

Hallmark of a liquid-liquid transition in supercooled water nanodroplets

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Since the introduction of the liquid-liquid critical point (LLCP) hypothesis in 1992 to explain the anomalous properties of liquid water, numerous studies have been conducted to validate it. However, the LLCP's occurrence at extremely supercooled temperatures and high pressures makes investigating the LLCP, and the associated liquid-liquid phase transition (LLPT) between a low-density liquid (LDL) and a high-density liquid (HDL), particularly challenging in experiments. Therefore, we adopt an alternative approach to observe LLCP manifestations in water nanodroplets, in which crystallization is suppressed, rather than in bulk water. Leveraging the Laplace pressure allows us to achieve high pressures by reducing nanodroplet radius. Employing the TIP4P/2005 water potential in molecular dynamics simulations, we identify hallmarks of a LLCP in nanodroplets containing only a few hundred molecules [1,2]. However, the small size required to produce the critical pressure of 185 MPa calculated for the model prevents a clear observation of a LLPT. We extend our study to water droplets ranging from a thousand to tens of thousands of molecules using the WAIL water model, revealing a critical pressure in nanodroplets at $P_c=37$ MPa. Bulk-like behavior is observed in nanodroplets of size $N \geq 1000$, and so we observe a sharp LLPT in droplet sizes of approximately $N_c \approx 15,000$. These findings are significant because if the LLPT in real water occurs at $P_c \leq 100$ MPa, it opens the possibility of detecting a LLPT in water nanodroplets in experiments conducted at ambient pressure. To further investigate, we explore the potential for inducing a LLPT in nanodroplets containing tens of thousands of molecules using an inert gas as a pressurizing medium. Preliminary results indicate a transformation from LDL to HDL in the droplet core, as shown in Fig. 1, further supporting the feasibility of experimental LLPT detection in the absence of crystallization.

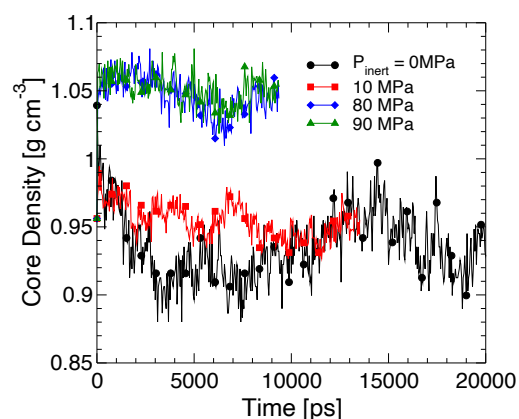


Fig. 1: Time dependence of core density for various values on inert pressure

[1] S.M.A. Malek, P.H. Poole, and I. Saika-Voivod, Nat. Commun. 2018, 9, 2402

[2] S.M.A. Malek, P.H. Poole, and I. Saika-Voivod, J. Chem. Phys. 2019, 150, 234507