Patterns of Thermodynamic Property Extrema under Supercooled and Stretched Conditions for Classical Water Models

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We analyzed the results of accurate MD simulations performed for three popular atomistic water models, TIP4P/2005, TIP5P, and ST2, in supercooled and deeply stretched (doubly metastable) regions. The two-structure EOS that incorporates the liquid-vapor spinodal was used to describe the thermodynamic anomalies associated with the liquid-liquid transitions in the supercooled metastable states of these models. We found that the patterns of property extrema around the liquid-liquid transition lines are controlled by three major factors: the distance between the liquid-liquid critical point and the vapor-liquid spinodal, the pressure/temperature slope of the transition line, and the difference in energies of the alternative structures. We made an attempt to fit the patterns of extrema loci for these water models to master curves by corresponding-states-like rescaling of the temperature and pressure coordinates. Such rescaling results in collapse of extrema loci of the density, isothermal compressibility, and isobaric heat capacity into a universal pattern. We also discuss the possibility of observing such universality in other tetrahedral systems.