Limit of metastability of supercooled water

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ABSTRACT

The fate of deeply supercooled liquid water has been the topic of intense research and fruitful disputes. The heat capacity and compressibility of liquid water increase in the supercooled region, apparently following a power law that would diverge at about 228 K, just below the experimental temperature of homogeneous nucleation of ice, T_H = 232 K. Fast ice crystallization has prevented the experimental characterization of the structure and thermodynamics of liquid water at temperatures between 140 and 232 K, a region known as water's "no-man's land". Due to the slow dynamics of supercooled water, this region is also very challenging to probe with atomistic simulations. We used molecular simulations with the mW model of water to investigate the relationship between the structure, anomalies and crystallization rate of water and to elucidate the fate of liquid water in "no-man's land".[1,2,3] The simulations indicate that the continuous structural transformation of liquid water into a four-coordinated liquid is responsible for the thermodynamic anomalies of liquid water and also controls the crystallization rate. The simulations predict that the crystallization rate of water reaches a maximum at a temperature T_x just below T_H, a result that is also supported by calculations using classical nucleation theory with experimental free energy and diffusivity data for water. The maximum crystallization rate at T_x is due to a crossover between a nucleation-dominated regime (above T_x) and a growth-dominated regime (below T_x). The results of the simulations are supported by calculations using Classical Nucleation Theory and experimental data for the temperature dependence of the excess free energy and diffusivity of liquid water. Our results indicate that at temperatures below Tx = 225 K, liquid water cannot be equilibrated because the time scale of crystallization is comparable to the time scale of relaxation of the liquid. Our results imply that bulk supercooled water reaches a kinetic limit of metastability in "no-man's land" at around 225 K.

1. Moore, E. B. & Molinero, V. Structural transformation in supercooled water controls the crystallization rate of ice. *Nature* **479**, 506–508 (2011).
2. Moore, E. B. & Molinero, V. Ice crystallization in water's 'no-man's land'. *J Chem Phys* **132**, 244504 (2010).
3. Xu, L. & Molinero, V. Is there a liquid-liquid transition in confined water? *The Journal of Physical Chemistry B* **115**, 14210–14216 (2011).