On the phase behavior of stretched, supercooled and glassy water, its dependence on confinement, and its relation to that of other network and molecular systems.

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1. Introduction

There are at least two forms of amorphous solid water, one much denser than the other, and with density dependent on the pressure of vitrification\(^1\)\(^-\)\(^2\). There is controversy over all aspects of these glassy states, including the importance of confinement which allows very subdivided states of water to avoid crystallization during slow cooling. There is also controversy concerning the behavior of stretched water, particularly the evidence for a large difference in density between the states of water that cavitate homogeneously, depending on the direction of temperature change\(^3\)\(^-\)\(^5\). States that reach their tensile limit on isochoric cooling from high temperatures, cavitate at much lower densities than states that cavitate during isochoric heating from low temperatures.

2. Experimental/theoretical methods

We discuss the experimental approaches that have been used in the study of glassforming properties, supercooled and stretched liquid properties, and confinement effects.

3. Results and discussion

We review the results of various methods and present some unpublished results in each area. We then show how these results can be reconciled using the “critical-point-free scenario” for water’s anomalies\(^6\). In particular, we show how this scenario allows us to understand the controversially feeble glass transition of vitreous water obtained by hyperquenching in terms of a narrowly avoided second critical point. This striking behavior is attributed to the cooperative formation of strong hydrogen bonds that is permitted under constant pressure (but not constant volume) condition.

Seeking evidence of related behavior in other network liquids, we study the heat capacity of the ionic network glassformers, BeF\(_2\) and SiO\(_2\). In these cases a related, but much more damped form of the same behavior, (feeble glass transition, and heat capacity maximum at higher temperatures), is observed. However, in these cases the anomalies occurs at temperatures far above the melting points. Looking at weaker networks and non-network glassformers, we observe only increases in (non-vibrational)
heat capacity with decreasing temperature. The heat capacity rise is cut off by a first order transition to the glassy state. The relations are shown in Figure 1. [7]

FIG. 1: Plots of heat capacity and entropy in excess of glassy (vibrational) contribution, for liquids of different classes (fragile on left and strong on right), with water and analogs Si and Ge showing sharp $C_p$ peaks or weak first order L-L transitions, in the center.

Finally, we show how closely the strong network system behavior (best represented by the case of BeF$_2$), relates to the behavior of classical metallic binary alloy systems undergoing their order-disorder transitions.

4. Conclusions

The much-discussed “uniquely anomalous” behavior of water, is interpretable.

5. References

[5] F. Caupin, (private communication)