diffusion can be interpreted as a high-density phenomenon, specifically as the approach to a double-glass transition. Many-body interactions manifest themselves in a striking way in the dynamics of the small species: releasing excluded-volume constraints, their mobility is reduced at long times, rather than enhanced.

The appearance of two kinds of glasses – one where both particle species freeze, one where the smaller one stays mobile – has been predicted [19–21] using mode-coupling theory of the glass transition (MCT) [22], and indicated in colloidal experiments [23, 24] and molecular-dynamics (MD) simulations [25]. MCT qualitatively explains fast-ion diffusion in sodium silicate melts [26] as a precursor of this scenario. The two transitions have different microscopic origins: while the slow dynamics of the larger species is dominated by caging on the nearest-neighbor scale, the single-particle dynamics of the smaller species exhibits a continuously diverging localization length. This latter leads to the appearance of power-law-like anomalous diffusion. A similar transition also appears in a recent extension of MCT where big particles are immobile from the outset [27, 28].

The exemplary off-lattice model for particle localization is the Lorentz gas (LG), a single classical point particle moving between randomly distributed, fixed hard-sphere obstacles. At a critical obstacle density, the particle undergoes a localization transition understood as a critical dynamic phenomenon [29]. Close to the transition, a power-law asymptote for the mean-squared displacement is explained by continuum percolation theory, as demonstrated in recent extensive simulations [30–32]. We shall embark on the subtle connection between the LG and true binary mixtures below.

We performed molecular-dynamics (MD) simulations of an equimolar binary mixture of purely repulsive soft spheres, with interaction potential $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(r/\sigma_{\alpha\beta})^{-12} - (r/\sigma_{\alpha\beta})^{-6}] + \alpha_{\beta}$ for $r < r_- = 2^{1/6}\sigma_{\alpha\beta}$ (zero else), $\alpha, \beta \in \{1, 2\}$. Diameters are chosen additively, $\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/2$, $\sigma_{11}$ setting the unit of length, and $\epsilon_{11} = 0.35$. Nonadditive energetic interactions further decouple the species, $\epsilon_{12} = \epsilon_{21} = 1$ but $\epsilon_{i\alpha} = 0.1$. We set the temperature $k_B T = 2/3$, and all masses equal, $m_1 = m_2 = 1$: no time-scale separation exists between the two species at short times.

The smoothened potential $V(r) \times [(r - r_-)/h]^4/[1 + (r - r_-)/h]^4$ with $h = 0.005\sigma_{11}$ provides continuity of energy and forces at the cutoff $r_-$. Newton’s equations of motion were integrated for $N_1 = N_2 = 1000$ particles with the velocity form of the Verlet algorithm (time step $\delta t = 0.005/\sqrt{48} \text{ in units } t_0 = [m_i\sigma_i^2/\epsilon_{i\alpha}]^{1/2}$). To avoid crystallization, big-particle diameters were sampled equidistantly from the interval $\sigma_{11} \in [0.85, 1.15]$, retaining $\sigma_{12} = (1 + \sigma_{ss})/2$. At each number density $\rho$, four
in Fig. 1 is a fit to $D_{\text{MCT}}$, critical density and $\gamma$ density, due to a faster slowing down in particles which becomes more pronounced with increasing decoupling between the motion of large and small particles still retains a diffusive regime, allowing us to extract small-particle MSD even though this could technically be called anomalous diffusion, where $\langle \delta r_s(t)^2 \rangle \sim t^{\alpha}$ for the big particles, we observe big-particle diffusion has is about 2.5 orders of magnitude higher than in $\rho l$ by a power law as predicted by $S_{\text{ss}}(\rho)$ for the disparate-sized binary mixture. The fit yields $D_{\text{ss}}$ at two different densities as indicated, as functions of $q^{-1/3}$. The dotted line is $S_{\alpha}(q)$ for non-interacting small particles at $\rho = 2.19$.

independent runs were performed. Up to $\rho \leq 2.296 \sigma_{\text{ll}}^{-3}$, the system was fully equilibrated, requiring equilibration runs over at least $10^6$ and up to $2 \times 10^8$ time steps, followed by production runs of the same length. During equilibration, temperature was held constant by coupling the system periodically to a stochastic heat bath; production runs were done in the microcanonical ensemble. At the highest density $\rho = 4.215 \sigma_{\text{ll}}^{-3}$, over $10^9$ time steps were performed. No runs showed signs of demixing or equilibrium phase transitions.

Figure 1 displays the self-diffusion constants $D_\alpha$ obtained from the simulated mean-squared displacement (MSD), $\delta r_\alpha^2(t) = \langle (i \delta r_\alpha(t) - i \delta r_\alpha(0))^2 \rangle$ for a singled-out particle at $\vec{r}_\alpha(t)$ via the Einstein relation, $\delta r_\alpha^2(t \to \infty) \sim 6D_\alpha t$, where possible. The diffusion coefficients show a decoupling between the motion of large and small particles which becomes more pronounced with increasing density, due to a faster slowing down in $D_l$ than in $D_s$. At $\rho = 2.296$, $D_s$ is about 2.5 orders of magnitude higher than $D_l$, and at $\rho \geq 2.568$, big-particle diffusion has ceased over the entire simulation time window. Yet, the small-particle MSD still retains a diffusive regime, allowing us to extract $D_s > 0$ up to $\rho = 3.257$. Also shown in Fig. 1 is a fit to $D_l$ by a power law as predicted by MCT, $D \sim D_0(\rho_c - \rho)^\gamma$. The fit yields $\rho_c = 2.23$ for the critical density and $\gamma = 2.1$ for the critical exponent. A similar fit to $D_s$ is not satisfying and yields much larger $\gamma$ and $\rho_c$. $D_s(\rho)$ also clearly differs from an Arrhenius law, although a fit with two exponentials would be possible.

The slowing down visible in Fig. 1 and discussed in the following is purely dynamic; no essential changes in the static structure of the system were observed, despite the drastic compression employed. This is demonstrated by the partial static structure factors $S_{\alpha\beta}(q)$, showing little change with density if plotted as functions of $q^* = q\rho^{-1/3}$ to eliminate a trivial change in length scale (inset of Fig. 1).

The MSD corresponding to these transport coefficients are shown in Fig. 2. For the big particles, we observe a standard glass-transition scenario: a two-step process gives rise to a plateau over an increasingly large time window, crossing over to diffusion at increasingly large time, and at a length scale associated with dynamic nearest-neighbor cageing, typically at about 10% of a particle diameter (Lindemann’s criterion). Indeed, from the plateau of $\rho = 2.296$ curve one reads off the corresponding cage localization length $l_\alpha^* = \sqrt{\delta r_\alpha^2/6} \approx 0.66 \sigma_{\text{ll}}$, which decreases at larger $\rho$ due to compression. Although this could technically be called anomalous diffusion, we reserve that term for the behavior shown by the small particles: Around $\rho_c$, the small-particle MSD behave quite differently, with no sign of a two-step glassy dynamics. Instead, they show subdiffusive growth and cross over to ordinary diffusion at increasingly large length and time scales when increasing $\rho$. This indicates that nearest-neighbour cageing is not the dominant mechanism for their slowing down. The subdiffusive regime can be described by power-law variation, $\delta r_\alpha^2(t) \sim t^\mu$ with some effective $0 < \mu < 1$ that seems to decrease with increasing density.

The small-particle dynamics qualitatively agrees with previous MD results [25]. It also agrees with the dynamics found in the Lorentz gas [30–32]. There, subdiffusive growth with apparent density-dependent exponents $\mu$ is due to the approach to an asymptotic power law, $\delta r_s^2(t) \sim t^\mu$, that extends to $t \to \infty$ at the localization critical point. Careful simulations [30] could establish
x = 2/6.25 for the LG. To estimate a critical exponent x from Fig. 2 is tempting, but preasymptotic corrections render it impossible. It appears that a description of our data in terms of the LG asymptote is not convincing.

Our binary mixture differs from the LG *inter alia* through the finite density of interacting small particles. To establish the effect of this distinction, we switch off interactions among small particles, setting $\epsilon_{ss} = 0$ while keeping their number constant. Within simulation accuracy, structure and dynamics of the big particles are unchanged in this ‘transparent-small’ mixture.

Figure 3 compares the small-particle MSD of the two systems. Initially, the transparent small particles show weaker localization, intuitively expected as they have larger free volume available. This trend prevails at low densities. Surprisingly, at high $\rho$, switching off interactions leads to significantly slower diffusion compared with the fully interacting case as $t \to \infty$.

This is emphasized by the lower panel of Fig. 3: the effective exponent $\mu(t) = d[\log(\delta_{g}^2(t))]/d[\log(t)]$ crosses over from $\mu(0) = 2$ (ballistic short-time motion) to $\mu(\infty) = 1$ for ordinary diffusion or $\mu(\infty) = 0$ for arrested particles. For the LG model, $\mu(t) \approx x$ for increasingly large time windows close to the localization treshold. No clear plateaus are seen in our data, but switching off small–small interactions at fixed density $\rho$ systematically reduces $\mu(t)$ at long times. For comparison, we have indicated in Fig. 3 the predictions $x = 1/2$ for single-file diffusion and $x = 2/6.25 = 0.32$ from the LG model.

One could rationalize this finding as follows: excluded-volume constraints dominate the exploration of the small-particles’ local surroundings. In the long run, however, the exploration of all the cul-de-sacs for the noninteracting small particles in the frozen structure becomes vastly less effective than an interaction-mediated transport: interacting small particles have a larger probability to visit spaces where another small particle has just left, thereby channeling motion along ‘preferential paths’ known from ion-conducting melts [33].

No exact results are known for our binary mixture. MCT describes the slow glassy dynamics well, but a small-wave-vector divergence forbids its application to the localization transition [34, 35], and hence to a discussion of $x$. Still, the predicted double-transition scenario [19–21] is in line with our results. Thus, ignoring the asymptotic behavior close to the localization transition, let us focus on the effect of making the small particles ‘transparent’ in the binary mixture. The MCT equations for $\delta_{g}^2(t)$ are completely determined once the $S_{\alpha\beta}(q, t)$ are known: we take them from MD (cf. inset of Fig. 1). The difference in interactions enters the theory only through these quantities. To focus on effects arising from finite wave numbers, we only show MCT solutions on a finite grid $q_i = (i - 1/2)\Delta q \sigma^{-1}$ with $i = 1, \ldots, 120$, $\Delta q = 0.2$ and additional low-$q$ cutoff $q_0 = 4\sigma^{-1}$. Discretization of $q$ in fact yields $z_{MCT} = 1/2$ [21, 36].

Figure 4 shows the $\delta_{g}^2(t)$ for the two binary mixtures considered. Remarkably, the theory reproduces
three qualitative trends seen in the MD data, Figs. 2 and 3: (i) while the big-particle MSD exhibits the ordinary glassy two-step behavior (localization length around 0.1σl), δr^2(t) shows a different signature in the time windows accessible to the simulation. This is the precursor of the double-transition scenario. (ii) At low densities, transparent-small diffusion (dashed) is faster than the one for interacting small particles (solid lines), as expected from the reduced scattering frequency. This also holds for high densities at intermediate times. (iii) For large t and high ρ, transport of transparent small particles is much slower than in the fully interacting case. Within the MCT picture, the latter arises from a small shift of ρc ≈ 2.293 (γ ≈ 2.9) to lower ρ, rendering transport slower at fixed ρ. From our MD data, we cannot rule out whether this MCT picture is qualitatively correct, or whether one may indeed surmise that the change in dynamics is due to a cross-over from single-particle dynamics akin to the Lorentz-gas model to a many-particle interaction-assisted transport.

Let us summarize the main results. We studied a disparate-size mixture of purely repulsive soft spheres whose dynamics can be understood as the approach to two distinct, purely dynamical arrest transitions: (i) an ordinary glass transition connected with big-particle transport, where small-particle diffusion does not vanish, and (ii) a localization transition for small-particle transport at a higher density. As a precursor, a window over increasingly large length scales appears in the small-particle mean-squared displacement, exhibiting power-law anomalous diffusion, δr^2(t) ∝ t^{1/2}. This naturally explains an order-of-magnitude decoupling between diffusion coefficients, rendering our binary soft-sphere mixture a minimal model for fast ion transport in amorphous materials. Further experiments on specifically catered colloidal suspensions [23, 24] would be highly promising.

The anomalous diffusion in our binary mixture is a many-particle phenomenon: upon switching off interactions between the small particles, effective power-law exponents appear to decrease. As a consequence, excluded-volume interactions between the small particles accelerate their transport in the binary mixture. This is remarkable, since in the high-density regime one usually expects excluded volume to hinder individual particle motion; to understand the origin of this effect remains as a challenge for future work.

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