

Contact Line Pinning Effects Influence the Determination of the Line Tension of Droplets Adsorbed on Substrates

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Lattice density functional theory (LDFT) and Constrained LDFT

In lattice density functional theory (LDFT), the grand potential^{1,2} can be expressed as

$$\Omega = k_B T \sum_i [\rho_i \ln \rho_i + (1 - \rho_i) \ln(1 - \rho_i)] - \frac{\epsilon_{ff}}{2} \sum_i \sum_a \rho_i \rho_{i+a} + \sum_i \rho_i (\varphi_i - \mu) \quad (1)$$

with k_B the Boltzmann constant, T the temperature, ρ_i the local density at site i , ϵ_{ff} and ϵ_{sf} the fluid/fluid and the solid/fluid interaction strength, respectively, and φ_i is the sum of the solid/fluid interaction over the nearest neighbor of site i . At a given chemical potential, the density distribution at equilibrium (i.e., at a stable or metastable state) can be obtained by solving $\partial\Omega/\partial\rho_i = 0$. The constrained LDFT³ is an advanced method with an constraint on the volume of droplets/bubbles, which reads

$$\Omega' = \kappa[N_L^0 - N_L] \quad (2)$$

. Here, κ is a Lagrange multiplier, N_L^0 is the volume of nanobubble/droplet, and $N_L = \sum_i x_i$, with the functional x_i defined as

$$x_i = \begin{cases} 0 & \rho_i < 0.5 \quad i \in \text{vapor} \\ 1 & \rho_i > 0.5 \quad i \in \text{liquid} \end{cases}$$

to distinguish the liquid phase from vapor phase. The constrained grand potential is defined as

$$\Omega^C = \Omega + \Omega' = k_B T \sum_i [\rho_i \ln \rho_i + (1 - \rho_i) \ln(1 - \rho_i)] - \frac{\epsilon_{ff}}{2} \sum_i \sum_a \rho_i \rho_{i+a} + \sum_i \rho_i (\varphi_i - \mu) + \kappa[N_L^0 - \sum_i x_i] \quad (3).$$

By solving the equations $\partial\Omega^C/\partial\rho_i = 0$ and $\partial\Omega^C/\partial\kappa = 0$, the local density ρ_i can be obtained

as

$$\rho_i = \frac{1}{1 + \exp(\epsilon \sum_a \rho_{i+a} - \varphi_i + \mu + \kappa \frac{\partial x_i}{\partial \rho_i})} \quad (4)$$

Finally, the local density ρ_i and the Lagrange multiplier κ can be obtained by using an iterative algorithm.

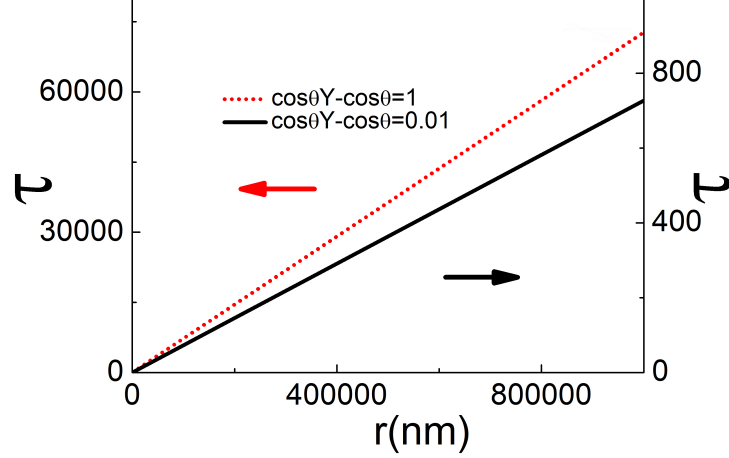
The method to determine the contact angle of droplets

Before determining the contact angle, first we need to identify the vapor-liquid interface for the given droplet, which can be fitted by using circle approximation. With the obtained vapor-liquid interface and the height of the droplet, we can easily determine the contact angle using a simple geometrical relationship.

Eliminating the non-equilibrium effect and lattice effect

The nanodroplets studied in this work are modeled as critical nuclei at the given temperature and chemical potential, with advantages of bias free and free of non-equilibrium effect. The non-equilibrium effect for microscopic droplets cannot be neglected due to the evaporation and condensation. To eliminate the effect, at the given temperature and chemical potential we used the corresponding critical nuclei, for which the chemical equilibrium is achieved in our constrained LDFT calculations,³ as the nanodroplets for our study. For highly curved liquid/vapor interface, the LDFT method would cause a small difference between two different orientations, which is called the lattice effect. In this work we chose a high temperature of $T = 1.2$ to reduce the lattice effect, and our calculations indicate that the effect becomes negligible at such a high temperature.

Using modified Young's equation induces unreasonably large line tensions for large droplets in metastable state



Firstly, we set the surface tension to 72.75 mN/m, and varied $\cos\theta_Y - \cos\theta$ from 0.01 to 1. The modified Young's equation (see Eqn. 1 in text) can be used to determine the line tension with $\tau/r_p = (\cos\theta_Y - \cos\theta)\gamma_{lv}$, following the same approach as in most experimental measurements. According to this equation, we can find that $\tau \propto r_p$ at the given $\cos\theta_Y - \cos\theta$. Therefore, as the base radius of the droplet increases from 1 nm to 1 mm, the line tension increases linearly with droplet size at the given contact angle hysteresis, giving the fitted line tension $10^{-13} \sim 10^{-11}$ J/m (nm) to $10^{-7} \sim 10^{-5}$ J/m (mm). This clearly shows that the incorrect use of Eqn. 1 would lead to unreasonable large line tension. For nano-scale droplets, the measured line tension is normally in the range of $10^{-11} \sim 10^{-10}$ J/m.^{4,5} For the micron size droplets, the obtained line tension ranges from 1.2×10^{-9} J/m to 2.4×10^{-6} J/m.⁶ As for millimeter-sized droplets under the same pinning effect, the magnitude of the line tension is about 10^{-6} J/m.^{7,8} This effect might be relevant to explain the large variation in the experimental results (2-5 orders) and possibly the differences with respect to the theoretical results. Again, we note that in equation $\cos\theta = \cos\theta_Y - \frac{\tau}{r_p\gamma_{lv}} - \frac{\tilde{f}_p}{\gamma_{lv}}$, $\frac{\tau}{r_p\gamma_{lv}}$ can introduce a negligible contribution for sufficiently large droplets, and therefore it could be

ignored in many practical situations. In this case, $\tilde{f}_p/\gamma_{lv}$ would play an important role in determining the contact angle or contact angle hysteresis.

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