Size-Dependent Surface Free Energy and Tolman-Corrected Droplet Nucleation of TIP4P/2005 Water

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Nucleation is the phenomena by which the first embryos of a stable phase emerge from a metastable phase to initiate a phase transition. The kinetics of nucleation are critical for a wide range of industrial and natural processes – ranging from crystallization to cloud formation. Classical nucleation theory (CNT) is commonly employed to predict nucleation rates which, when using the planar surface free energy, typically differ from experimentally measured rates by many orders of magnitude. Since predicted nucleation rates are extremely sensitive to the surface free energy, this discrepancy is often attributed to a size-dependency of the surface free energy – which can differ significantly between nanoscale droplets and a planar interface. Therefore, accounting for a size-dependent surface free energy in CNT may improve predictions of nucleation kinetics.

For homogeneous droplet nucleation from vapor, Tolman proposed that the surface free energy is dependent on the droplet curvature [1]:

$$\frac{\gamma(R)}{\gamma(\infty)} = 1 - \frac{2\delta}{R}$$

where $\gamma(R)$ is the surface free energy of a droplet of radius R, $\gamma(\infty)$ is the planar surface free energy, and δ is the Tolman length. Even with the advent of molecular dynamics, density functional theory, and faster computers, obtaining accurate values of the Tolman length remains a challenge – the sign of δ for a Lennard Jones fluid is still disputed. As experimental measurements of γ in the nanometer-sized regime are extremely difficult, countless computational studies (see references within ref. [2]) have been performed to calculate the Tolman length of simple fluids.

Although numerous studies on water droplet nucleation indicate large discrepancies between experiment and CNT, the size-dependence of the surface free energy for water droplets has been relatively unexplored until recently. To improve predictions of nucleation kinetics, we examine the size-dependence of the surface free energy for TIP4P/2005 water nanodroplets (radii ranging from 0.7 to 1.6 nm) at 300 K [3]. We employ the mitosis method, in which a water droplet is reversibly separated into two subclusters. We calculate the Tolman length to be -0.56 ± 0.09 Å, in agreement with an experimental estimate of -0.47 Å [4]. Our result indicates that the surface free energy of water droplets we investigated is 5-11 mJ/m^2 greater than the planar surface free energy. We incorporate the computed Tolman length into a modified classical nucleation theory, δ-CNT, which yields improved predictions compared to CNT for the critical size and nucleation rate. We expect our results to be applicable to the hydrophobic drying transition, in which liquid-vapor interfaces have similar curvatures to those we examine.

[1] Tolman, R.C. The Effect of Droplet Size on Surface Tension. *J. Chem. Phys.* **1949**, *17*, 333-337.

[2] Malijevský, A.; Jackson, G. A Perspective on the Interfacial Properties of Nanoscopic Liquid Drops. *J. Phys-Condens. Mat.* **2012**, *24*, 464121.

[3] Joswiak, M.N.; Duff, N.; Doherty, M.F.; Peters, B. Size-Dependent Surface Free Energy and Tolman Corrected Droplet Nucleation of TIP4P/2005 Water. *J. Phys. Chem. Lett.* **2013**, *4*, 4267-4272.

[4] Azouzi, M.E.M.; Ramboz, C.; Lenain, J.F.; Caupin, F. A Coherent Picture of Water at Extremely Negative Pressure. *Nat. Phys.* **2013**, *9*, 38-41.