Dynamics of a Molecular Glass Former: Diffusion and the Potential Energy Landscape for Ortho-Terphenyl

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Abstract

Introduction

- Diffusion constants of many supercooled liquids display anomalous super-Arrhenius behaviour. Ortho-terphenyl (1,2-diphenylbenzene, OTP) is a typical example.
- Attempts to explain this and other dynamic phenomena of glass formers using the Potential Energy Landscape (PEL) approach are well-established. [1]
- Previous work in our group[2, 3] established the existence of high-barrier ‘cage-breaking’ rearrangements for atomic glass formers, which dominate diffusion in the moderately supercooled regime.
- In this temperature regime, particles reside within cages of their nearest-neighbour particles. A cage break corresponds to a significant change in the nearest-neighbour environment of one or more particles.
- This is a 3-site rigid-body model using the Lennard-Jones potential to model ring-ring interactions.

Cage-breaking Transitions

- To identify cage breaks (CBs), we quench a Molecular Dynamics (MD) trajectory to the parent local energy minima. This freezes out vibrational noise.
- We maintain independent nearest neighbour lists for each site in every OTP molecule.
- Nearest neighbours of each site are identified using the Solid Angle Nearest Neighbour (SANK) method. [6]
- A CB occurs when all sites within a molecule simultaneously change 2 or more nearest neighbours.
- A ‘productive’ cage break is a CB which is not subsequently reversed, either by another CB or by non-cage-breaking rearrangements.
- Computing diffusion constants from only productive cage-breaking displacements reproduces the correct translational diffusion constants in the moderately supercooled regime.
- So cage-breaking rearrangements dominate diffusion at these temperatures.

Cage-breaking in the Potential Energy Landscape

- Configurations were quenched from a locally ergodic MD trajectory and connected using the OPTIM package. [7]
- This builds a database of minima and transition states (TSs), which can be represented by a disconnectivity graph.
- A TS is described as cage-breaking if any molecule undergoes a CB during the corresponding rearrangement.
- These disconnectivity graphs exclude particular types of TS, causing the tree to fragment. Fragments are coloured by energy.
- Cage breaking transitions are sufficient and necessary to traverse large regions of the landscape (top two figures).
- The lowest figure shows non-CB and reversed-CB TSs. The landscape is separated into a hierarchy of connected regions, bounded by productive cage breaks.
- Transitions between these regions are rarely reversed, so should follow an approximate random walk.
- The regions possibly correspond to metabasins. [8]

Super-Arrhenius Behaviour Arises From Negatively Correlated Motion

Correlation Angles

- Neighbours definition
- Productive cage breaks define by nearest neighbour changes give a reasonable approximation to translational diffusion constants in the moderately supercooled regime.
- The same cage breaks are both necessary and sufficient to traverse the PEL, demonstrating importance for long-time diffusion.
- Productive cage breaks reveal hierarchical ordering in the PEL. The regions of phase space bounded by these transitions may correspond to metabasins. [8]
- Super-Arrhenius behaviour in translational diffusion of OTP arises from negative correlations in particle displacement over short time scales.
- This negative correlation behaviour is the same effect that we attempt to capture by excluding reversed cage breaks.

Conclusions

- Cage breaks defined by nearest neighbour changes give a reasonable approximation to translational diffusion constants in the moderately supercooled regime.
- The same cage breaks are both necessary and sufficient to traverse the PEL, demonstrating importance for long-time diffusion.
- Productive cage breaks reveal hierarchical ordering in the PEL. The regions of phase space bounded by these transitions may correspond to metabasins. [8]
- Super-Arrhenius behaviour in translational diffusion of OTP arises from negative correlations in particle displacement over short time scales.
- This negative correlation behaviour is the same effect that we attempt to capture by excluding reversed cage breaks.

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Bibliography