Cooperative motion in Lennard-Jones binary mixtures below the glass transition

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(June 8, 2000)

Abstract

Using the activation-relaxation technique (ART), we study the nature of relaxation events in a binary Lennard-Jones system above and below the glass transition temperature \( T_g \). ART generates trajectories with almost identical efficiency at all temperature, thus avoiding the exponential slowing down below \( T_g \) and providing extensive sampling everywhere. Comparing these runs, we find that the number of atoms involved in an event decreases strongly with temperature. In particular, while in the supercooled liquid activated events are collective, involving on average thirty atoms or more, events below \( T_g \) involve mostly single atoms and produce minimal disturbance of the local environment. These results confirm the interpretation and the generality of recent NMR results by Tang et al (Nature 402, 160 (1999)). PACS numbers: 61.43.Dq, 82.20.Pm, 82.20.Wt

Typeset using REVTEX
Atomic motion in solids is largely determined by the nature of the local network. While atomic diffusion in crystals is constrained by symmetry and can be described in terms of well-defined displacements leaving the overall structure of the network unaffected, diffusion in disordered materials offers a much more complex picture. These materials present a wide range of local environments and diffusion can take place in principle through an equally large number of mechanisms.

This has made understanding the nature of diffusion and relaxation mechanisms in compact glasses, such as metallic and Lennard-Jones glasses, a difficult task. Nevertheless, significant progress regarding the details of the dynamics in these dense glasses has been achieved recently. On the theoretical side, simulations have been used extensively to investigate this problem. [1–5] Studies on supercooled model binary glasses have established clearly that as a liquid becomes supercooled a change in the dynamics takes place and diffusion starts to proceed by jumps. [1,2] More recent work has provided further characterization of these mechanisms, showing that in the supercooled regime moves are collective [3,4] and occur in highly correlated sequences. [6]

Experimental measurements are also challenging; diffusion takes place on a long time scale and the data represent only an average over a distribution of barriers and pre-factors. This makes it difficult to identify directly specific mechanisms. A search for diffusion mechanisms in multinary metallic glasses, using standard slicing techniques, has led to conflicting results. [7,8] More direct probes to identify local changes around atoms, such as NMR, have also been used recently. [9–13] In particular, the work of Tang et al. [12] implies that there is a qualitative change in the diffusion mechanism of Be atoms as the Zr-Ti-Cu-Ni-Be samples are brought below the glass transition temperature ($T_g$): from mostly collective, jumps become localized and clearly atomistic. This last result is of great interest because it demonstrates a qualitative distinction between the supercooled regime and the dynamics below $T_g$.

A numerical reproduction of this phenomenon, necessary to establish the validity of the explanation and its generality, is difficult to achieve using standard techniques: in the low
temperature regime, the time scale covered by molecular dynamics is insufficient to ensure a satisfactory exploration of the space of configurations. The activation-relaxation technique (ART) [14] offers a way to go beyond these limitations and to sample the phase space of disordered systems even at low temperatures.

We show here that ART can generate trajectories in Lennard-Jones glasses without suffering from exponential slowing down below $T_g$. Comparing events above and below $T_g$, we also find that the number of atoms involved in relaxation and diffusion decreases significantly with temperature, going from many tens to one or two at the lowest $T$ studied here.

ART by-passes the description of the phonon vibrations to concentrate on activated mechanisms: it looks directly for paths connecting minima in a high-dimensional energy landscape. Starting from a local minimum, the whole configuration is first pushed away from it, until a negative eigenvalue appear, and then directed to a nearby saddle point – the activation. The configuration is then brought to a new minimum, providing a complete event with initial, saddle and final configurations. The new move is then accepted or rejected with Boltzmann probability $\exp(\Delta E/k_BT$, where $\Delta E$ is the energy difference between final and initial configuration and $T$ the simulation temperature.) A more detailed description of the original algorithm can be found in Ref. [15].

In order to ensure a better control of the trajectory in this dense material, we use here a modified version of the algorithm. In the activation stage, the configuration is now pushed against the force corresponding to the to the lowest (negative) eigenvalue of the hessian matrix, the second derivative of the total configurational energy. Since an exact diagonalization of the $3N \times 3N$ matrix is computationally too demanding for the 1000-atom simulation presented here, a Lanczos algorithm is used to project out eigenvectors corresponding to the lowest eigenvalues only. [16] In spite of the efficiency of the Lanczos algorithm, this approach remains numerically more intensive than the standard ART. However, ART nouveau ensures a direct convergence to the saddle point and provides a better control on the trajectory, which is particularly useful in dense systems such as metallic or Lennard-Jones
This algorithm is applied to a 1000-atom Lennard-Jones binary $A_{80}B_{20}$ mixture using the parameters introduced in Ref. [5] but with shifted energy and forces to ensure continuity of the energy and the first derivative at the cut-off. [17] Energy has units of $\epsilon_{AA}$, temperature of $\epsilon_{AA}/k_B$, length of $\sigma_{AA}$ and time of $(m\sigma_{AA}/48\epsilon_{AA})$.

The simulation procedure is as follows. We start with a randomly-packed configuration and first relax it at constant volume and $T = 0.50$, a temperature slightly above the glass transition, until thermalization, i.e., until the configurational energy reaches a plateau. This takes place in about 5000 ART-events. The last configuration of the initialization run is then used as a starting point for further runs at $T = 0.25$, 0.50 and 1.00, i.e., well below, slightly above and well above $T_g$, respectively. $T_g$, here, is defined as in Ref. [18], by a sharp low-temperature break in the inherent-structure energy curve. [19]

The overall acceptance ratio for these runs is about 20 %. This includes exchange events, accounting for about 6 % at all temperatures, where two or more atoms switch position, leaving the final configuration structurally indistinguishable from the original. Although physically relevant in the study of self-diffusion, these events do not contribute to the relaxation of the lattice per se and they excluded from the analysis below. Accepted events are therefore only those resulting in a final configuration structurally different for the initial one. The acceptance rate for these events is about 20 % at $T = 1.00$, 10 % at $T = 0.50$ and 4-5 % at $T = 0.25$.

Figure 1 shows the energy sequence of the accepted events at the three temperatures considered here. As the model is initially prepared at $T=0.50$, this sequence is already thermalized. The thermalization at $T = 1.00$ takes about 300 events while that at $T = 0.25$ is longer, about 500 events. It is not formally possible to talk of equilibrium below the glass transition, however all quantities described below have been tested over different intervals at $T = 0.25$ and found to be insensitive to the specific subset of events chosen past event 400. The exact value of the configurational energies after thermalization with ART is significantly lower than that of models relaxed with molecular dynamics. Starting with a configuration
equilibrated at $T = 1.5$ and slowly cooling down, (at $10^{-5} \epsilon_{AA}$/time unit), the inherent structures stabilize at an energy per atom of about $-6.738$ at $T = 1.00$, $-6.817$ at $T = 0.50$ and $-6.858$ at $T = 0.25$. The corresponding values for the ART run are $-6.810$, $-6.844$ and $-6.870$, respectively. ART is not expected to fully describe the liquid phase since it is event-based and does not include all entropic contributions. This means that many dynamical distributions, such as those presented below, obtained with ART should be sharper than those generated with MD in the liquid and supercooled liquid. ART and MD should meet in the solid phase where the dynamics is almost exclusively activated. At low temperatures, entropic contributions should be minimal and the lowest energy configurations should be sampled, which we see in the ART trajectory at $T = 0.25$. The energy difference between ART and MD at at $T = 0.25$ is therefore due, in large part, to the much better sampling of the energy landscape achieved by ART.
FIGURES

FIG. 1. Configurational energy sequence of the accepted events, i.e., after removing atomic exchanges. The thermalization for T=1.00 and T=0.25 takes about 300 and 500 events respectively.

FIG. 2. Mean-squared displacement per atom, from the initial configuration, as a function of accepted event number above, around and below the glass transition. As mentioned in the text, the diffusion due to atomic exchanges, which is significant at low temperatures, is not included. For comparison, a 2-million time step MD simulation at T = 0.25, with exchanges allowed, produces a $\langle r^2 \rangle = 0.035\sigma^2$/atom.

At all temperatures, the sampling of the energy surface is significant. Figure 2 shows the root-mean-square displacement per atom as a function of accepted events. Diffusion is linear in this quantity, following an Einstein-like relation with a “diffusion constant” almost independent of the temperature. In terms of accepted events, i.e., without even including atomic exchanges, the sampling of the phase space proceeds therefore at a constant rate.
ART clearly overcomes the exponential slowing down of the dynamics in these metallic glasses.

![Diagram of van Hove correlation function](image)

**FIG. 3.** Self-part of the van Hove correlation function. $n$ is taken as the difference between two configuration numbers. (a) $G_s$ at $T=0.25$ for 4 different intervals: 20, 100, 200 and 300, starting with a solid line, dotted line, dash-dotted and dashed. In inset, the same function is plotted for the run at $T=1.00$. (b) Comparison of the $G_s(r,t=300)$, at $T=0.25$, 0.50 and 1.00. For both plots, the correlation function is measured in the second part of the run, i.e., after 300 accepted events. The features of the correlation function are not sensitive to the subset of accepted events selected.

With the properties of the sampling established, we can study the the nature of the
relaxation and diffusion mechanisms as a function of temperature. The self part of the van
Hove correlation function,

\[
4\pi r^2 G_s(r, n) = \frac{4\pi r^2}{N} \langle \sum_i \delta (r - |r_i(0) - r_i(n)|) \rangle
\]

provides the probability of finding an atom \( r \) away from it initial position at event \( n \).

In Figure 3(a), the correlation is plotted as a function of event number \( n \) at two different
temperatures. The distributions at all temperatures are significantly sharper than those
generally obtained in molecular dynamics [1, 5, 6]. Because ART concentrates exclusively on
activated events, the thermal contribution to the peak around \( r = 0 \) are eliminated.

![Log-log plot of the average number of atom per event moving by more than a given
threshold. At T=1.00, 30.4 atoms move by more \( r = 0.1\sigma \), while 8.9 do so at T=0.5 and only 3.8
at T=0.25.](image)

At \( T = 1.00 \) (inset), the distribution is initially bimodal with broad peaks and evolves
into a single wide peak, indicating relaxation mechanisms with a range of of lengths. The
distribution at \( T = 0.25 \), on the other hand, is narrow and evolves by adding new peaks at
integer multiples of \( r = 1.05\sigma \). This behavior is underlined in Fig. 3(b), which compares
the long time distribution at all temperatures: as the temperature lowers, the atomic dis-
placements become more and more discrete: the jumps take place on a disordered but rigid
lattice. The \( T = 0.50 \) model, well into the supercooled region, is not yet as discrete: the
distribution is broad and smooth beyond the first peak.

In order to get a better understanding of the events, it is useful to plot the average number of atoms involved in an event. [20] Figure 4 gives the full distribution as a function of a threshold displacement. As discussed elsewhere, [20] the slope of the curve is universal. There is a strong temperature dependence on the pre-factor, however, which relates to the rigidity of the network sampled locally: the events become more and more collective as the temperature increases. At \( r = 0.1\sigma \), events involve more than 2 times more atoms at \( T = 0.50 \) and eight times more atoms at \( T = 1.00 \) than at \( T = 0.25 \).

over, there are essentially no atoms moving by \( 0.2 < r/\sigma < 1.0 \) in the \( T = 0.25 \)-run, as indicated by a flat curve: atoms moving have to jump by a nearest-neighbor distance, anything less is not possible. A similar phenomenon can be seen in the \( T = 0.50 \) curve, but for \( 0.6 < r/\sigma < 1.0 \), and a slope still relatively high: as an atom jumps by a nearest-neighbor distance, atoms in the local environment relax by up to \( \sigma = 0.6 \). Although the degree of collectivity in the events varies strongly with temperature, the three curve come together at \( r = 1.0\sigma \). At all temperatures, the activated dynamics is therefore controlled by nearest-neighbor jumps. This characteristic can also be seen in the self-part of the van Hove correlation (Fig 3): for small intervals, \( t = 20 \), the \( T = 1.00 \) distribution shows a strong peak at \( r = 1.05\sigma \), identical to that at \( T = 0.25 \).

How do these results fit with those on heterogeneities in glasses obtained by MD? The conclusions of these simulations can be summarized as follows: heterogeneities exist in glasses but they are not associated with a given scale; their spatial extent depends directly on the time scale selected, leading to homogeneities in the long run. [21,22] Similar results are found here. Comparing the first and the last half of the run at \( T = 0.25 \), for example, we find that 226 atoms move by more than \( r = 0.2 \) in the first half of the last 400 events, and 212 in the second, with 75 atoms belonging to the two sets, in agreement with MD work.

Where ART and MD differ, however, is in the definition of “collective” event. [6,22] Certain groups have concluded that the dynamics becomes more and more collective as the temperature decreases, [23,22] in apparent contradiction with our results. However, the
adjective collective is applied there for events taking place over an extended time period and pertains more to time correlation between events than to the nature of each activated jump. As such, ART and MD conclusions are not contradictory. Further analysis is currently underway to see whether ART produces the same long time correlations. [19]

In summary, we have performed a simulation of a binary Lennard-Jones glass above and below the glass transition temperature. We first show that ART can explore the phase space below $T_g$ without encountering exponential slowing down. We also find that there is a qualitative change in the nature of the mechanisms as one goes from above to below $T_g$. Although all events seem to be centered around a few atoms jumping over a lattice spacing, the total number of atoms involved in an event decreases by an order of magnitude as the temperature goes down. These results support the interpretation of recent NMR experiments. [12] Although these results are likely to be valid for metallic glasses in general, we can expect different behavior from less dense glasses such as network glasses.

Acknowledgments. I would like to acknowledge numerous discussions with G. T. Barkema, S. de Leeuw, Y. Limoge, Y. Wu, as well as D. Drabold. This work is supported in part by the NSF, under grant DMR-9805848. Part of these simulations where run on the computers of HPoC at TU Delft.
REFERENCES

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[17] This model has been used extensively in the recent years as a standard glass model. The original version of this potential is not fully continuous, however, and we use a potential
shifted in both energy and force to ensure continuity of the first and second derivative at the cut-off. Energies and temperature cannot therefore be compared directly with that found using Ref. [5].


