

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



CHEMICAL ENGINEERING **UC SANTA BARBARA**

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Classical Nucleation Theory

Theory Overview

Classical Nucleation Theory (CNT) partitions the free energy of nucleus formation into favorable bulk and unfavorable surface contributions. For spherical droplets:

 $F_{CNT}(R) = -\frac{4}{3}\pi R^3 \rho \Delta \mu + 4\pi R^2 \gamma$

Major assumptions of CNT include

- Unvarying shape



Mitosis Method

<u>Aim</u>: Calculate the work required to reversibly separate a droplet into two equal sized subclusters. Use δ -CNT framework to calculate the Tolman length.

sub-cluster

Assume bulk density $\longrightarrow R_1 = 2^{-1/3}R_0$ $\Delta F_{mit} = 2F(R_1) - F(R_0)$ $\frac{\Delta F_{mit}}{4\pi R_0^2 \gamma(\infty)} = (2^{1/3} - 1) - (2^{2/3} - 1) \left(\frac{2\delta}{R_0}\right)$

The nucleation rate is particularly sensitive to γ and is often cited as a major source of discrepancy between CNT predicted and experimental rates. While other sources of error exist, in this study we focus on the errors associated with a size independent γ .

Water Droplet Nucleation Rates

Experimental nucleation rates can differ from CNT predictions (assuming the planar value of γ) by many orders of magnitude.

At 300 K, CNT over-predicts the nucleation rate. This may indicate that the surface free energy of droplets is *greater* than the planar surface free energy.

 $\gamma(R)$

 $\overline{\gamma(\infty)}$

T⁻¹/10⁻³K⁻¹ Wölk et al. *J. Chem. Phys.* 2002

The work required to separate the subclusters is calculated from the potential of mean force, $F_L(r)$.

To achieve a reversible separation, we perform bias sampling (hybrid MC/MD) along an order parameter which is a measure of the amount of contact between the subclusters. We simultaneously record the subcluster separation distance, r, in order to calculate the joint (q, r) probability.

Split along r (jump out)

Results

Free Energy Surface 2n = 128 molecules

Potentials of Mean Force

To improve predictions of nucleation kinetics, a size dependent surface free energy should be introduced.

 $F(R) = -\frac{4}{3}\pi R^3 \rho \Delta \mu + 4\pi R^2 \boldsymbol{\gamma}(\boldsymbol{R})$

Tolman Equation

The surface free energy of a liquid droplet in equilibrium with its vapor depends on the droplet curvature and the Tolman length, δ .

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

 δ is on the order of a molecular diameter. The sign of the Tolman length is still disputed even for a LJ fluid.

Estimates of the Tolman length for water:

- $\delta = -0.47$ Å at $T \approx 330$ K : water cavitation in quartz inclusions (Azouzi et al. Nat. Phys. 2013)
- $\delta = -1.4$ Å : lattice model of water (Vaikuntanathan & Giessler, PRL 2014)
- $\delta \approx 0 \text{ Å at } T = 298 \text{ K}$: mW water model (Factorovich et al. JACS 2014)
- $\delta > 0$ Å at 200 < T < 240 K : analysis of nucleation rates (Holten et al. J. Chem. Phys. 2005)

CNT + Tolman Eq = δ -CNT

Incorporating the Tolman equation into CNT leads to first-order expressions for the critical size and barrier height.

Example free energy profiles for TIP4P/2005 water: Supersaturation = 3

 $\delta < 0$

We investigated nanodroplet radii ranging from 0.7 to 1.6 nm.

We construct the plot of

From the slope, we find that

$$\delta = -0.56 \pm 0.09$$
 Å

Exp. Estimate: $\delta = -0.47$ Å (Azouzi et al. *Nat. Phys.* 2013) Our findings suggest that γ is 5-11 mJ/m² higher than the planar surface free energy for droplets with radius 1.6 to 0.7 nm, respectively.

Incorporating our Tolman length into δ -CNT yields good agreement with independently measured nucleation kinetics.

size reflects errors.

To compare with experiments, we assume our calculated δ applies to water. At a supersaturation of 4, we obtain good agreement with experiment.

 $J_{\delta-CNT} / J_{CNT} \approx J_{exp} / J_{CNT} \approx 10^{-8}$

Accounting for a size-dependent surface free energy can lead to a significant change in the barrier height. An accurate calculation of the Tolman length can lead to more accurate predictions of nucleation kinetics.

References

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Summary

CNT rate predictions often differ from experimental measurements by orders of magnitude, which may be a result of assuming a size independent γ .

 δ -CNT accounts for a size dependent surface free energy via the Tolman equation. Reasonable estimates of δ can significantly alter predicted nucleation kinetics.

We employed the mitosis method with a δ -CNT framework and calculated the Tolman length to be -0.56 ± 0.09 Å. This indicates that the surface free energy for nanometer-size water droplets is approximately 5-11 mJ/m² higher than the planar surface free energy.

Our calculated Tolman length leads to good agreement between independently measured nucleation kinetics and δ -CNT predictions.

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