Slow dynamics in random media: Crossover from glass to localization transition

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Abstract – We study slow dynamics of particles moving in a matrix of immobile obstacles using molecular-dynamics simulations. The glass transition point decreases drastically as the obstacle density increases. At higher obstacle densities, the dynamics of mobile particles changes qualitatively from glass-like to a Lorentz-gas-like relaxation. This crossover is studied by density correlation functions, nonergodic parameters, mean square displacement, and nonlinear dynamic susceptibility. Our finding is qualitatively consistent with the results of recent numerical and theoretical studies on various spatially heterogeneous systems. Furthermore, we show that slow dynamics is surprisingly rich and sensitive to obstacle configurations. Especially, the reentrant transition is observed for a particular configuration, although its origin is not directly linked to the similar prediction based on the mode-coupling theory.

Transport phenomena in inhomogeneous systems are of great importance in physics, chemistry, biology, and engineering [1]. Many biological systems and composite materials consist of components of various sizes. The interplay between the broad range of length and time scales is essential to their dynamical properties. Recently, slow dynamics and the glass transition of such systems has attracted much attention. One reason is that it is interesting to understand the effect of the generic disorder of inhomogeneous systems on dynamic arrest [2]. Another reason is the extremely rich phenomenology that such systems exhibit near the glass transition point. For example, the colloidal suspensions with the short-range attractive potentials often show a crossover from the glass transition at high densities to gelation at lower densities, which is triggered by the spatial disorder due to aggregation of the colloidal particles [3–6]. Other examples include peculiar glassy dynamics in binary colloidal mixtures with disparate size ratios [7–9], star polymer mixtures [10], or anomalous ion transport in silicate glasses [11–13]. However, the presence of multiple length/time scales have hampered elucidation of the origin of these interesting behaviors. For this reason, it is desired to study a simple model system where inherent complexities are pruned down as much as possible. The possibly simplest model is a mixture of mobile and immobile spherical particles. This system is a minimal model of spatially heterogeneous systems such as a fluid absorbed in porous media. It can also be seen as a model of a binary mixture where the characteristic time scales of constituent particles of each component are well separated. The slow dynamics of this model is interesting in its own right; in the dilute limit of immobile particles, dynamic arrest or the glass transition takes place at finite densities of mobile particles. The opposite limit where a single mobile particle moves in a matrix of immobile particles is a classic Lorentz gas model. In this case, the mobile particle undergoes a localization transition at a finite immobile particle density, whose origin is purely geometric [14,15]. Recently, Krakoviack studied this model theoretically for arbitrary densities of mobile/immobile components by combining the replica method with the mode-coupling theory (replica MCT or RMCT) [16–18]. Two important predictions have been made in his studies. One is the crossover of dynamics from the glass to localization transition. When the volume fraction of mobile particles, \( \phi_m \), is large and the volume fraction of immobile particles, \( \phi_i \), is small, the system undergoes a glass transition, where the onset of slow dynamics is signaled by the discontinuous emergence of two-step relaxation, over all wavelengths, in the density correlation functions. This transition is referred to as

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Type-\(B\) transition in the glass transition community \[19\]. As \(\phi\) increases, the glass transition point \(\phi_n\) decreases drastically. At even larger \(\phi\), dynamics near the transition point qualitatively changes; one-step slow relaxation sets in at large wavelengths, where the amplitude of the relaxation curve grows continuously and progressively propagates toward the shorter wavelengths as \(\phi_m\) increases. This dynamics is called Type \(A\). The crossover from Type \(B\) to \(A\) is especially interesting since it is ubiquitous in many heterogeneous systems such as colloidal gels \[4,6\] and systems with disparate size ratios \[9\]. Another prediction of RMCT is the existence of the reentrant pocket in the low \(\phi_m\) and high \(\phi_i\) region, in which the dynamics of mobile particles is accelerated as \(\phi_i\) increases. This counter-intuitive result was rationalized as being caused by dephasing of the dynamics of the caged particles due to multiple collisions with other mobile particles \[16–18\].

In this letter, we investigate slow dynamics of mixtures of mobile/immobile particles by extensive numerical simulations. Our goals are twofold; first, we study the crossover from the glass to localization transition, exploring the whole range of parameter space of \((\phi_i, \phi_m)\). Slow dynamics of mobile particles near the transition line is analyzed using the density correlation functions, nonergodic parameters, and mean square displacement. We also calculate the dynamic susceptibility in order to probe the dynamic heterogeneities around this crossover. The second goal is to study the sensitivity of the dynamics of mobile particles to a geometry of random configurations of the immobile particles. To see this, we investigate two types of protocols to generate random configurations. In the first protocols which we refer to as Quenched-Annealed \((QA)\), we prepare the immobile particles, let them run for some time steps and, after they are equilibrated, we quench their motions. Then, the mobile particles are inserted into the void spaces of the matrix of immobile particles. This \(QA\) protocol is appropriate to study dynamics in a porous medium. This is the protocol that has been adopted in RMCT analysis \[16–18\]. In the second protocol which we call Equilibrated Mixture \((EM)\), we first run all of particles until they are equilibrated and then freeze the motion of a fraction of the particles while keeping the others mobile. We design this protocol in order to mimic binary mixtures with disparate time scales \[7–9,20\] and to study the dynamics of the faster \((lighter)\) component, which would be analogous to that of mobile particles in an EM system. In our study, we observe no sign of the reentrant transition for QA systems, which is contrary to the RMCT prediction \[16–18\]. Surprisingly, however, we do find the reentrant transition for EM systems. The physical origin of this reentrance is purely geometric and no direct connection with the RMCT prediction is inferred.

We carried out molecular-dynamics \((MD)\) simulations for two systems. The first one consists of an equal number of two types of particles. The reason to use the bidisperse system was to avoid crystallization in large \(\phi_m\) and small \(\phi_i\) regions. Our system is composed of \(N = N_1 + N_2 = 1000\) particles in a cubic box with dimension \(L = V^{1/3} = 10.8\) under periodic boundary conditions \((PBC)\). They interact via the soft potential \(v_{\alpha\beta}(r) = \epsilon(\sigma_{\alpha\beta}/r)^{12}\), where \(\sigma_{\alpha\beta} = (\sigma_a + \sigma_b)/2\) and \(a, b \in \{1, 2\}\). The size and mass ratio were \(\sigma_2/\sigma_1 = 1.2\) and \(m_2/m_1 = 2\), respectively. The units of length, time, and temperature were taken as \(\sigma_1, \sqrt{m_1\sigma_1^2}/\epsilon, \) and \(\epsilon/k_B\), respectively. \(N_1 (N_m)\) immobile (mobile) particles were chosen from the \(N_1 + N_2\) particles for each simulation run. We used the volume fractions defined by \(\phi_i = \pi N_i \sigma_{\alpha\beta}^3/6V\) and \(\phi_m = \pi N_m \sigma_{\alpha\beta}^3/6V\) as the system parameters, where \(\sigma_{\alpha\beta} = (\sum_{a,b} \sigma_{\alpha\beta}^3/4)^{1/3}\) is the effective diameter of particles \[21\]. The states investigated here were \(\sigma_{\alpha\beta}^3 = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.15, 1.2, 1.3, 1.4,\) and \(1.45\). The corresponding temperatures were \(T = 21.61, 10.42, 5.624, 3.207, 2.058, 1.350, 0.992, 0.772, 0.651, 0.473, 0.352,\) and \(0.306\), respectively.

We controlled \(\phi_i\) and \(\phi_m\) by changing \(N_i, N_m, \) and \(\sigma_{\alpha\beta}\). The minimum number of mobile particles was chosen as \(N_m = 10\). The time steps used were \(0.001–0.005\). The second system we investigated is the monatomic hard spheres. This system was employed in order to clarify the origin of the configuration dependence of the dynamics without being obscured by the bidispersity and softness of the continuous potential. The system includes \(N = 1000\) hard spheres with mass \(m\) and diameter \(\sigma\) in a cubic box of volume \(V\) under PBC. \(\sigma\) and \(\sqrt{m\sigma^2}/k_BT\) were used as the units of length and time, respectively. The temperature was fixed as \(k_BT = 1\). The volume fractions \(\phi_i\) and \(\phi_m\) were controlled by changing \(N_i, N_m, \) and \(V\). For both systems, we carefully checked the sample dependence of the observables throughout the study.

We first performed simulations of EM systems of the bidisperse soft-sphere system to observe the dynamics for the whole \((\phi_i, \phi_m)\)-space. In fig. 1, the dynamic phase diagram is plotted as a function of \(\phi_i\) and \(\phi_m\). This is drawn by calculating the self part of the intermediate
scattering function (ISF) for mobile particles defined by $F_s(k,t) = N^{-1}_m \langle \sum_{i=1}^{N_m} e^{i \vec{k} \cdot \vec{r}_i(t) - \vec{r}_i(0)} \rangle$. Here $\vec{k}$ is the wave vector, $k = |\vec{k}|$, and $\vec{r}_i(t)$ is the position of the $i$-th particle. We define the Liquid-Arrest (LA) line that delineates the liquid and arrested (glass or localization) phase in fig. 1 as the points at which the structural relaxation time $\tau_\alpha$ reaches $10^3$. Here $\tau_\alpha$ is defined by $F_s(k=2\pi/\xi, \tau_\alpha) = 0.1$. It is seen that, in the small $\phi_i$ regime, the LA line (or the glass transition points) drastically decreases as $\phi_i$ increases. This behavior is in accordance with the results of simulations [22-25] and RMCT [16-18]. This trend is sustained up to the small $\phi_m$ regime, beyond which a small reentrant pocket is observed. We shall discuss this reentrance later in detail.

In fig. 2 (a)–(c), we show $F_s(k,t)$ for the mobile particles along the three cuts across the LA line, as marked by arrows (a)–(c) in fig. 1. We also calculated the collective part of the ISF, $F(k,t)$ and found its behavior is qualitatively the same as $F_s(k,t)$ except at small wave vectors, the details of which will be explained elsewhere [26]. Figure 2 clearly demonstrates the existence of two types of distinct dynamics depending on the immobile particle densities. As shown in fig. 2(a), at small $\phi_i$, $F_s(k,t)$ exhibits a typical glassy behavior; the two-step relaxation with a plateau. This plateau or the nonergodic parameter (NEP) appears discontinuously over the whole wavelength range at an onset density, followed by a mild increase of the plateau heights as the densities $(\phi_i, \phi_m)$ increase along the arrow. This is typical Type-B behavior. At large $\phi_i$, on the other hand, the ISFs show a single-step relaxation with a long tail. Its amplitude or NEP continuously grows as $(\phi_i, \phi_m)$ increases across the LA line, as seen in fig. 2(c). The $k$-dependence of the NEP is plotted in the inset of fig. 2(c). NEP (calculated from $F(k,t)/F(k,0)$) emerges from zero continuously at small $k$, as $(\phi_i, \phi_m)$ approach the LA line. As $(\phi_i, \phi_m)$ increase further, NEP grows and this trend propagates progressively toward larger $k$. These behaviors are the hallmark of Type A or the localization transition predicted by RMCT and also demonstrated by simulations for various spatially heterogeneous systems such as colloidal gels [6,9]. The behavior of the mean square displacement (MSD) defined by $\delta^2(t) = N^{-1}_m \langle \sum_{i=1}^{N_m} \Delta \vec{r}_i^2(t) \rangle$, where $\Delta \vec{r}_i(t) = \vec{r}_i(t) - \vec{r}_i(0)$, also qualitatively changes as the dynamics changes from Type B to A. It is well known that, in the Type-B regime, MSD shows a plateau caused by the cage effect (the results not shown). On the other hand, at the low $\phi_m$ limit, where the system becomes a Lorentz gas, the anomalous subdiffusive behavior is observed at long times, which can be explained in terms of percolation theory [15]. The latter behavior is observed for the MSD in the Type-A regime, as shown in fig. 2(d). The MSD shows regular diffusive behavior in the liquid region, but near the LA line around $(\phi_i, \phi_m) \approx (0.377, 0.042)$, it becomes subdiffusive; $\delta^2(t) \approx t^{0.3}$, the exponent of which is consistent with 0.32 predicted for a Lorentz gas [27,28].

We next investigated the nonlinear dynamic susceptibility or 4-point correlation function, $\chi_4(k,t)$, for mobile particles [29–31], which is a good measure of the dynamic heterogeneities. $\chi_4(k,t)$ is defined as the variance of the fluctuations of the self part of the ISF by $\chi_4(k,t) = N^{-1}_m [\langle \hat{F}_s(k,t)^4 \rangle - (\langle \hat{F}_s(k,t) \rangle)^4]$. Here $\hat{F}_s(k,t) = (\hat{F}_s(k,t))$. In the literature [30], $N^{-1}_m \langle \sum_{i=1}^{N_m} \cos(\vec{k} \cdot \Delta \vec{r}_i(t)) \rangle$ is used as the definition of $\hat{F}_s(k,t)$. With this definition, however, $\chi_4(k,t)$ decays to $1/2$ at $t \to \infty$. On the other hand, as we demonstrate here, the peak of the dynamic susceptibility for the Type-A regime grows more mildly than for the Type-B regime. In order to demonstrate this suppression of the peak and thus the dynamic heterogeneities in the Type-A regime without being obscured by a constant plateau at large $t$, we have adopted an alternative definition of $\hat{F}_s(k,t)$ which is $N^{-1}_m \langle \sum_{i=1}^{N_m} \sin(\vec{k} \cdot \Delta \vec{r}_i(t))/|\Delta \vec{r}_i(t)| \rangle$. Of course, both definitions of $\hat{F}_s(k,t)$ lead to the identical averaged value $F_s(k,t) = (\hat{F}_s(k,t))$. With this new definition, $\chi_4(k,t)$ decays to 0 at $t \to \infty$. In fig. 3, the time evolution of $\chi_4(k,t)$ is plotted for the three states (a)–(c) in fig. 1. In the glass (Type-B) regime at (a), $\chi_4(k,t)$ exhibits behavior well-known for the bulk glass, i.e., a pronounced peak at the $\alpha$-relaxation time, whose height grows rapidly as the density increases, preceded by algebraic growth in the $\beta$-relaxation regime. In the localization (Type-A) regime at (c), on the other hand, $\chi_4(k,t)$ does not grow nor show a strong peak, even at long times. This implies that dynamic heterogeneities play a minor role in the slow transition.
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Fig. 3: (Colour on-line) Dynamic susceptibility $\chi_4(k, t)$ at $k = 2\pi$ for three states on each cut (a)–(c) indicated in fig. 1(a)–(c) from top to bottom.

dynamics in this regime. A similar behavior of $\chi_4(k, t)$ has been reported for colloidal gels whose slow dynamics is caused by geometrical frustrations [32,33].

Finally, we examine the sensitivity of the above results to the configurations of immobile particles by comparing results for the Equilibrated Mixture (EM) with those using the Quenched-Annealed (QA) protocol. Hereafter, we mainly focus on the moderately small-$\phi_m$ regime, because little protocol dependence is observed at large $\phi_m$. Here we switch the system to the monatomic hard sphere system to keep physical interpretation from being obscured by the bidispersity and continuous potential of the previous system. We checked that the results remain unchanged for the bidisperse soft-sphere systems. Dynamic phase diagrams of both QA and EM systems are plotted in fig. 4. Here the LA line is determined as the points beyond which the MSD does not exceed $10^2$ in a time within the simulation time $t = 10^4$. First, from the simulation for the lowest $\phi_m$ of our study ($\phi_m = 0.026$), we estimate the percolation point to be $\phi^p_i \approx 0.25$ for both QA and EM systems, which is close to 0.24 determined by Voronoi tessellation [24]. In the proximity of $\phi^p_i$, the MSD again shows subdiffusive behavior $\delta r^2(t) \approx t^{0.3}$ [27,28]. Details of these results will be explained elsewhere [26]. We here note that to check the finite size effects we performed the same simulations for $N = 10000$ and confirmed that overall behavior is almost the same in both the QA and EM systems.

As seen in fig. 4(a), no reentrant transition is observed for QA systems, contrary to the RMCT prediction. The LA line monotonically decreases as $\phi_i$ increases, which is compatible with the recent numerical simulations for the related QA system [34]. This result is hardly surprising, considering that the slow-down of mobile particle dynamics is mainly due to the geometrical confinement by the immobile particles. Krakoviack has conjectured that the reentrant pocket predicted by RMCT is caused by the dephasing of the trajectories of the caged mobile particles by collision with other mobile particles [16–18]. This effect may be too small to manifest itself as reentrance, if any. On the other hand, surprisingly, the EM system has the reentrant pocket, as clearly seen in fig. 4(b) and also in fig. 1. In other words, the dynamics of the mobile particles is accelerated as the number of mobile particles increases. The physical origin of the reentrant pocket for EM systems is clear. The random configuration of the immobile particles is generated by quenching their motion after both mobile/immobile particles are equilibrated together. Therefore immobile particles adjust themselves so that the free volume of both components is entropically maximized and leaves more available geometrical pathways for mobile particles, which pushes the percolation point $\phi^p_i$ to larger values and thus results in faster dynamics of mobile particles. The sensitivity of the percolation point on the protocols used to generate the configuration has been studied in several contexts [23–25]. However, its interplay with the dynamics of mobile particles, especially the reentrant transition, has not been explored, to the best of
our knowledge. It is worth mentioning that an analogous reentrant behavior has been found for a distinct system, i.e., a binary mixture consisting of large/small particles studied by MD simulations [20]. It has been observed that the diffusion of small particles becomes slower when the interactions between small particles are switched off [20]. We believe that this counter-intuitive observation is closely related to our finding of the reentrant pocket for EM systems; this switch-off leaves small particles “invisible” from each other and the large ones feel as if there are fewer small particles around them. Therefore, the equilibrium configurations of the large (thus less mobile) particles would leave less void spaces and pathways for small particles than before the switch-off. This consideration and the results of the present study naturally lead to a speculation that the separation of timescales, rather than the disparity of particle sizes, is a more essential element behind anomalous dynamics (such as reentrance) in heterogeneous systems.

In summary, we have carried out MD simulations to study the slow dynamics in random media for a broad range of parameter space. Two types of dynamics, A and B, have been observed and quantified in terms of various dynamic quantities, which supports RMCT predictions qualitatively. The dynamic susceptibility clearly demonstrates the minor roles of dynamic heterogeneities in the Type-A regime. We did not observe any evidence of the reentrant transition for the system for which RMCT has been originally applied. Contrary, we do observe the reentrant transition for the system with configurations generated with a different protocol. However, the physical origin of this reentrance is not directly linked to the similar prediction based on RMCT. Our study suggests that anomalous dynamics common in the heterogeneous systems might be, more often than not, explained well by a maximally simplified model such as the one in the present study.

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