Transport Properties of Stable and Supercooled Water: Two-State Analysis of Experiments and Simulations

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Thermodynamic anomalies of water, such as its negative expansion coefficient, or the increase of its isobaric heat capacity upon cooling, become exacerbated in the supercooled liquid, below the equilibrium melting temperature of ice. Among the proposed explanations, the second critical point scenario involves a first-order transition between two distinct liquid phases, terminating at a critical point. According to molecular dynamics simulations, the critical point lies deep in the supercooled region, making it difficult, if not impossible, to observe in experiments. Nevertheless, the liquid properties at temperatures above the critical point temperature remain influenced by its existence. This has suggested a phenomenological description of the properties of water with a two-state model, which regards water as a non-ideal solution of two rapidly inter-converting species, whose relative fraction depends on temperature and pressure. This description is able to reproduce quantitatively all available thermodynamic data within a broad pressure and temperature range. We discuss the extension of this model to dynamic properties. Indeed, transport properties of water are also anomalous: the shear viscosity η decreases with applied pressure, whereas the self-diffusion coefficient *D* increases, in contrast with the behavior of other liquids. Although *D* has been measured under pressure and deep in the supercooled region, η of supercooled water was known only at ambient pressure. We have recently measured η of supercooled water under pressure. A simple extension of the two-state thermodynamic model is able to quantitatively reproduce the transport properties. To gain more insight on the connection with a possible liquid-liquid critical point, we have used molecular dynamics simulations with the TIP4P/2005 model for water, for which the situation was similar to real water: a two-state thermodynamic model was available, and η was largely unknown in the low temperature region. We have obtained *D* and η from simulations in a wide temperature and density range. As for real water, a simple extension of the thermodynamic two-state model is able to describe transport properties at positive pressure. However, some discrepancies exist at negative pressure and call for further investigations.