Correlation Effects in Super-Arrhenius Diffusion

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Overview

Introduction
Strong and Fragile Glasses
Simulation Details

A Quantifiable Correlation Effect
Non-Ergodic Diffusion Constants
The Relationship between $D(\tau)$ and $D(\infty)$
Correlation, $\cos(\theta_{jk})$
Recovering Super-Arrhenius Behaviour

Arrhenius Diffusion
Non-Ergodic Arrhenius Diffusion
Arrhenius $\rightarrow$ Super-Arrhenius Behaviour
Fitting to Super-Arrhenius Behaviour

Glassy Landscapes
Reversibility in the Energy Landscape
Cage-Breaking
Non-Diffusive Connections
Diffusive Connections
‘Super-Arrhenius’ behaviour
For some supercooled liquids, the temperature dependence of relaxation times or transport properties such as the diffusion constant, $D$, is stronger than predicted by the Arrhenius law.

<table>
<thead>
<tr>
<th></th>
<th>Arrhenius</th>
<th>Super-Arrhenius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature dependence</td>
<td>Arrhenius Law</td>
<td>VTF equation</td>
</tr>
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<td></td>
<td>$\eta = \eta_0 \exp[A/T]$</td>
<td>$\eta = \eta_0 \exp[A/(T - T_0)]$</td>
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<td>Angell’s classification</td>
<td>Strong</td>
<td>Fragile</td>
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</table>
Strong and Fragile Glasses

\begin{align*}
\log_{10}\eta/\text{poise} & \\
T_g/T & \\
-4 & 0 & 4 & 8 & 12 & 0 & 0.2 & 0.4 & 0.6 & 0.8 & 1
\end{align*}

Strong

Fragile

\begin{tabular}{|c|c|c|}
\hline
 & Arrhenius & Super-Arrhenius \\
\hline
Temperature dependence & Arrhenius Law & VTF equation \\
 & \eta = \eta_0 \exp[A/T] & \eta = \eta_0 \exp[A/(T - T_0)] \\
\hline
Angell’s classification & Strong & Fragile \\
\hline
\end{tabular}
Simulation Details

Binary Lennard-Jones mixtures

Number densities of 1.1, 1.2 and 1.3 $\sigma_{AA}^{-3}$

- **60-atom**: 48 type A and 12 type B particles
- **256-atom**: 204 type A and 52 type B particles

Interaction parameters:

\[
\sigma_{AA} = 1.0, \quad \sigma_{AB} = 0.8, \quad \sigma_{BB} = 0.88
\]
\[
\epsilon_{AA} = 1.0, \quad \epsilon_{AB} = 1.5, \quad \epsilon_{BB} = 0.5
\]

used with the **Stoddard-Ford quadratic cutoff**

- Microcanonical Molecular Dynamics simulations with a time step of
  \[
  0.005 \left( \frac{m\sigma_{AA}^2}{\epsilon_{AA}} \right)^{1/2}
  \]
- The Mountain and Thirumalai energy fluctuation metric for the average energy was used to diagnose broken ergodicity.
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Einstein’s relation for diffusion should be used in the limit $t \to \infty$.

Non-ergodic diffusion constants, $D(\tau)$: short, non-ergodic time intervals averaged over an ergodic trajectory.

\[ \tau = 25 \left( m\sigma_{AA}^2 / \epsilon_{AA} \right)^{1/2} \]
As $\tau$ increases, expect $D(\tau) \rightarrow D(\infty)$

Super-Arrhenius curvature is recovered as expected

$\tau = 25, 250 \text{ and } 2500$

$(m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$
The Relationship between $D(\tau)$ and $D(\infty)$

$$D = \lim_{t \to \infty} \frac{\langle \Delta r_i(t)^2 \rangle}{6t}$$

If the total trajectory is divided into $m$ time intervals of length $\tau$ and

$$\Delta r_i(j) = r_i(j \tau) - r_i(j \tau - \tau),$$

$$\Delta r_i(t)^2 = \sum_{j=1}^{m} \Delta r_i(j)^2 + 2 \sum_{j<k} \Delta r_i(j) \cdot \Delta r_i(k)$$

$$= \sum_{j=1}^{m} \Delta r_i(j)^2 + 2 \sum_{j<k} |\Delta r_i(j)||\Delta r_i(k)| \cos \theta_{jk}$$
\[ k = j + 1 \]

\[ k = j + 2 \]

\[ \langle \cos \theta_{jk} \rangle \neq 0 \text{ for adjacent time intervals only.} \]

\[ \langle \cos \theta_{jk} \rangle \text{ is negative, an atom is most likely to move backwards relative to the displacement vector in the previous time window.} \]
If only the average behaviour of $\langle \cos \theta_{j,j-1} \rangle$ is important:

$$\Delta r_i(t)^2 = \sum_{j=1}^{m} \Delta r_i(j)^2 \times (1 + 2\langle \cos \theta_{j,j-1} \rangle)$$

$$D(\tau)^* = D(\tau) \times (1 + 2\langle \cos \theta_{j,j-1} \rangle)$$
Recovering Super-Arrhenius Behaviour

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\[
\Delta r_i(t)^2 = \sum_{j=1}^{m} \Delta r_i(j)^2 \times (1 + 2 \langle \cos \theta_{j,j-1} \rangle)
\]

\[
D(\tau)^* = D(\tau) \times (1 + 2 \langle \cos \theta_{j,j-1} \rangle)
\]

Super-Arrhenius behaviour is recovered.
The effect extends to larger system sizes

Finite size effects are small

The correction is sufficient except at the shortest time scales
A Quantifiable Correlation Effect

- The diffusion constant is overestimated for time windows that are too short to register negative correlations in atomic positions.
- The correct super-Arrhenius behaviour can be recovered:
  a) in the limit of long time intervals
  b) with a correction containing the average angle between steps
- We can directly link negative correlation with an increase in effective activation energy at low temperature.
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Non-Ergodic Arrhenius Diffusion

Arrhenius forms can be found over a range of timescales

Exclude ergodic and ‘caged’ results
Arrhenius → Super-Arrhenius Diffusion

\[ \text{gradient/intercept} = a(\ln(\tau/\tau_0 + 1))^b + c \]

\[ \ln D(T, \tau) = \frac{-a(\ln(\tau/\tau_0 + 1))^b - c}{T} + d(\ln(\tau/\tau_0 + 1))^e + \ln D_0 \]
Minimisation gives an ergodic time and an ergodic diffusion constant:

\[
\frac{t_{\text{erg}}}{\tau_0} = \exp \left( \frac{h}{T^j} \right) - 1
\]

\[
\ln D_{\text{erg}} = - \left( \frac{m}{T} \right)^n - \frac{c}{T} + \ln D_0
\]
$D(T, \tau)$ is linked to the local behaviour of the mean square displacement.

$$\langle r^2(T, \tau) \rangle = 6\tau \exp(\ln D(T, \tau))$$
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\[
\langle r^2(T, \tau) \rangle = 6\tau \exp(\ln D(T, \tau))
\]
\[ \ln D_{\text{erg}}(T) = -\left(\frac{m}{T}\right)^n \frac{c}{T} + \ln D_0 \] can be used to fit ergodic diffusion constants.

Arrhenius component and a correction, \(-\left(\frac{m}{T}\right)^n\).
A Quantifiable Correlation Effect

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Arrhenius Diffusion

- Non-ergodic diffusion is described by a time-dependent Arrhenius form.

- A formalism is introduced to describe super-Arrhenius behaviour based on Arrhenius and non-Arrhenius contributions to the diffusion constant.
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Glassy Landscapes

- Quench configurations from an MD trajectory
- Connect the resulting minima via double-ended searches

Many disordered minima at similar energies separated by high barriers
Reversibility in the Energy Landscape

A wide spectrum of potential energy barriers exists which can be loosely divided into diffusive and nondiffusive processes.\[1,2\]

- **NONDIFFUSIVE** Nearest neighbour coordination shells do not change
- **DIFFUSIVE** One or more atoms change their nearest neighbours

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<th>Negative correlation is present in minima to minima transitions[3]</th>
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<td>Correlated diffusive processes</td>
</tr>
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<td>The landscape can be coarse-grained into a random walk between metabasins[4]</td>
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Sequence of **minimum – transition state – minimum** for a cagebreaking event.

The cagebreaking atom (shown in red) is identified by the loss and gain of neighbours during the cagebreaking event.
Minima connected by **non-cagebreaking** paths

Changes in colour show disconnected branches – highly disconnected
Non-Diffusive Connections - 205

−205 −210 −215 −220 −225 −230

−205 −210 −215 −220 −225 −230

Correlation Effects in Super-Arrhenius Diffusion – p.24/27
Minima connected by *cage-breaking* paths

Changes in colour show disconnected branches – highly connected
Summary

**Glassy Landscapes**

- Disconnectivity trees have a highly frustrated appearance, with a large number of potential energy funnels separated by relatively high barriers.
- There are no clear differences between trees at different temperatures and for systems with differing fragility (density) suggesting that a more subtle characterisation of the landscape is needed.
- We can identify cage-breaking or diffusive moves and find that these provide an accurate description of the exploration of the PEL.
- Reversals are evident in these diffusive moves and they increase with decreasing temperature as found for previous studies of ‘jumps’ in a trajectory.
*Correlation Effects and Super-Arrhenius Diffusion in Binary Lennard-Jones Mixtures*

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

*Diagnosing broken ergodicity using an energy fluctuation metric*