

The Density Anomalies of Supercooled Confined Water

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Although water is so essential and familiar to all known forms of life, there are still more than 60 fascinating properties that can not be well understood, especially the supercooled water below the homogeneous nucleation temperature, $T_H = 235$ K. Our group has developed a well ordered nano porous silica material, MCM-41-S-15. By exploiting the confined space, the homogeneous nucleation of water can be avoided and the so-called “no man’s land” is finally reachable.

Our collaboration in Massachusetts Institute of Technology, Prof. Sow-Hsin Chen *et al.*, have performed a series of small angle neutron scattering (SANS) experiments on the supercooled water confined in our nano porous materials. One of the most outstanding results showed that D_2O has an unfamiliar density minimum around 210 K [1]. The origin of the thermodynamic anomalies of water could be explained by the hypothetical existence of a liquid-liquid critical point (LLCP) hidden in the deeply supercooled region at an elevated pressure.

Because of the small scattering length density (SLD) and strong incoherent scattering of H_2O , it is hard to measure the density of H_2O by neutron techniques. On the other hand, there are no such limitations in X-ray scattering. Therefore, we tried to use X-ray scattering to acquire the density of water (H_2O) in MCM-41-S-15 under deeply supercooled condition in this project. Since the scattering intensity is proportional to the square of SLD contrast between water and the silica matrix, and based on the fact that the SLD is proportional to mass density, we can obtain the density of supercooled water by measuring the intensities of X-ray scattered by full hydrated MCM-41-S-15.

Figure 1 showed the densities of H_2O at various temperatures measured by X-ray scattering. The highly superimposed of these two sets of cooling and heating scan data presented that our experiments are duplicable. The densities of bulk water at temperatures higher than T_H and the data obtained by an independent optical scattering experiment with our confined matrix were also shown on the same Fig. [2]. The X-ray scattering patterns of dry MCM-41-S-15 at different temperatures were also collected. The intensities of dry sample did not change through entire temperature range, which proved the trend of X-ray scattering intensity only varied with the water density change. One can find these results are quite similar. Even though there is small deviation at deeply cooled region between Mallamace’s and our data, these two systems still both exhibited a clearly density minimum and comparable trend. Besides, the SANS measurements of D_2O also showed highly resemblance.

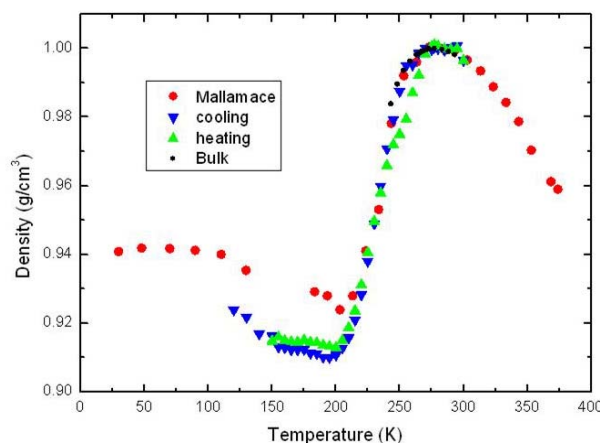


Fig. 1: Densities of H_2O at various temperatures. The blue and green triangles are the cooling and heating scan, respectively, measured in this project. The red circles are the optical scattering results done by Mallamace *et al.* with the same confined matrix. The black dots are the density of bulk water.

In the near future, we are going to reveal more physical and chemical properties of supercooled water. The most crucial issue would be sample environment. At present, the sample environment can only access low temperature condition. Without the high pressure environment, it is impossible to shed light on the complete phase diagram of supercooled water, which so many thermodynamic questions are embedded in. Although it may be hard to achieve, our next step will try to locate the LLCP at low temperature and elevated pressure.

References

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