

## Liquid-liquid phase separation of water: A molecular dynamics study

Water is one of the most studied liquids because it has many peculiar properties. It is known that the isobaric heat capacity of water sharply increases with decreasing temperature down to 235 K. A leading hypothesis to explain this anomaly is the liquid-liquid phase transition theory. This theory attributes the divergent behavior of thermodynamic response functions to the hypothesized second critical point at  $T_c \sim 220$  K. Although many computer simulations and experiments seem to support the liquid-liquid phase transition scenario, this is still a controversial issue.

The liquid-liquid phase transition hypothesis suggests that supercooled water exists as either a low density liquid (LDL) or high density liquid (HDL) for  $T < T_c$ . If the system is at constant volume and the density is intermediate between those of the low and high density phases, a spontaneous phase separation is expected to occur at  $T \sim T_c$  in the course of decreasing temperature. To the best of our knowledge, however, there has been no study which clearly demonstrates the liquid-liquid phase separation of water, because of the fact that the two liquid phases are quite similar to each other and thus it is difficult to distinguish them.

To observe the liquid-liquid phase separation of water, we performed very long isochoric-isothermal (NVT) molecular dynamics simulations. We classified water molecules based on the hydrogen bond network rearrangement dynamics, and found that the liquid-liquid phase separation indeed takes place at temperatures below the second critical point. Our results strongly support the liquid-liquid phase transition hypothesis.