Thermodynamics of Nanoscale Water Systems

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Thermodynamic properties of small systems are known to deviate for those determined at large scale due to the large surface-to-volume ratio. In this work, we have studied the surface and shape effects of small systems, and how extensive thermodynamics properties are no longer proportional with the volume as the size of the system becomes significantly smaller than in the thermodynamic limit. We investigate how Hadwiger's theorem[1] of volume- and surface terms can be used to explain fluctuating properties in the grand-canonical ensemble. The properties are analyzed using Hill's nanothermodynamics[2], and it is shown that the properties can be resolved in a surface and a volume term. The surface satisfies the thermodynamics of a flat surface, as described by Gibbs[3]. Using molecular simulations, we show how the size and shape changes the properties of TIP4P/2005 water. We calculate the isothermal compressibility and the thermodynamic factor, and show that values scaled to the thermodynamic limit deviate within 2 % of the values obtained from experiments[4].

References:

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