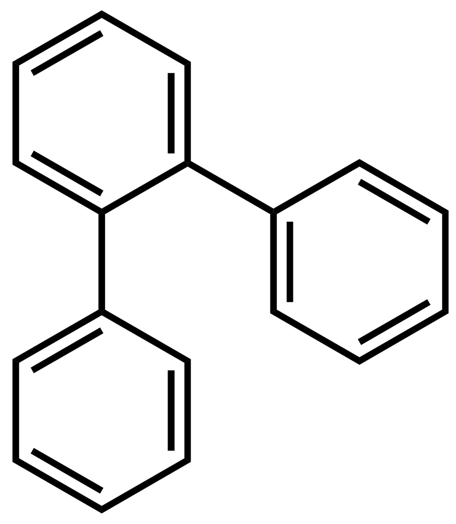

Dynamics of a Molecular Glass Former: Diffusion and the Potential Energy Landscape for Ortho-Terphenyl

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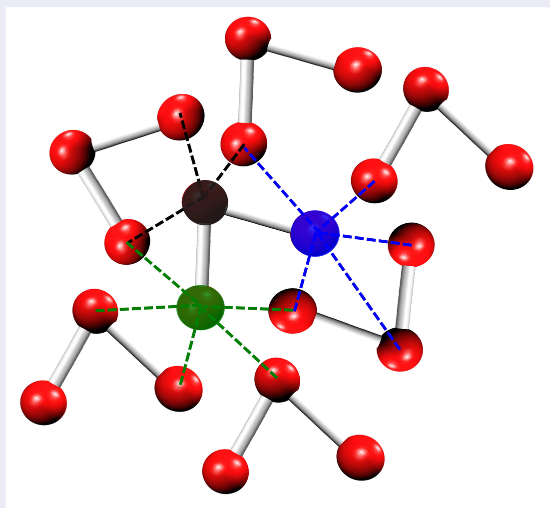
Introduction

- 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.
- Here[4] we extend our neighbour-based definition of cage-breaking rearrangements to a molecular system: the Lewis-Wahnström model for OTP. [5]
- This is a 3-site rigid-body model using the Lennard-Jones potential to model ring-ring interactions.

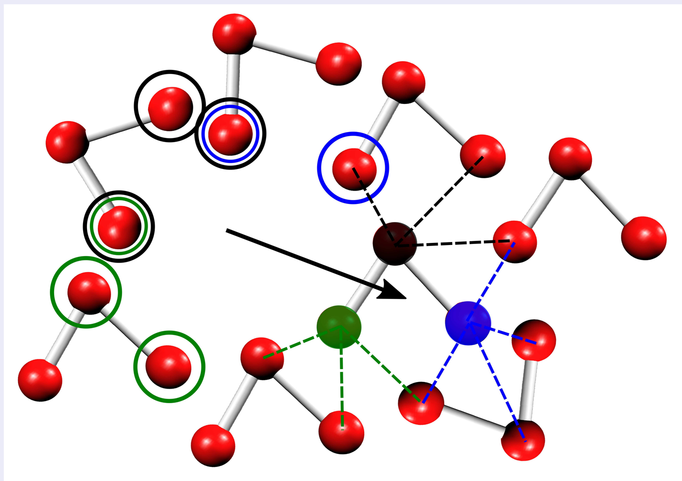
Cage-breaking Transitions

- 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 (SANN) 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.

Schematic Cage Break

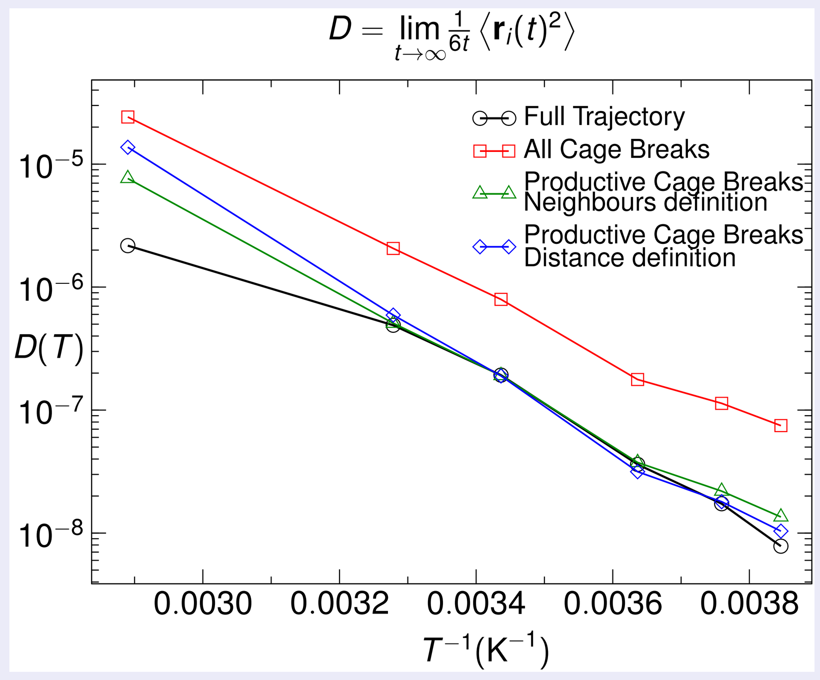


Before a Cage Break. Nearest neighbours are shown for the three interaction sites on the central molecule (dashed lines, different colours for each site).



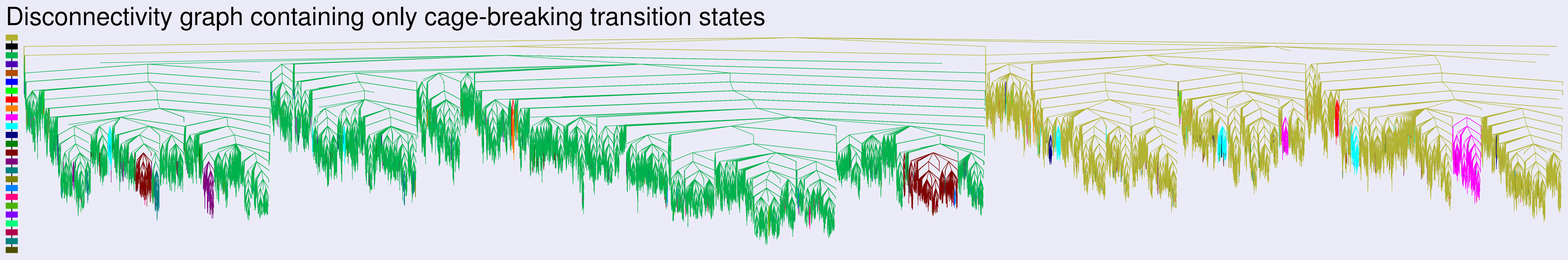
After the rearrangement. New nearest neighbours are shown as before. Old nearest neighbours lost during the transition are circled. Each atom has changed at least two neighbours, so a Cage Break has taken place.

Cage-breaking Diffusion Constants

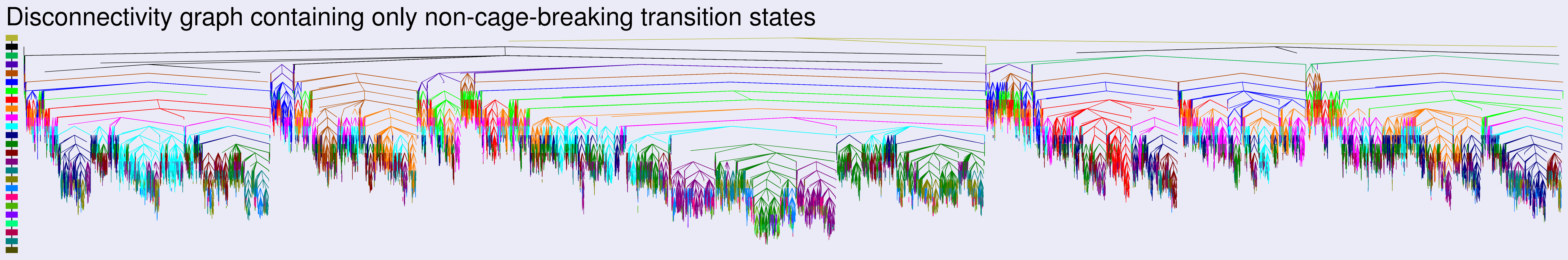


Cage-breaking in the Potential Energy Landscape

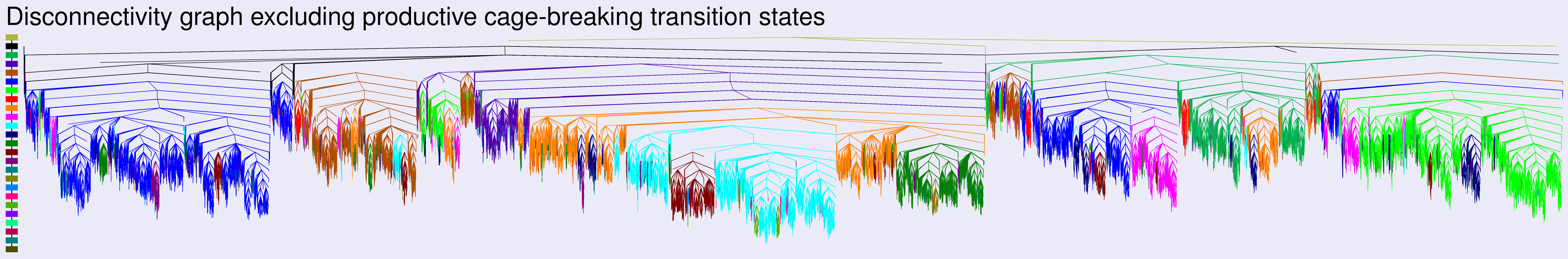
Disconnectivity graph containing only cage-breaking transition states



Disconnectivity graph containing only non-cage-breaking transition states



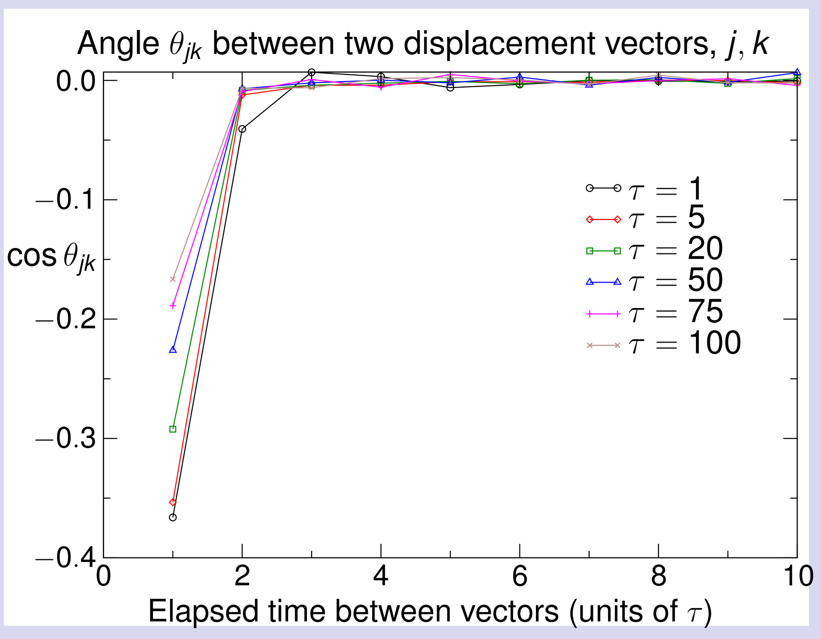
Disconnectivity graph excluding productive cage-breaking transition states



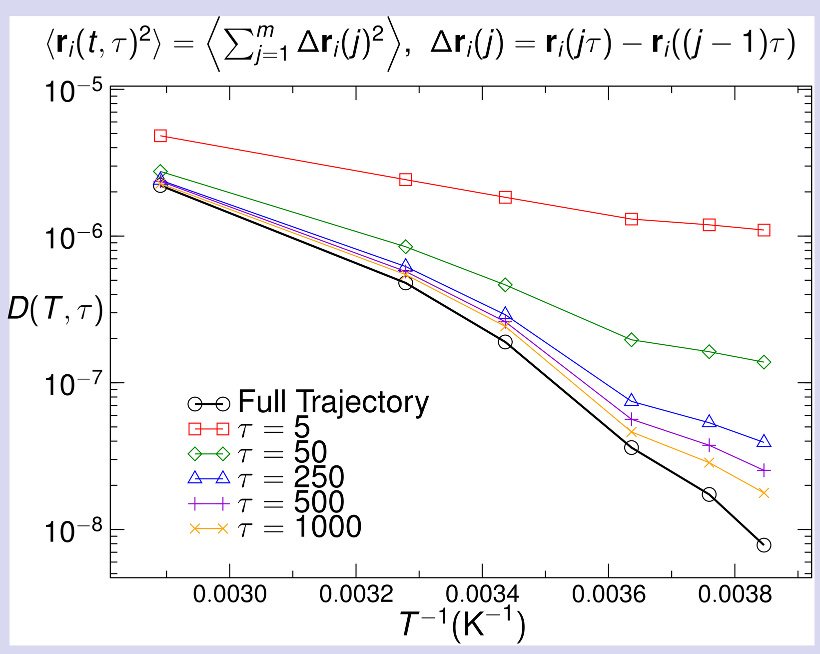
- Configurations were quenched from a locally ergodic MD trajectory and connected using the OPTIM package. [7]
- This builds a database of minima and transition states (TSs), which can be represented by a disconnectivity graph.
- A TS is described as cage-breaking if any molecule undergoes a CB during 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

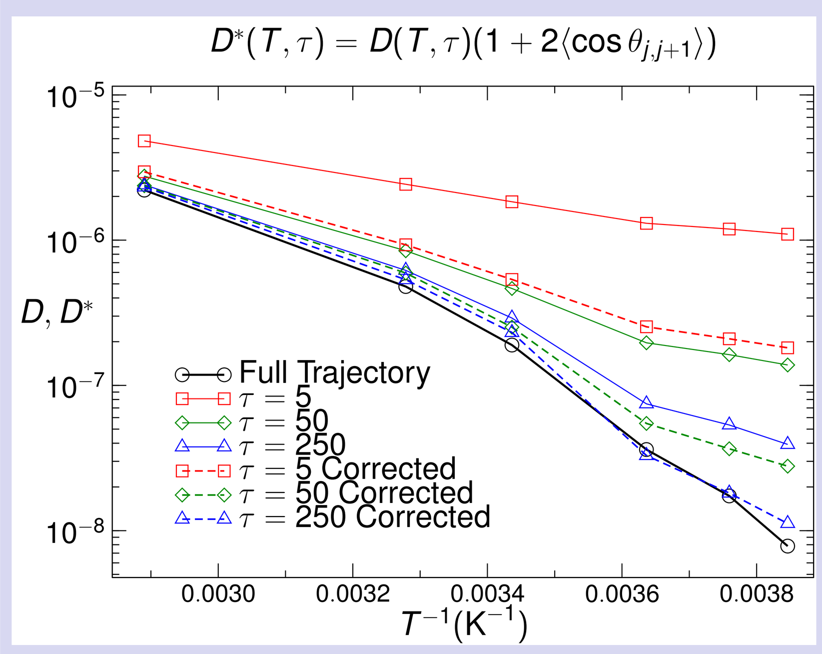
Correlation Angles



Reduced-Timescale Diffusion



Correlation-Corrected Diffusion



- Translational motion shows strong negative correlation on short time scales, and negligible correlation at longer times (left panel).
- Calculating diffusion constants over short time intervals of length τ excludes negative correlation behaviour. The second panel shows that this calculation removes super-Arrhenius behaviour (small τ).
- Adding a simple correction term accounting for short-time correlations is sufficient to restore super-Arrhenius behaviour (right panel, dashed lines).

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.

Acknowledgements

This work was supported by the University of Cambridge and by the ERC.
The program used to identify cage breaks may be obtained from http://www-wales.ch.cam.ac.uk/CCD.html

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