

Super-Arrhenius Diffusion in an Undercooled Binary Lennard-Jones Liquid Results from a Quantifiable Correlation Effect

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On short time scales an underlying Arrhenius temperature dependence of the diffusion constant can be extracted from the fragile, super-Arrhenius diffusion of a binary Lennard-Jones mixture. This Arrhenius diffusion is related to the true super-Arrhenius behavior by a factor that depends on the average angle between steps in successive time windows. The correction factor accounts for the fact that on average, successive displacements are negatively correlated, and this effect can therefore be linked directly with the higher apparent activation energy for diffusion at low temperature.

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Super-Arrhenius temperature dependence of transport properties such as the diffusion constant is a characteristic of “fragile” supercooled liquids in Angell’s classification [1]. In such systems the effective activation energy increases as the temperature falls, and the Vogel-Tammann-Fulcher (VTF) equation is commonly used to fit such behavior. In this Letter we show that for the binary Lennard-Jones (BLJ) glass former, it is possible to separate out an Arrhenius dependence that occurs on a shorter time scale than the ergodic super-Arrhenius behavior. The short-time-averaged results can be quantitatively corrected by taking into account the correlation between displacements in successive time windows.

Molecular dynamics simulations were performed for 60- and 256-atom binary mixtures of 48 type A and 12 type B particles, and 204 type A and 52 type B particles, respectively, interacting via a Lennard-Jones potential in a periodically repeated cell [2–7]. Number densities of 1.1 and 1.3 in reduced units of σ_{AA}^{-3} (used throughout) were considered for interaction parameters $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.8$, $\sigma_{BB} = 0.88$, $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, and $\epsilon_{BB} = 0.5$ along with the Stoddard-Ford quadratic cutoff [8], which ensures that both the potential energy and its first derivative are continuous. Cutoffs of half a box length were used, and a velocity Verlet algorithm was employed to propagate the trajectory with a time step of 0.005 in reduced units of $(m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$ (used throughout). For the 256-atom system, each microcanonical run at constant energy included 10^5 initial steps followed by 10^6 steps of data collection. For the 60-atom system, 10^7 initial steps were followed by 10^7 steps of data collection in each run. The final configuration at a particular energy was used as a starting configuration for the subsequent simulation, with the total energy decreased by $10\epsilon_{AA}$ each time for 60 atoms and $50\epsilon_{AA}$ for 256 atoms.

Self-diffusion coefficients, presented previously [9], were obtained using Einstein’s proportionality relation for the mean square displacement of a particle as a function of observation time in the limit that $t \rightarrow \infty$. The gradient

was calculated by linear regression. All results are presented for the majority A atoms, although the B atoms exhibit identical behavior.

To determine the time scale required to achieve effective ergodicity in a given simulation we employed the energy fluctuation metric $\Omega(t)$ [9,10]. This metric measures the deviation of the time-averaged energy of each individual particle from the average for that species. If the system is ergodic within a well-defined region of configuration space then $\Omega(t)$ vanishes for long times. Ergodicity can be diagnosed by requiring smooth, monotonic decay of $\Omega(t)$ with time and comparing results for simulations at different energies [9]. There is then no heterogeneity in the distribution of average particle energies or mobilities. However, for computer simulations of supercooled liquids and glasses over finite time intervals this ergodic limit may not be accessible, especially at low temperature. Instead $\Omega(t)$ reaches an almost constant value, indicating that the energy per particle is not self-averaging [11,12]. Heterogeneous dynamics [13–23] are therefore associated with nonergodic averaging intervals in the present work. Complementary information is provided by the non-Gaussian parameter [24]

$$\alpha_2(t) = \frac{3\langle\Delta r^4(t)\rangle}{5\langle\Delta r^2(t)\rangle^2} - 1, \quad (1)$$

which decays to zero for ergodic trajectories. Here $\langle\dots\rangle$ denotes an average over all atoms of a particular type and all time origins. $\alpha_2(t)$ vanishes when the atomic motion is homogeneous, which occurs during ballistic motion at $t \rightarrow 0$ and ergodic diffusion at $t \rightarrow \infty$.

In order to characterize differences between the most mobile and immobile particles, we considered time scales over which $\Omega(t)$ indicates nonergodicity, and the non-Gaussian parameter does not decay to zero. Here we define mobility in terms of the displacement between the two end points. If the entire trajectory is ergodic, we can divide the total time, t_{total} , into m shorter nonergodic segments of length τ . We then consider the result of calculating the

diffusion constant, $D(\tau)$, from the average mean square displacement over different time scales, τ . The total mean square displacement at the end of the trajectory is given by

$$\langle \mathbf{r}^2(t_{\text{total}}) \rangle \equiv \frac{1}{N} \left\langle \sum_{i=1}^N \Delta \mathbf{r}_i(t_{\text{total}})^2 \right\rangle, \quad (2)$$

where here and subsequently, $\langle \dots \rangle$ denotes an average over all time origins. The mean square displacement used to calculate $D(\tau)$ is given by $\langle \sum_{j=1}^m \sum_{i=1}^N \Delta \mathbf{r}_i(j)^2 \rangle / N$, where $m\tau = t_{\text{total}}$ and $\Delta \mathbf{r}_i(j) = \mathbf{r}_i(j\tau) - \mathbf{r}_i(j\tau - \tau)$.

Figure 1 shows $D(\tau)$ for the 10 most mobile and the 10 least mobile atoms for $\tau = 25$ in a 60-atom BLJ mixture of number density 1.3. On this time scale $D(\tau)$ for all the atoms, whether more or less mobile, exhibits Arrhenius temperature dependence. Furthermore, $D(\tau)$ calculated for individual atoms runs parallel to the true diffusion constant at high temperature, but deviates at low temperature. The deviation occurs where curvature in the true diffusion constant becomes apparent, around $T = 1.0\epsilon_{\text{AA}}/k_B$. This is roughly the temperature where the system may enter a “landscape-influenced” regime, and the average potential energy of minima sampled starts to fall significantly [2].

As τ increases, and ergodicity is reached, $D(\tau)$ should tend to the true diffusion constant, whether calculated for individual atoms, or averaged over all of them. Figure 2 shows $D(\tau)$ calculated for the average over all (A) atoms at several values of τ . Super-Arrhenius curvature is recovered with increasing τ , and we see that it is only the lower temperature results that change. At high temperature it appears that ergodicity was already reached on the shortest

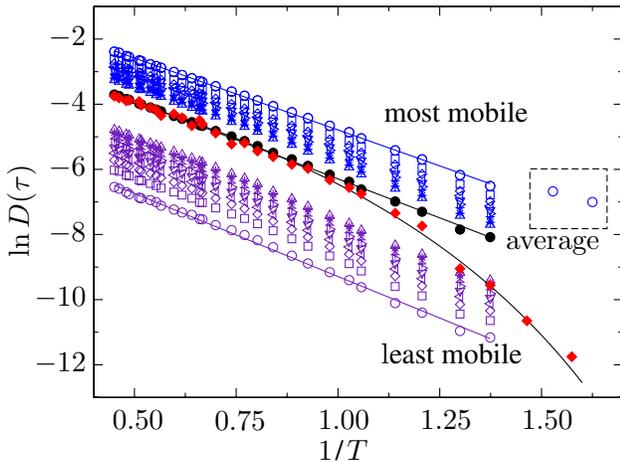


FIG. 1 (color online). Variation of $\ln D(\tau)$ with $1/T$ for the ten most mobile atoms, the ten least mobile atoms and the average over all A atoms (filled circles) determined over a time interval of $\tau = 25$ in a 60-atom BLJ mixture of number density 1.3. Linear regression fits are shown. The dashed box encloses results for the most mobile atom where $\Omega(t)$ indicates nonergodicity over the entire trajectory. The true diffusion constant obtained by averaging over all A atoms on an ergodic time scale is shown by filled diamonds together with a VTF fit.

time scale considered. $\Omega(t)$ reveals that for the four lowest temperatures, ergodicity is approached at a time around 2500 (not shown).

Arrhenius behavior is observed on time scales for which the low temperature results are nonergodic. On averaging over longer time windows super-Arrhenius behavior is progressively recovered. However, we find that this super-Arrhenius diffusion does not result from averaging over a distribution of particles that each behave in Arrhenius fashion but with different barriers. Instead, the analysis below shows that super-Arrhenius behavior is caused by a negative correlation between the atomic displacements in successive time windows. If the windows are too short then there is insufficient time for reversals in direction to be registered in lower temperature trajectories, and the calculated $D(\tau)$ is too large. The magnitude of the discrepancy increases with decreasing temperature, in agreement with the suggestion that non-Arrhenius transport properties are linked to the increasing time scale required to achieve effective ergodicity at low temperature [7].

Further insight can be obtained by considering the physical significance of the mean square displacement employed to calculate $D(\tau)$. We can rewrite the total mean square displacement in terms of atomic displacements in m time intervals of length τ ,

$$\begin{aligned} \Delta \mathbf{r}_i(t_{\text{total}})^2 &= \sum_{j=1}^m \Delta \mathbf{r}_i(j)^2 + 2 \sum_{j < k} \Delta \mathbf{r}_i(j) \cdot \Delta \mathbf{r}_i(k) \\ &= \sum_{j=1}^m \Delta \mathbf{r}_i(j)^2 + 2 \sum_{j < k} \Delta r_i(j) \Delta r_i(k) \cos \theta_{jk}. \end{aligned} \quad (3)$$

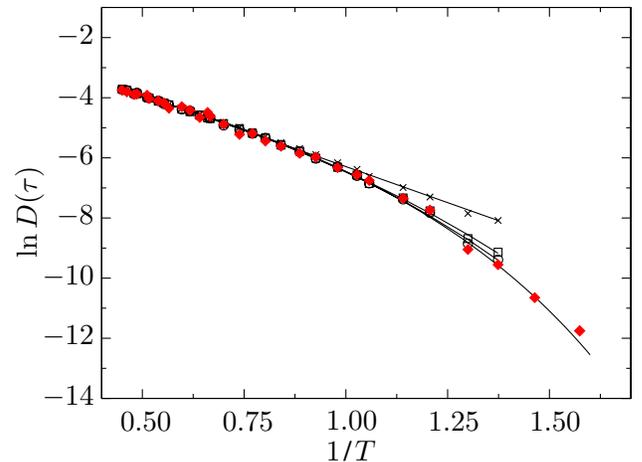


FIG. 2 (color online). Variation of $\ln D(\tau)$ with $1/T$ for the average over all A atoms in a 60-atom BLJ mixture of number density 1.3. The $D(\tau)$ were calculated over time intervals of 25, 250, and 2500, represented by crosses, squares, and circles, respectively. The true diffusion constant obtained by averaging over all A atoms on the longest time scale is shown by filled diamonds.

When calculating $D(\tau)$ we include the first term in Eq. (3) but not the second term. For $\tau = 25$ we find $\langle \cos\theta_{jk} \rangle \neq 0$ only for adjacent time intervals (Fig. 3). At low temperatures $\langle \cos\theta_{j,j-1} \rangle$ is negative, and an atom is most likely to move backwards relative to the displacement vector in the previous time window. $\langle \cos\theta_{j,j-1} \rangle$ tends to zero as τ increases sufficiently for ergodicity to be achieved.

If we assume that m is large and the displacements in adjacent steps are similar, such that only the average behavior of $\cos\theta_{jk}$ is important, we obtain:

$$\langle \mathbf{r}^2(t_{\text{total}}) \rangle \approx \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^m \Delta \mathbf{r}_i(j)^2 \right\rangle \times (1 + 2\langle \cos\theta_{j,j-1} \rangle). \quad (4)$$

Using this formula, which adjusts the mean square displacement, we can recover the correct super-Arrhenius behavior for different values of τ , as shown in Fig. 4.

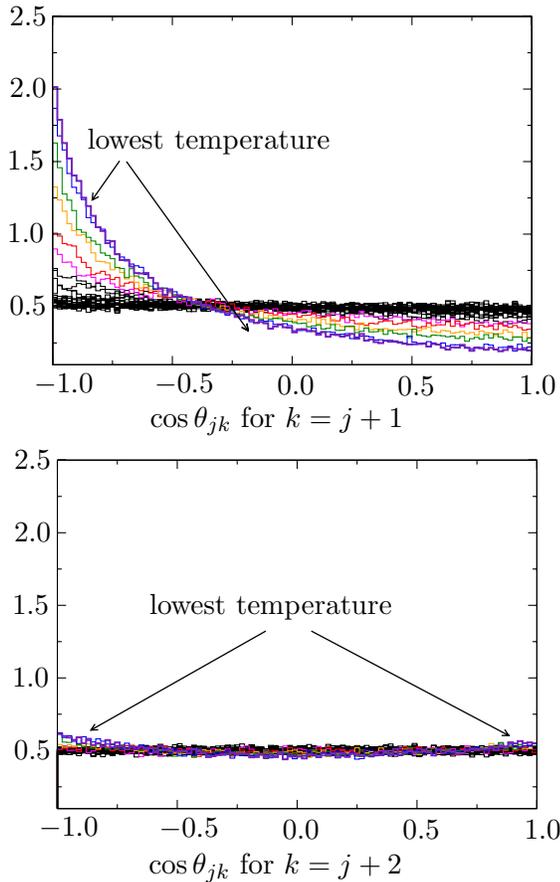


FIG. 3 (color online). Normalized probability distribution of $\cos\theta_{jk}$ between displacements in different time intervals of length 25 are shown for adjacent time windows, $k = j + 1$, and for time windows separated by one intervening window, $k = j + 2$. The distributions for the lowest temperature are shown in bold. For $k = j + 2$, there is little temperature dependence or bias towards positive or negative $\cos\theta_{jk}$.

The above analysis was repeated for the 256-atom BLJ system at various number densities with analogous results. Figure 5 shows $D(\tau)$ calculated for several different values of τ , with and without the $\langle \cos\theta_{jk} \rangle$ correction for the higher density. The correction again recovers the correct diffusion constants for all but the shortest values of τ . This result is easily understood, since at low temperatures for the shortest times, a plateau in the mean square displacement shows that the particles are still caged. If $D(\tau)$ is calculated while the non-Gaussian parameter is still following a power law of the form $\alpha_2(t) \propto \sqrt{t}$ [25], i.e., during caging, the $\langle \cos\theta_{jk} \rangle$ correction is not sufficient to recover the true super-Arrhenius behavior.

Negative correlation for successive transitions between local BLJ minima is evident in Fig. 6 of Ref [26]. Studies by Keyes and Chowdhary for a 32-atom Lennard-Jones system [27] and Doliwa and Heuer for a 65-atom BLJ system [5,28] also suggest that negative correlation exists, in agreement with the present work. Our results provide a quantitative link between negative correlation and the higher apparent activation energy for diffusion in fragile glasses at low temperature. A similar effect has been seen in a model with a simple hierarchical landscape [29] and has been suggested for $\text{Cu}_{33}\text{Zr}_{67}$ [30,31], BLJ [32], and for hard spheres [33]. For the BLJ systems considered here the negative correlation may be a direct result of a reduced number of connections between local potential energy minima that are sampled at lower energy [26,34]: if the number of connections is limited then return to a previous minimum becomes more likely.

In summary, the present work establishes a quantitative connection between super-Arrhenius diffusion, correlated atomic motion, heterogeneity, and ergodicity in a binary

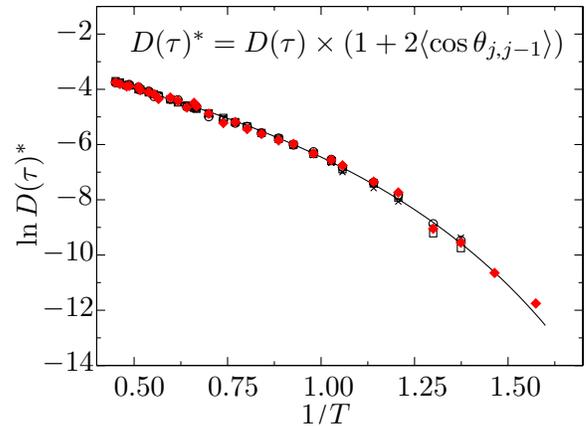


FIG. 4 (color online). Variation of $\ln D(\tau)^*$ with $1/T$ averaged over all A atoms in a 60-atom BLJ mixture with number density 1.3, calculated using the $\langle \cos\theta_{jk} \rangle$ correction in Eq. (4). The results are for $\tau = 25$, 250, and 2500, represented by crosses, squares, and circles, respectively. The long-time diffusion constant averaged over all A atoms is shown by filled diamonds, and the solid line shows the long-time VTF fit.

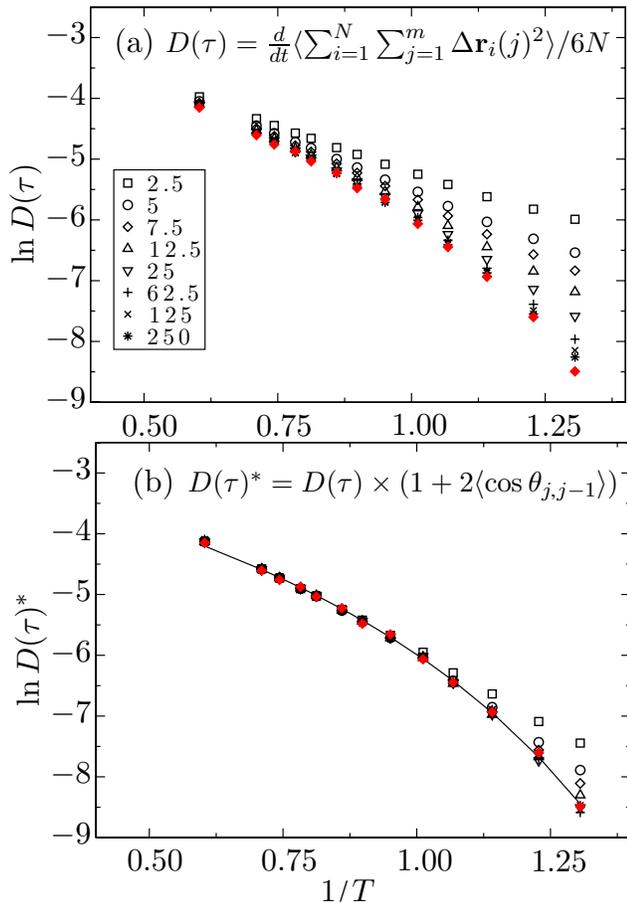


FIG. 5 (color online). $D(\tau)$ for a 256-atom BLJ mixture at a number density of 1.3 calculated for different time intervals, τ , as shown in the legend. Filled diamonds show the true diffusion constants for the ergodic trajectory. (a) $D(\tau)$ calculated for a range of τ ; (b) $D(\tau)$ corrected by a factor containing the average angle between successive displacements.

Lennard-Jones system. For short time scales and low temperatures, over which the dynamics are nonergodic and heterogeneous, the short-time-averaged diffusion constant exhibits Arrhenius behavior. The mean-squared displacement, and hence the diffusion constant, is overestimated for time windows that are too short to register negative correlations in atomic positions. The correct super-Arrhenius behavior is recovered in the limit of long time intervals, and the short-time-averaged results can also be corrected by including a factor containing the average angle between steps in successive time windows. Negative correlation is therefore directly linked to the increase in effective activation energy at low temperature for this fragile glass former.

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