Topological characterization of rearrangement events in supercooled water

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Abstract

Molecular dynamics simulations of super-cooled, low-density, ST2 water are analysed from the perspective of rearrangements in the bonding network. A sequence of inherent structures is represented by their geometrically determined bond-networks. These networks are then compared to find minimal clusters of molecules involved in each reorganization event. The topology of the change in each cluster is classified according to the coordination defects involved, net bond creation, and size distributions are determined for each category. We find a significant proportion of events in all three top-level categories: clusters with net bond breaking or formation; clusters which globally conserve bonds but the number at individual molecules changes; and clusters where all molecules retain their original number of bonds but the network is topologically different. Trends toward the first categories are identified as the temperature is reduced. We also note enhanced activity near molecules with coordination defects.

Introduction

How are the dynamics of a super-cooled liquid be most simply described? This is the region between the strongly heterogeneous rare events of the rigid amorphous solid and the continual tumbling of the high temperature liquid.

For a network liquid such as water in its low density phase, we can characterize flow events as changes to the topology of the network itself. This neglects the short time dynamics involved in vibrations and the momentum effects that cause correlations with subsequent events, but both of these diminish in importance as the super-cooling increases.

Even in this simplified topological space, a vast array of events occur, leading us to the following questions:

- Can these be put into tractable categories as has been done in the defect theories used for crystalline materials[1]?
- Are the events simple enough to describe and enumerate (e.g. for implementation in Monte Carlo algorithms)?
- Are there any local network features that promote nearby activity, and determine the heterogeneity of the system?

Models and Methods

Model
1728 molecules, at a density of 0.83 g/cm^3, interacting according to the ST2 model for water. 10 ps quenched snapshots were produced during MD runs of around 4 ns (high temps) to 40 ns (low temps)[2].

Method
Hydrogen-bonding networks were assigned to each snapshot based on geometric criteria requiring both oxygen proximity and a co-linear hydrogen. Any bonds that changed from frame to frame were identified and clusters identified and characterized.

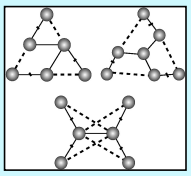

Fig 1: Examples of conservative topological rearrangements

Results

Network properties

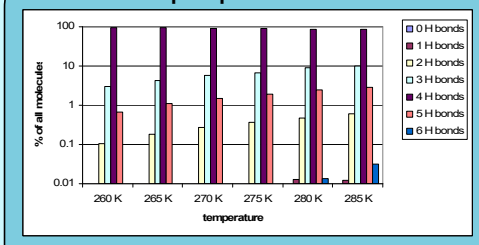

Fig 2: The equilibrium fraction of molecules with each coordination number, as a function of temperature.

A small fraction of molecules have less than four hydrogen bonds, and an even smaller fraction have more. The equilibrium defect concentrations decrease as the temperature is decreased. Because the occurrence of more extreme defects is so small, under-coordination will hereafter be referred to as 3-defects and over-coordination as 5-defects.

Validation of robust clusters

Overlaps within the time period?

10 ps periods are sufficiently long that it is reasonable to question whether multiple events are occurring in an overlapping location in between snapshots.

We have excluded temperatures above 270 K because at those temperatures, over 25% of molecules were involved at least once during each period, and thus the probability of cluster overlap was high.

At 260K we find around 30 clusters per frame, involving around 6% of molecules in total. This suggests they will usually be separate events, but we are currently doing a validation study using 0.1 ps periods.

Are the inherent (quenched) structures representative?

The same analysis has been done on the unquenched structures. These show additional clusters, but they are overwhelmingly 2 molecule clusters (single bond breaks or makes). We suggest that these are simply reversible vibrations which momentarily break our geometric definition of a hydrogen bond, and are not of long lived significance.

Cluster sizes

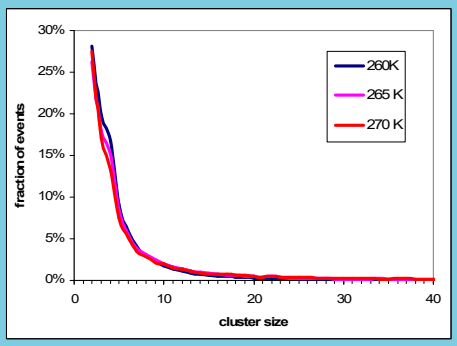

Fig 3: The fraction of all events with a given cluster size.

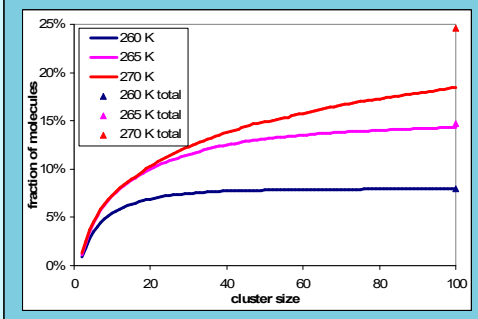

Fig 4: The cumulative fraction of all molecules which are participating in clusters up to a specified cluster size during a 10 ps period.

10 ps periods are short enough for the majority of molecules to retain their local environment in temperatures up to 270 K. Those molecules which do participate in a rearrangement are usually in clusters of less than around 10 molecules, and this is increasingly true as the degree of super-cooling is increased. Such small cluster sizes suggest that a complete enumeration of possible topological events could be constructed.

Cluster categorization

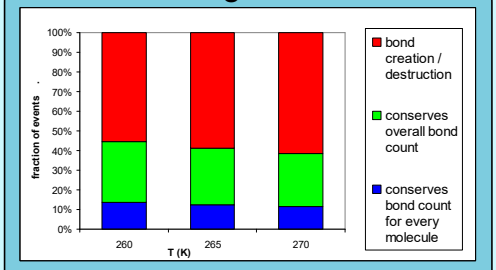

Fig 5: The fraction of clusters categorized according to their effect on the H-bond count of involved molecules.

Even at the lowest temperature, the majority of clusters are in the catch-all category of net bond creation or destruction. This appears to preclude simple enumeration, (as was previously been done for conserved mechanisms in silicon[3]), but the good news is that the majority of these events are trivial bond formation between a pair of 3-defects, or the reverse, bond breaking between 4-bonded molecules.

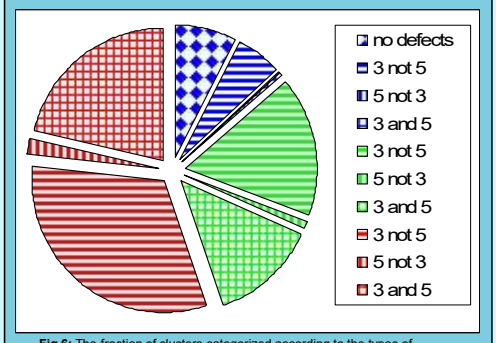

Fig 6: The fraction of clusters categorized according to the types of defects involved, as well as their effect on the H-bond count of involved molecules (colours refer to the same categories as the previous figure).

3-defects are nearly always present in a rearrangement (either before, after, or both), vastly out of proportion to their concentration.

Conclusions

- Low density water near its freezing point is well represented by a continuous random network of hydrogen bonded molecules, primarily 4-bonded, with a small fraction under-bonded, and an even smaller fraction over-bonded.
- When super-cooled, rearrangements of this network usually involve less than around 10 molecules.
- There is a strong preference for reorganization involving defect molecules, particularly under-bonded defects.
- There are a wide variety of types of event including bond-conserving, defect-transport, defect-creation and recombination. As the temperature decreases, there is a trend toward bond conservation and defect transport.

References

1) H. J. Frost and M. F. Ashby, *Deformation-Mechanism Maps, The Plasticity and Creep of Metals and Ceramics*, Pergamon Press, Oxford (1982).
2) P. H. Poole, I. Saika-Voivod and F. Sciortino, *J. Phys.: Cond. Mat.* **17**(43), L431-L437(1), (2005).
3) T. S. Hudson and P. Harrowell, *J. Chem. Phys.* **126**, 184502 (2007).