

Liquid-like and gas-like components in the dynamics of supercritical water

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In recent years, interest in supercritical water has been growing because of its importance in biological and geological sciences and because of its wide application in biochemical industries. Underlying many of these applications is the large tunability of the density and solvation properties of supercritical water near its critical point. A thorough physical understanding of these properties is needed in order to further exploit them to facilitate a variety of chemical processes. However, while the thermodynamics of supercritical fluids is relatively well-understood, with the “Widom line” indicating a rapid crossover between liquid-like and gas-like states in the supercritical region, details of their microscopic dynamics are less clear. This reveals a lack of experimental data and theoretical understanding of the dynamics of supercritical fluids.

Therefore, in this work, we study the molecular-scale dynamics in sub- to supercritical water with meV-resolved inelastic x-ray scattering measurements and molecular dynamics simulations. Contrary to commonly used models, we observe that the longitudinal current correlation spectra contain not one, but two main components: a low-frequency, gas-like component and a high-frequency, liquid-like component. Our analysis shows that, while the gas-like component is associated with free-particle motion, the liquid-like component arises from the O—O stretching mode between hydrogen-bonded molecules, which is reminiscent of the longitudinal acoustic mode in ambient water. With increasing temperature, the hydrogen-bond network diminishes and the spectral weight shifts from the liquid-like to the gas-like component, leading to a dynamical transition. The ratio between the two components can be used to describe quantitatively the microscopic dynamics of supercritical water, with a rapid crossover around the Widom line, thus drawing a connection between the dynamics and the thermodynamics of the system. The changing ratio between the components can also be used to explain the thermodynamic state dependence of physicochemical properties such as the dielectric constant, which has important implications for industrial applications of supercritical water. Further simulation results on other systems indicate that this two-component behavior is not specific to water and its hydrogen-bonding network, but a general phenomenon among supercritical fluids.