Decoupling of exchange and persistence times in atomistic models of glass formers

Lester O. Hedges
School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom

Lutz Maibaum and David Chandler
Department of Chemistry, University of California, Berkeley, California 94720-1460, USA

Juan P. Garrahan
School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom

(Received 15 August 2007; accepted 4 October 2007; published online 3 December 2007)

With molecular dynamics simulations of a fluid mixture of classical particles interacting with pairwise additive Weeks-Chandler-Andersen potentials, we consider the time series of particle displacements and thereby determine the distributions for local persistence times and local exchange times. These basic characterizations of glassy dynamics are studied over a range of supercooled conditions and were shown to have behaviors, most notably decoupling, similar to those found in kinetically constrained lattice models of structural glasses. Implications are noted. © 2007 American Institute of Physics. [DOI: 10.1063/1.2803062]

Facilitated dynamics, as encoded in various kinetically constrained lattice models (KCMs), implies a general picture of structural glasses in which never-ending excitation lines coalesce, branch, and percolate throughout space time. Particles cannot move except when intersected by these excitation lines. As such, principal signatures of glassy dynamics can be viewed as manifestations of the distribution of times for which a particle must wait to first encounter an excitation, and the distribution of times between subsequent encounters. These are what we have called the distributions of “persistence” times and “exchange” times, respectively. Definitions and behaviors of excitation lines, persistence, and exchange are most obvious in idealized lattice models. Nevertheless, these concepts have been proven useful for interpreting intermittent and heterogeneous dynamics and transport decoupling in continuous force model systems and real systems, suggesting that these concepts are not limited to KCMs. Here, we show that indeed, exchange and persistence are well defined in terms of classical trajectories of the sort computed from molecular dynamics or observed with microscopy, and for a specific continuous force model, the distributions for exchange and persistence times behave similarly to those we have previously gleaned from KCMs.

Figure 1 illustrates our main result. It shows the distributions of persistence and exchange times for particle displacement events obtained from molecular dynamics simulations of an atomistic model. A local dynamical event or excitation is defined as a displacement beyond a specified cutoff length (see below). As the liquid becomes increasingly supercooled, the two distributions decouple and the typical persistence time becomes much larger than the typical exchange time. This decoupling occurs because excitations or mobilities and their associated excitation lines become relatively sparse at low temperatures. As such, for low enough temperatures, the time extent of space-time regions devoid of excitation lines (regions that dominate persistence processes) is typically very long compared to that for regions bridging the width of excitation lines (regions that dominate exchange processes). Thus, the origin of this decoupling is the same as that of dynamic heterogeneity.

This decoupling is reflected, for example, in observed breakdowns in mean-field transport relations such as the Stokes-Einstein inverse proportionality between diffusion constant $D$ and structural relaxation time $\tau_s$. In particular, when decoupling occurs, diffusion is much faster than would be predicted from $D \propto 1/\tau_s$ because diffusion, being an exchange process, has $1/D$ proportional to the first moment of the exchange time distribution, while $\tau_s$ is the first moment of the persistence time distribution.

The model study is a variation of the binary Lennard-Jones mixture of Ref. 18, which has been extensively studied as a model of supercooled liquids (see, e.g., Ref. 19). We modify this system by removing the attractive part of the Lennard-Jones interaction by adopting the Weeks-Chandler-Andersen (WCA) separation of the pair potential. We consider a mixture of two particle species $A$ and $B$ in a cubic simulation box of side length $L$ and volume $V=L^3$. The potential energy is the sum of the pairwise interactions between two particles of species $\mu, \nu \in \{A, B\}$,

$$V_{\mu\nu}(r) = 4\varepsilon_{\mu\nu}\left[\left(\frac{\sigma_{\mu\nu}}{r}\right)^{12} - \left(\frac{\sigma_{\mu\nu}}{r}\right)^{6} + \frac{1}{4}\right],$$

if their separation $r$ is less than $2^{1/6}\sigma_{\mu\nu}$ and $V_{\mu\nu}(r)=0$ otherwise. Following Ref. 18, we choose $\sigma_{AA}=1$, $\sigma_{BB}=5/6$, $\sigma_{AB}=(\sigma_{AA}+\sigma_{BB})/2$, and $\varepsilon_{AA}=\varepsilon_{BB}=\varepsilon_{AB}=1$. The particle masses are $m_A=2$ and $m_B=1$. Lengths, times, and temperatures are reported in units of $\sigma_{AA}$, $m_\mu\sigma_{AA}^2/\varepsilon_{AA}$, and $1/\sigma_{AA}^2$.
As a function of systems. Static density correlations are stationary over plateaus, and stretching observed in simulations of similar characteristic low temperature features of increasing slowing down respectively, as a function of time. The curves display the characteristic low temperature features of increasing slowing down, plateaus, and stretching observed in simulations of similar systems. Static density correlations are stationary over the range of temperatures considered, which suggest that nothing of thermodynamic significance is happening throughout the simulation. The density correlation functions decay to their uncorrelated values at lengths much smaller than the simulation box length, and its structure factor shows no anomalies at small wave vectors. These facts indicate that the system remains a liquid mixture throughout the simulation and does not evolve toward a crystallized or phase-separated state. Dynamical quantities show typical liquidlike behavior when measured over long enough time scales. For instance, the small wave vector incoherent scattering function is fully consistent with diffusive relaxation. This fact also supports the conclusion that the system is not evolving towards a crystallized or phase-separated state.

Figure 2 demonstrates that the WCA mixture has the standard phenomenology associated with glass formation. The figure presents results from two-point time-correlation functions for varying temperatures ranging from the normal liquid regime to the supercooled regime. It helps us study a reasonably large system at significantly supercooled conditions.

Figure 2 shows the mean-squared displacement of Fig. 2 demonstrates that the WCA mixture has the standard phenomenology associated with glass formation. The figure presents results from two-point time-correlation functions for varying temperatures ranging from the normal liquid regime to the supercooled regime. It helps us study a reasonably large system at significantly supercooled conditions.

Due to the shortness of the interaction range, $2^{1/6} \sigma = 1.12 \sigma$, each particle interacts only with its nearest neighbors, significantly reducing the computational overhead of calculating forces. We find that this feature makes the WCA mixture up to one order of magnitude faster to simulate than the corresponding Lennard-Jones mixture. It helps us study a reasonably large system at significantly supercooled conditions.

To obtain the distributions shown in Fig. 1, we monitor the time series of events for each particle in the system, defining the occurrence of an event as a particle is displaced beyond a cutoff length $d$. Consider particle $i$, at the initial time $t=0$, when we start the observation, its position is $\mathbf{r}_i(0)$. The first event time for that particle $t_1$ is the first time that particle $i$ has moved far enough so that $|\mathbf{r}_i(t_1)−\mathbf{r}_i(0)|=d$. A second event occurs for that particle at time $t=t_1+t_2$, when particle $i$ manages to move again a distance $d$.

FIG. 1. (Color) Decoupling of exchange and persistence times in the WCA mixture. A local event is defined as a particle moving at a distance larger than $d$. We show results for $d=0.5$. (Top) The distributions of exchange times and of persistence times for particle species $A$ and $B$ for various temperatures $T$. (Bottom) Ratio of the average persistence time $\tau_p=(t_p)$ to the average exchange time $\tau_e=(t_e)$ as a function of $T$. The inset shows $\tau_p$ and $\tau_e$ for both species as a function of $1/T$.
its position at $t_1$, i.e., $|\mathbf{r}_i(t_1 + t_2) - \mathbf{r}_i(t_1)| = d$. A third event takes place after a further wait $t_3$, and so on.

This convention establishes a set of waiting times between events for the $i$th particle $\{t_1, t_2, t_3, \ldots\}$. Notice, however, that $t_1$ has an important physical difference from $t_2, t_3, \ldots$. The time $t_1$ is the time for the first event to take place without condition on when the previous event occurred. The times $t_2, t_3, \ldots$ are times between events. As noted, we call the time $t_1$ a persistence time, and the times $t_2, t_3, \ldots$, exchange times.

Figure 1 (top) shows the distributions of exchange and persistence times for the two kinds of particles in the WCA mixture, for temperatures ranging from the normal liquid regime to the supercooled one. We choose the cutoff length $d$ to be comparable with the particle size, so as to probe particle motion relevant to structural relaxation and diffusion. As argued in the previous work, dynamic facilitation features emerge only after a suitable coarse graining of short scale motion. The length $d$ plays the role of a coarse-graining length. The distributions of Fig. 1 are for $d=0.5$. We have obtained similar results for $d$ in the range $d=0.5-1.0$. At high temperatures, the exchange and persistence time distributions coincide. This is the situation where the distribution of exchange times is exponential. As the temperature is decreased, the two distributions become distinct, that for persistence moving toward longer times. Figure 1 (bottom) shows the ratio $\tau_p/\tau_e$, where $\tau_p = \langle \tau_p \rangle$ is the average persistence time and $\tau_e = \langle \tau_e \rangle$ is the average exchange time. At low temperatures, the average persistence time becomes much larger than the exchange time. This decoupling mirrors that of the breakdown of the Stokes-Einstein relation of Fig. 2.

The decoupling of exchange and persistence times in the WCA mixture is similar to that observed in KCMs. These distributions reflecting the time series of individual particle displacement events are non-Poissonian. Event times cluster with periods of quiescence followed by periods of high activity. This clustering of event times is one way to view dynamic heterogeneity, or more precisely, a coexistence in space time between active and inactive dynamical phases. Phase separation in trajectory space is a distinguishing prediction of dynamic facilitation. Decoupling of persistence and exchange processes is a consequence of this phase separation.

By describing dynamics in terms of exchange and persistence, one is able to picture particle motion as a continuous-time random walk. An individual particle makes random walk steps at random times drawn from the persistence and exchange time distributions. Along with the accounting for the breakdown of Stokes-Einstein relations, this simple picture also accounts for the non-Fickian to Fickian crossover and the shape of the van Hove correlation function in a wide range of systems.

In carrying out this work J.P.G. was supported by EPSRC under Grant No. GR/S40704/01. L.M. was supported by DOE grant under Contract No. DE-AC02-05CH11231, and D.C. was initially supported by NSF under Grant No. CHE-0543158 and currently supported by ONR under Grant No. N00014-07-1-0689. Calculations were made possible through access to the NERSC super-computer facility at Lawrence Berkeley National Laboratory.

---

**FIG. 2.** (Color) (Top) Mean-squared displacement $\langle (\Delta x)^2 \rangle = \langle \Delta x(t)^2 \rangle$ for both particle species A and B as a function of time $t$ for various temperatures $T$. (Center) Incoherent scattering function $F(k, t) = \langle e^{i k \cdot \Delta r(t)} \rangle$, evaluated at the wave vector $k=k_0$ of the first peak in the partial structure factors, for both species at the same temperatures as above. (Bottom) Violation of the Stokes-Einstein relation (dashed line) for decreasing temperatures. The inset shows the corresponding relaxation times $\tau_p$ defined by the relation $F(k, \tau_p) = 0.1$, for each species as a function of inverse temperature $1/T$.

---

Molecular dynamics simulations were performed using a microcanonical Verlet algorithm for Fig. 1 and LAMMPS (Ref. 22) for Fig. 2, at temperatures \( T = 5.0 \pm 0.36 \) along a constant density path. The particle numbers and box length, \( N_x = N_y = 500 \) and \( L = 9.172 \) for Fig. 1, and \( N_x = N_y = 4000 \) and \( L = 18.344 \) for Fig. 2, were fixed in each run. The system was prepared at each thermodynamic state point by coupling to a heat bath for time \( t_{\text{cool}} \) using velocity rescaling or velocity reassigning every 50 time steps. No drift or aging was observed over the equilibration time \( t_{\text{equil}} \) in thermodynamic or dynamic observables before performing production runs. Both \( t_{\text{cool}} \) and \( t_{\text{equil}} \) were significantly longer than the structural relaxation time.

In the context of renewal processes (Ref. 25), exchange and persistence times are called total and excess lifetimes, respectively. If events occur over a very short time scale as compared to waiting times the distributions of persistence and exchange times are related by \( p(t_p) = (t_p)^{-1} \int_p^\infty p(t)dt \) (Refs. 6 and 25). In our case, where an event may be built up over time (a displacement of distance \( d \) does not occur instantaneously), this relation works only as an approximation. Nevertheless, application of this formula gives reasonable estimates of the behavior.