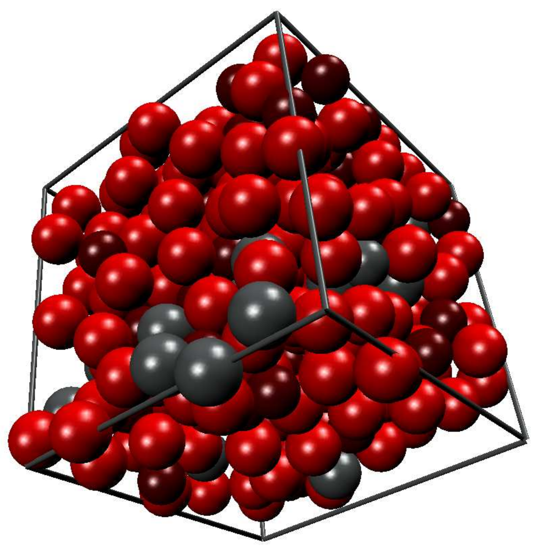

New Insights into the Pinned Glass Transition from an Energy Landscapes Approach

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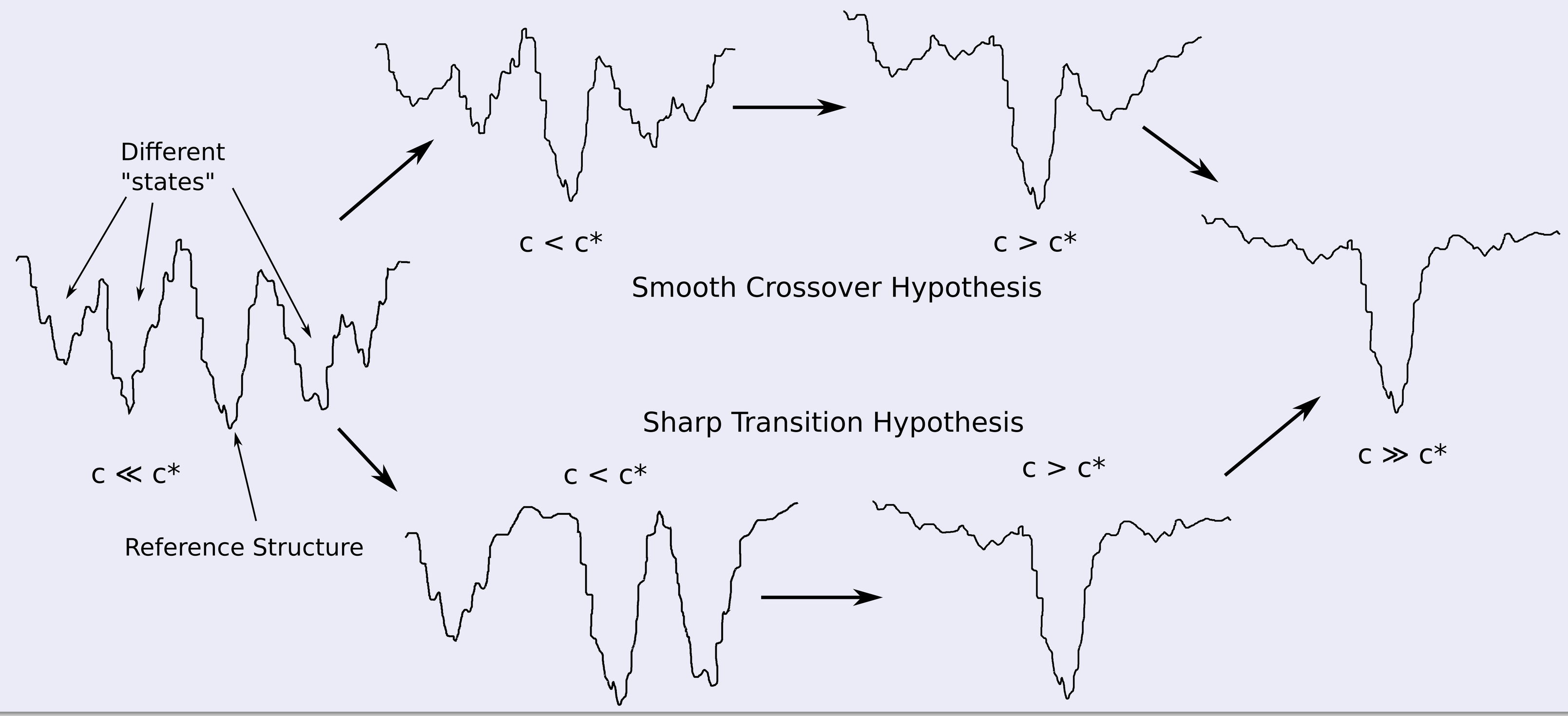
Introduction

- The laboratory glass transition is a kinetic phenomenon. Is there an associated thermodynamic "ideal glass transition" that we cannot access experimentally?
- Starting from a reference structure drawn from an equilibrated simulation, pinning a randomly selected[1] fraction c of the atoms (freezing their positions) reduces the number of thermodynamic states available to the system. This means that the configurational entropy decreases[2]. At high c, the number of states becomes small (sub-extensive).
- It has been suggested[2, 3] that this change represents a thermodynamic glass transition, as predicted by the RFOT theory[4, 5, 6, 7]. Extrapolating the corresponding critical temperature to the case $c = 0$ would give us the ideal transition temperature T_K.
- The dynamics of supercooled liquids are commonly described in terms of their Potential Energy Landscape (PEL)[8, 9]. How does pinning some particles affect the PEL?

Research Questions and Hypotheses

- We have studied a 256-particle Kob-Andersen liquid with periodic boundary conditions and number density 1.2.
- Many thermodynamic states are available at low c. Do these correspond to the superstructures ("funnels") on the PEL?
- At high pinning fraction c, only one state is populated at equilibrium (corresponding to the reference structure).
- How does the change between these two regimes take place?
- Smooth crossover hypothesis: gradual increase with c in energies of competing states, until only the reference structure is significantly populated.
- Sharp transition hypothesis: multiple low-energy states remain up to a critical $c = c^*$, at which all except the reference structure disappear. Energy barriers between states increase with c.
- The RFOT model[4, 5, 6, 7] implies that a sharp transition will be observed at low T.
- At higher T, a smoother crossover will be observed[10].



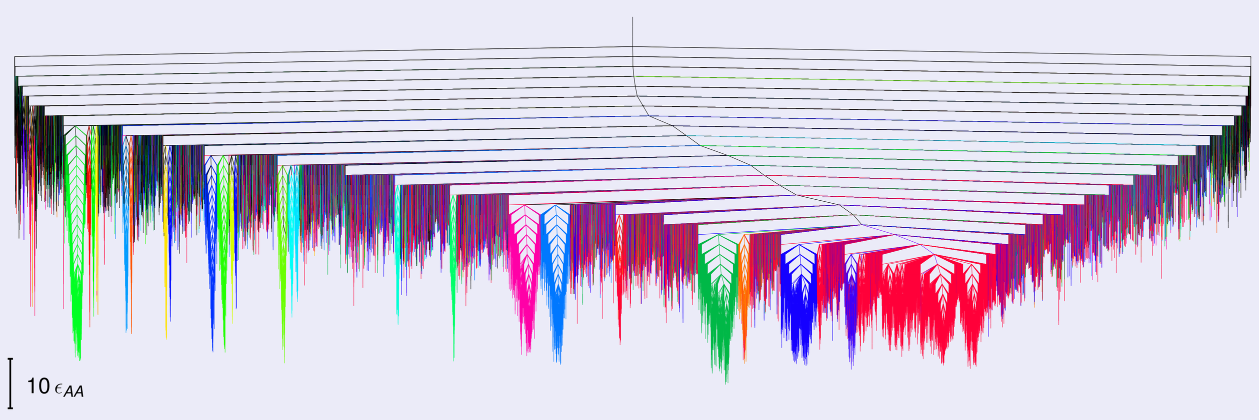
Distinct states on the landscape

Disconnectivity graph for $c = 0.15$. Minima are coloured according to different structures defined using mutual overlap[3, 11]:

$$Q_{ab} = \frac{1}{N_A}\sum_{i,j}^{N_A} \theta(0.3 - r_{ia,jb})$$

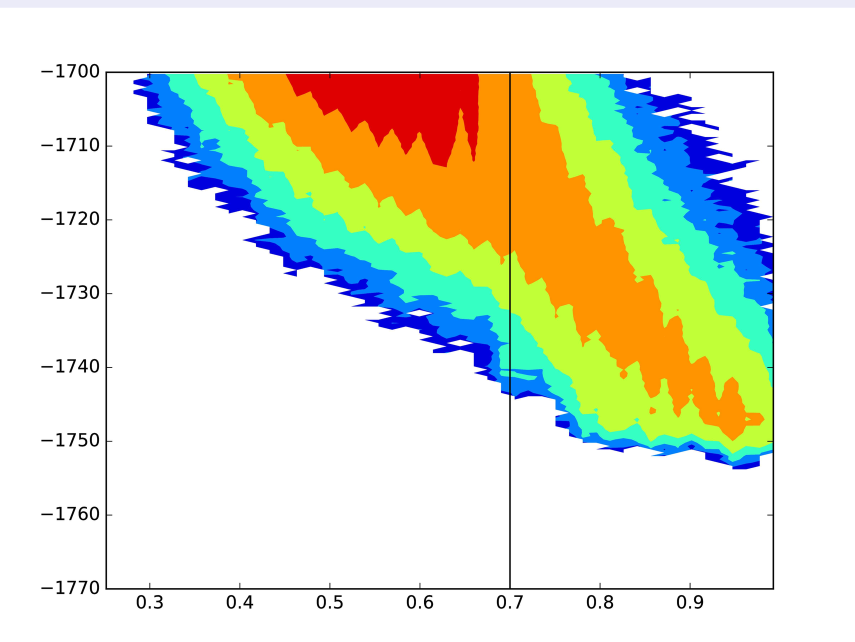
$r_{ia,jb}$ is the distance from atom i in configuration a to atom j in configuration b.

Configurations a and b belong to the same structure if $Q_{ab} > 0.7$.

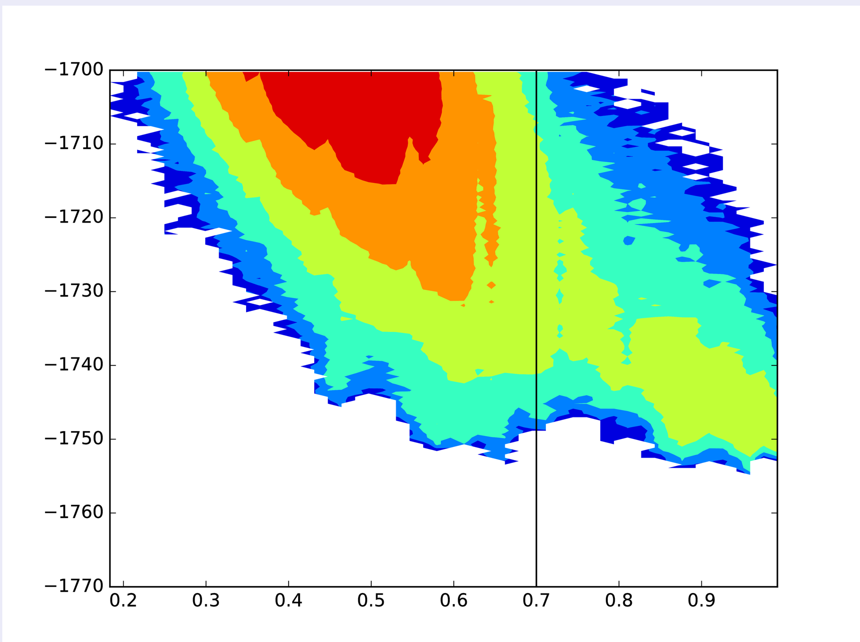


Basinhopping Results

Histogram of Q vs E for minima located by parallel tempering basin hopping (PTBH) at $c = 0.17$.

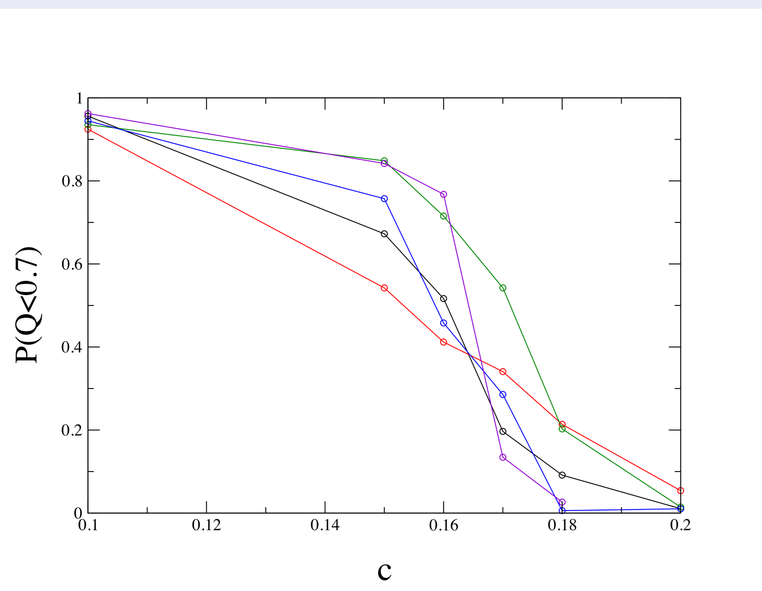


Histogram of Q vs E for minima located by PTBH at $c = 0.16$.



For any given reference structure and choice of pinned atoms, we can identify a maximum value of c where low-energy structures exist that are distinct from the reference.

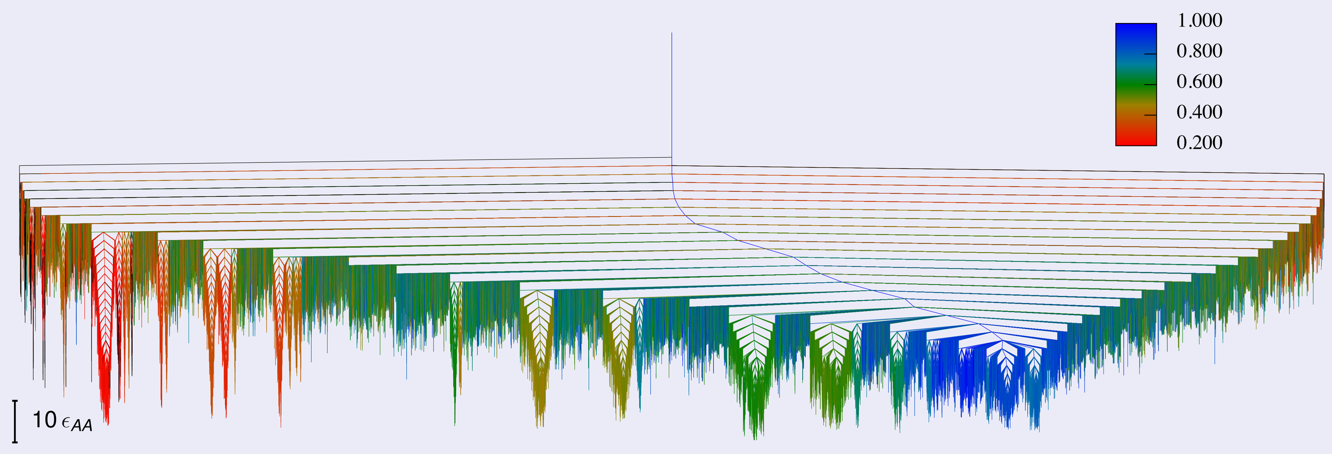
Variation between reference structures



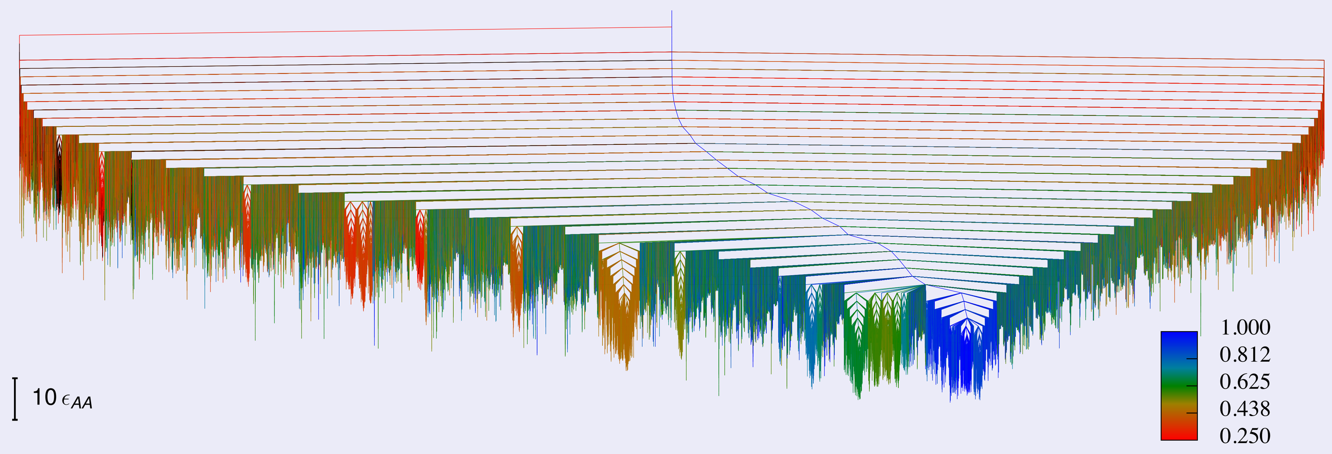
- Proportion of minima having overlap < 0.7 with the reference structure as a function of c.
- Results for 5 different sets of pinned atoms are shown.
- Only the 25% of minima with the lowest energies are used in each curve.
- Considerable variation is seen in the position and sharpness of the transition.

Observed structure of Pinned Landscapes

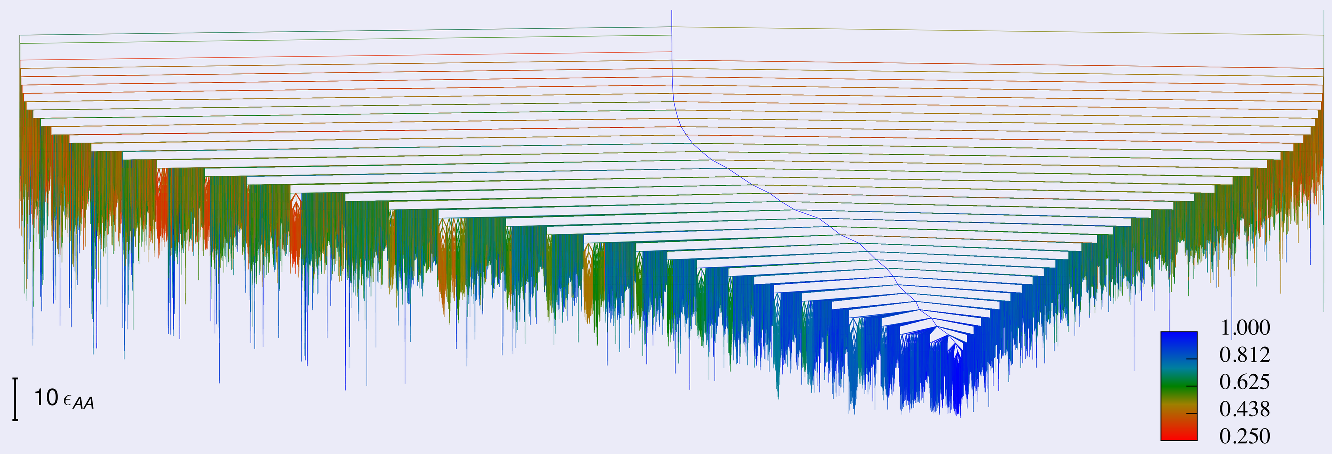
Disconnectivity graph for BLJ with 10% of particles pinned at random.



Disconnectivity graph for BLJ with 16% of particles pinned at random.



Disconnectivity graph for BLJ with 18% of particles pinned at random.



- Minima are coloured according to their overlap with the starting minimum.
- Most funnels on the disconnectivity graph are entirely one colour, so minima within a funnel have similar structures.
- The low-c graph is very similar to an unpinned landscape: many different funnels i.e. many different states.
- The $c = 0.16$ graph shows distinct states moving to higher energies, so their equilibrium population decreases.
- The high-c landscape also has multiple funnels with low overlap. But they are too high in energy to be significantly populated at equilibrium. So these do not constitute distinct thermodynamic states.

Conclusions

- Pinning a glass former changes the PEL dramatically, giving a well-defined global minimum state.
- Different structures, or "distinct packings" of the atoms may be identified with superstructures on the PEL.
- As pinning fraction is increased, structures distinct from the reference structure gradually increase in energy.
- At high pinning fractions, all states except one are too high in energy to be significantly populated at equilibrium.
- For a given structure, we can use the landscape to identify a region of pinning fractions c in which the behaviour changes from low-c to high-c behaviour.
- The change from many available states to one state appears to occur via a smooth crossover.

Outstanding Questions

- Is the observed smooth crossover a finite-size effect? How does this behaviour change with T?
- How is the landscape affected by choice of reference structure and pinned atoms?

Acknowledgements

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The pele software package may be obtained from https://github.com/pele-python/pele

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