Supplementary Information : Interfacial Thermodynamics of Spherical Nanodroplets: Molecular Understanding of Surface Tension via Hydrogen Bond Network

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ACCURACY OF EQUATION OF SURFACE TENSION

In the main text, we derive the equation of surface tension, $\gamma(R_\mathrm{s}) = \gamma_0 - 2\gamma_0\delta_0/R_\mathrm{s} + k_\mathrm{s}/R_\mathrm{s}^2$. Here let us estimate quantitatively the accuracy of the equation with respect to the DFT results. Figure S3 shows the accuracy and error between the DFT results at $T^* = 0.53$ and predictions obtained by the equation up to three different orders; $\gamma(R_\mathrm{s}) = \gamma_0$, $\gamma(R_\mathrm{s}) = \gamma_0 - 2\gamma_0\delta_0/R_\mathrm{s}$ and $\gamma(R_\mathrm{s}) = \gamma_0 - 2\gamma_0\delta_0/R_\mathrm{s} + k_\mathrm{s}/R_\mathrm{s}^2$. To quantify the error, we use the metric $\mathrm{Err} = (\gamma_\mathrm{DFT} - \gamma_\mathrm{Eq.})/\gamma_\mathrm{DFT}$, where γ_DFT is derived by DFT and γ_Eq is the prediction from the equations. Figure S3 (b) shows that the equation $\gamma(R_\mathrm{s}) = \gamma_0 - 2\gamma_0\delta_0/R_\mathrm{s} + k_s/R_\mathrm{s}^2$ has a remarkable accuracy with $\mathrm{Err} < 0.5$ %, in comparison with the other two lower-order equations. It clearly demonstrates the importance of second order term for the accurate prediction of surface tension.

COMPARISON WITH PREVIOUS STUDIES

We compare results of curvature dependent surface tension with previous studies. For the water nanodroplet, we compare the mitosis method with MD simulations of Lau *et al* at T = 300 K[1], and square gradient theory (SGT) calculations of Wilhelmsen *et al* at T = 290 K[2]. For the LJ nanodroplet, we compare perturbed chain statistical associating fluid theory (PC-SAFT) calculations of Rehner *et al* at T* = 0.7[3], and Monte Carlo (MC) simulations of Block *et al* at T* = 0.68[4]. Figure S4 shows that the results of various methods tend to agree quantitatively. One can expect that the surface tension of nanodroplet is smaller than that of the planar interface regardless of liquid interaction.

PREDICTION OF EXPERIMENTAL NUCLEATION RATES

We combine the surface tension of nanodroplet, $\gamma(r)$, with classical nucleation theory (CNT) to predict experimental nucleation rates of water at $T = 290$ K. From Wilhelmsen *et al.*[2], a nucleation barrier ΔW^* with nonzero Tolman length δ_0 and bending rigidity k_s is given by

$$\Delta W^* = \frac{4\pi\gamma_0 r_\mathrm{CNT}^{*2}}{3}\left(1 - \frac{6\delta_0}{r_\mathrm{CNT}^*}\right) + 4\pi\left(k_s + \delta_0^2\gamma_0\right), \qquad (1)$$

where γ_0 is surface tension of planar interface, and $r^*_{\mathrm{CNT}} = 2\gamma_0/(\rho_l k_{\mathrm{B}} T \ln S)$, where $]rho_l$ is water molecular density. The nucleation rate J is given by

$$J = J_0 \exp\left(-\frac{\Delta W^*}{k_{\mathrm{B}} T}\right). \tag{2}$$

J_0 is the kinetic prefactor and is given by Becker and Döring[5] as

$$J_0 = \frac{1}{\rho_l}\sqrt{\frac{2\gamma_0}{\pi m}}\left(\frac{P_g}{k_{\mathrm{B}} T}\right)^2, \tag{3}$$

where m is the mass of the water molecule, and P_g is the pressure of the gas.

Figure S5 shows that surface tension with curvature dependence $\gamma(r)$ gives prediction curve which are closer to experiments from Brus *et al.*[6]. It indicates that accurate characterization of curved surface tension can be applied to the nucleation theory.

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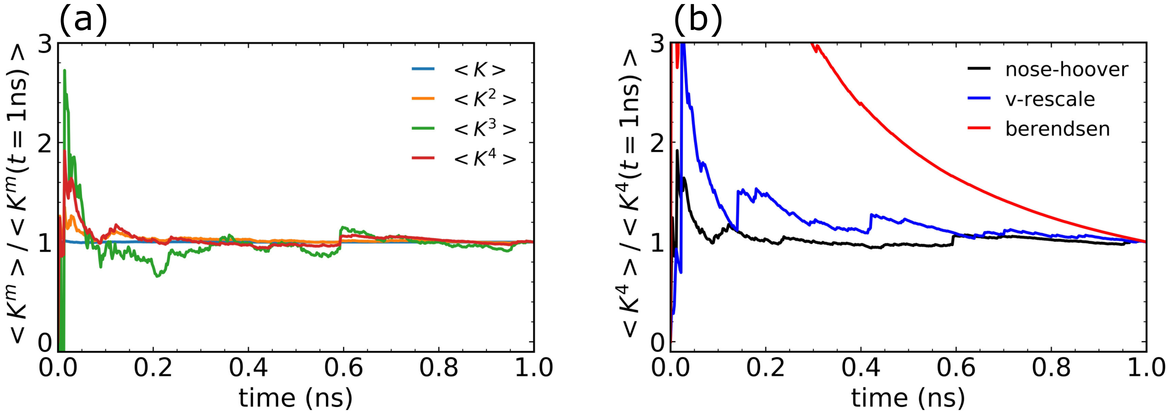

FIG. S1: (a) Fluctuation of average kinetic energy and second, third, and fourth moments of the kinetic energy fluctuations of $R_\mathrm{s} = 0.45$ nm ($N = 32$) nanodroplet. (b) Fluctuation of fourth moments of the kinetic energy fluctuations of $R_\mathrm{s} = 0.45$ nm ($N = 32$) nanodroplet with nose-hoover, v-rescale and berendsen thermostat.

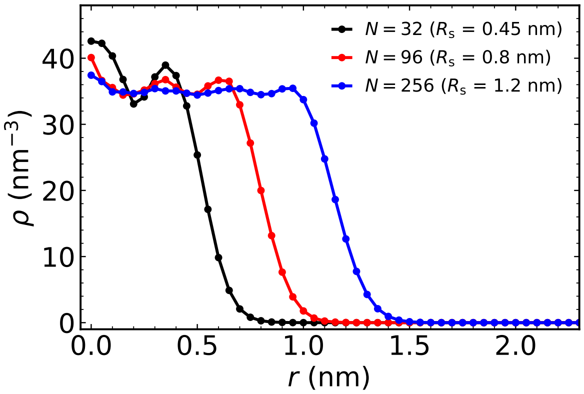

FIG. S2: Radial density profiles of $R_\mathrm{s} = 0.45$ nm ($N = 32$), $R_\mathrm{s} = 0.8$ nm ($N = 96$), and $R_\mathrm{s} = 1.2$ nm ($N = 256$) nanodroplet. Radial bin size is 0.5 $\AA$.

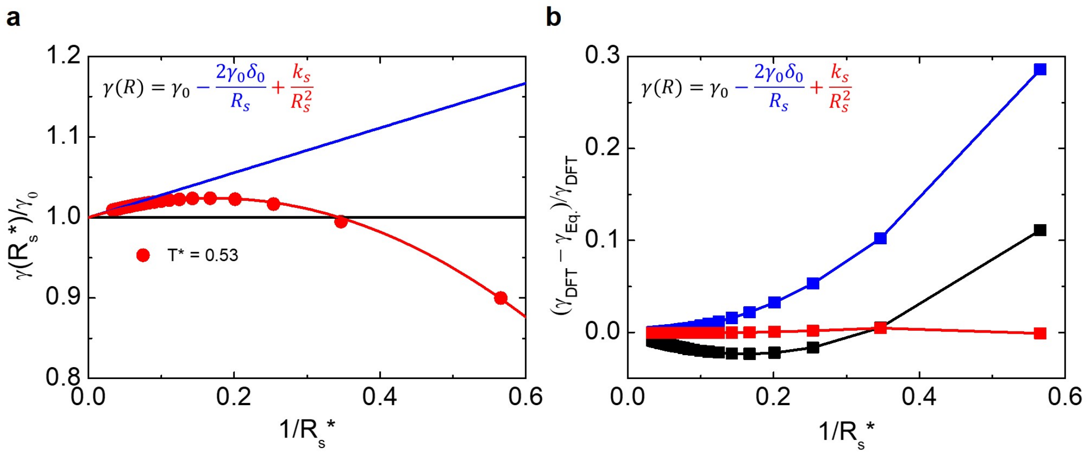

FIG. S3: (a) Comparison and (b) error between the values of surface tension obtained by DFT, γ_{DFT}, at $T^* = 0.53$ (dots) and those predicted by three equations of increasing orders, $\gamma(R_{\mathrm{s}}) = \gamma_0$, $\gamma(R_{\mathrm{s}}) = \gamma_0 - 2\gamma_0\delta_0/R_{\mathrm{s}}$, and $\gamma(R_{\mathrm{s}}) = \gamma_0 - 2\gamma_0\delta_0/R_{\mathrm{s}} + k_{\mathrm{s}}/R_{\mathrm{s}}^2$.

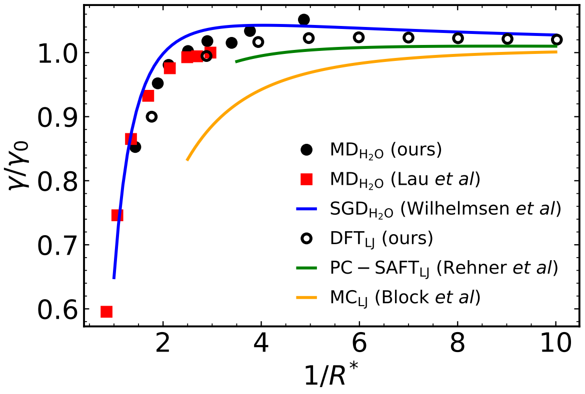

FIG. S4: The surface tension of water and Lennard-Jones nanodroplet from previous studies. For the water nanodroplet, we compare the mitotsis method with MD simulations of Lau *et al*[1] at $T = 300$ K, and SGT calculations of Wilhelmsen *et al*[2] at $T = 290$ K. For the LJ nanodroplet, we compare PC-SAFT calculations of Rehner *et al*[3] at $T^* = 0.7$, and MC simulations of Block *et al*[4] at $T^* = 0.68$.

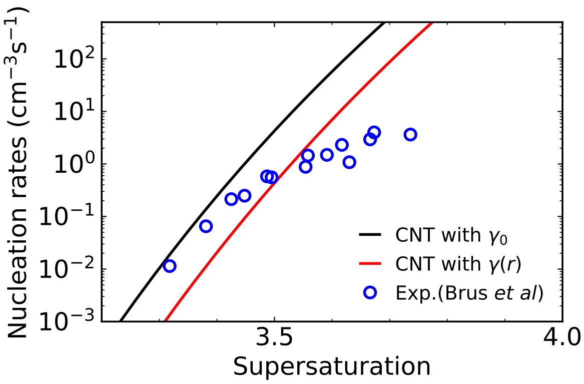

FIG. S5: Prediction capability of classical nucleation theory with γ_0 (black) and $\gamma(r)$ (red) for the experimental nucleation rates from Brus *et al*[6] (blue circle).

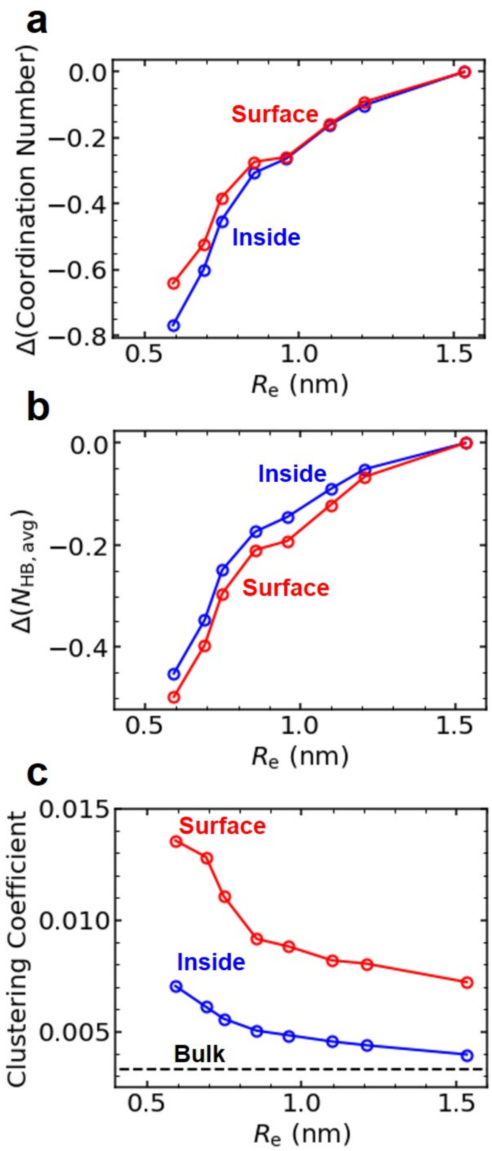

FIG. S6: Hydrogen bond (HB) network analysis of nanodroplets in terms of the equimolar radius R_{e}. Change of (a) the average coordination number and (b) the average number of HB, $\Delta N_{\mathrm{HB,avg}}$ with respect to those of $N = 512$ nanodroplet. (c) Average clustering coefficients of HB networks of nanodroplets in the inside region (blue) and in the surface region (red). Clustering coefficient of bulk water network is drawn for comparison. Here, we use the equimolar radius (R_{e}) to divide the inside and the surface region of nanodroplets, while we use the radius of surface of tension (R_{s}) in the main text, as shown in Fig. 4. Since the results of the main text and the supplement show the same tendency, we can conclude that the properties of HB of the surface and inside of nanodroplets are hardly affected by the definition of the surface.