Curvature-Dependent Surface Tension of a Growing Droplet

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A ghost interface simulation technique is developed and applied to supersaturated Lennard-Jones liquid-vapor interfaces. It is shown that the surface tension decreases approximately linearly with the supersaturation ratio and that it vanishes at the spinodal. The effect leads to a curvature-dependent surface tension since, it is argued, the local supersaturation of the vapor above a droplet is greater than in the bulk due to slow diffusion in the vapor phase. An analytic approximation is given for the local supersaturation ratio, and an analytic expression for this contribution to Tolman's length is derived. The theory gives a smaller critical radius and reduces the free energy barrier to nucleation compared to classical homogeneous nucleation theory, which have important implications for the kinetics of droplet and bubble formation.

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The growth of liquid droplets from a supersaturated vapor is described by homogeneous nucleation theory, which expresses the free energy of formation as the sum of two terms: the surface tension times the interfacial area, which opposes growth and dominates at small radii, and a term proportional to the droplet volume that arises from the decrease in free energy as gas molecules condense on the liquid drop [1,2]. The theory is very general and also applies to the nucleation of gas bubbles from a superheated liquid, the precipitation of crystals from a supersaturated solution, and the phase separation of a binary mixture, as examples. A major concern of the theory is the height of the free energy barrier to droplet formation, and the critical radius at which this barrier is located. These determine the rate at which droplets form as a function of the degree of supersaturation.

A crucial input is the interfacial tension, and this is usually taken as that of the planar liquid-vapor interface at coexistence. In principle, the surface tension depends upon curvature, but in practice these corrections are difficult to quantify. Tolman's length [2–4] is less than a molecular diameter in size [5–9] and is usually calculated from an approximate expression for the surface tension that is valid only to first order in curvature. There is no consensus on the form of the so-called replacement free energy, which is meant to account for losses of molecular degrees of freedom and edge effects [2]. Similarly controversial is the effect of the loss of macroscopic motion of the droplet, although this appears to be small [10,11].

Here a novel curvature effect is proposed that is distinct from the essentially geometrical contributions to Tolman's length that have previously been explored. It is based upon the effect of supersaturation on surface tension. A simulation technique is developed that gives formally exactly the surface tension of a planar interface and it is shown that the surface tension decreases with increasing supersaturation. This is consistent with earlier density functional work that showed that either the surface tension [12] or the barrier to liquid droplet formation [13] vanished approaching the spinodal line. The idea is particularly significant in view of the Laplace equation, which says that the vapor pressure above a droplet increases in inverse proportion to the droplet radius. A growing droplet is in a nonequilibrium state, and due to slow diffusion in the gas phase, one expects that the state of the vapor proximal to the droplet will be determined by the Laplace equation and will differ from the global supersaturation of the bulk vapor far from the droplet, (i.e., diffusion across the interface is much faster than diffusion from the droplet to the gas reservoir). The facts that the planar surface tension decreases with increasing supersaturation and that the local supersaturation above a droplet increases with increasing curvature lead to a novel curvature dependence in the surface tension. This proposal provides a physical interpretation of the observed decrease in surface tension with decreasing droplet radius [5–8], and it provides the basis for an analytic treatment of the problem.

Three expressions are required: the free energy of the growing droplet, the local supersaturation of the gas phase above the droplet, and the surface tension as a function of supersaturation. The capillarity approximation gives the constrained Helmholtz free energy of a single growing droplet as the sum of surface and bulk terms

$$F(N_l, R|N, V, T) = \gamma A + F(N_l, V_l, T) + F(N_g, V_g, T), \tag{1}$$

where the subscripts refer to the liquid and gas phases, N is number, V is volume, A is area, R is radius, T is temperature, and γ is the surface tension, which is conventionally taken to be the planar coexistence value. The notation indicates that N_l and R are constrained variables for the nonequilibrium thermodynamic potential [14]. The extremum of the constrained free energy is a saddle point (for an infinite system [11]). It is a minimum with respect to variations in radius at fixed number, which mechanical equilibrium is manifest in the

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Laplace equation,

$$p_l = p_g + \frac{2\gamma}{R}, \tag{2}$$

where p is the pressure. The derivative with respect to number vanishes when there is chemical potential equality, $\mu_l = \mu_g$.

Classical nucleation theory proceeds by assuming that the liquid is incompressible, $\mu_l = \mu^\dagger + (p_l - p^\dagger)/\rho_l$, where the superscript denotes the equilibrium state, and that the gas is ideal and forms a reservoir [1,2,8,11],

$$F(R|S,T) = \gamma A - \rho_l V_l k_B T \ln S + [S-1]p^\dagger V_l, \tag{3}$$

where the bulk supersaturation ratio is $S \equiv p_g/p^\dagger$, and k_B is Boltzmann's constant. The approximations involved here have been shown to be relatively accurate [11], with the exception of the assumption that the surface tension has its coexistence value, as shown below.

The growing droplet is in a nonequilibrium state characterized by the given variables. The present theory departs from the classical by recognizing that the gas phase is also in a nonequilibrium state, with the vapor pressure immediately above the surface of the droplet being determined by the fast diffusion across the interface rather than the slower diffusion into the bulk gas reservoir. Hence one has a local supersaturation ratio, $S^{\text{local}} \equiv p_g^{\text{local}}/p^\dagger$, and the stationary condition is $\mu_l = \mu_g^{\text{local}}$, which, with the ideal gas and incompressible liquid assumption, gives

$$p_l = p^\dagger + k_B T \rho_l \ln S^{\text{local}}. \tag{4}$$

Assuming mechanical equilibrium, inserting this into the Laplace equation generalizes the Kelvin equation,

$$S^{\text{local}} - 1 + 2\gamma(S^{\text{local}})/Rp^\dagger - [k_B T \rho_l/p^\dagger]\ln S^{\text{local}} = 0, \tag{5}$$

where an expression for the surface tension as a function of supersaturation will be given shortly. This is an explicit equation for droplet radius as a function of local supersaturation ratio. Replacing γ by $\gamma(R) \equiv \gamma(S^{\text{local}}(R))$ in Eq. (3) gives the thermodynamic potential of a droplet constrained to have radius R taking into account the dependence of the surface tension on the local atmosphere above the droplet. Note that it is S, not S^{local}, that appear in the remaining terms in Eq. (3) as these represent the transfer of gas from the reservoir to the droplet.

In place of the capillarity approximation of Eq. (1), the formally exact expression for the supersaturated surface tension is [11]

$$\gamma A = F(N_l, V_l|N, V, T) - V_l f(\rho_l^\ddagger, T) - V_g f(\rho_g^\ddagger, T). \tag{6}$$

Here appear bulk Helmholtz free energy densities of the metastable states at a given chemical potential $\mu^\ddagger$. Moody and Attard have recently shown that this may be rearranged to give the surface tension in a form suitable for computer simulation [11,15,16],

$$e^{-\gamma A/k_B T} = \frac{\langle e^{-U_{12}/k_B T}\rangle^0_{lg}}{\sqrt{\langle e^{-U_{12}/k_B T}\rangle^0_{ll}\langle e^{-U_{12}/k_B T}\rangle^0_{gg}}}. \tag{7}$$

The averages on the right-hand side are for the interaction potential U_{12} across the planar interface between two uncoupled phases (ghost interface) of the three types indicated by the subscripts. This result is the analog of Widom's expression for the chemical potential.

Briefly, the simulation protocol consisted of a preliminary Gibbs ensemble simulation of coupled liquid and vapor rectangular cells to determine the number of atoms at coexistence in each. These were then fixed for the subsequent three ghost interface simulations, which each involved two uncoupled or partially coupled simulation cells. The averages required above were obtained by multistage sampling (four to eight stages), with a nonlinear partial coupling of the Lennard-Jones interaction potential. Tail corrections for the truncation of the potential were invoked, and the results were insensitive to system size, the largest of which was $6 \times 6 \times 20\sigma$ with up to 600 atoms. After equilibration of each stage, the averages were collected over 4000 cycles. The two simulations for the averages involving the vapor phase were repeated for each value of supersaturation, which was studied by increasing the number of atoms in the vapor phase. (The number of liquid atoms was fixed at the coexistence value, which is justified because the liquid is incompressible, and it was shown that the procedure is insensitive to the choice of atom number.) Full details of the simulations will be given in another place [15].

In Fig. 1 it can be seen that the new simulation procedure yields a surface tension at coexistence in agreement with that obtained by the conventional Kirkwood-Buff theory. A unique feature of the ghost interface equation is that it can be used to obtain the surface tension of a supersaturated interface, which cannot be done with the Kirkwood-Buff theory. Figure 1 shows that the surface tension decreases with increasing supersaturation of the vapor phase, and that it vanishes approaching the spinodal, which is intuitively appealing and consistent with earlier density functional results [12,13]. To a good approximation the decrease is linear and well fitted by

$$\gamma(S) = \gamma^\dagger \frac{S^0 - S}{S^0 - 1}, \tag{8}$$

where $\gamma^\dagger$ is the planar coexistence surface tension and $S^0 > 1$ is the supersaturation ratio at the spinodal ($S = 1$ corresponds to coexistence). The spinodal supersaturation ratios used for the fit, $S^0 = 2.7$, 5.0, and 6.5, agree with those obtained from the Lennard-Jones equation of state [17], $S^0 = 2.2$, 6.3, and 14.8, respectively. The discrepancy is likely due to the limited validity of the equation of state in the spinodal regime.

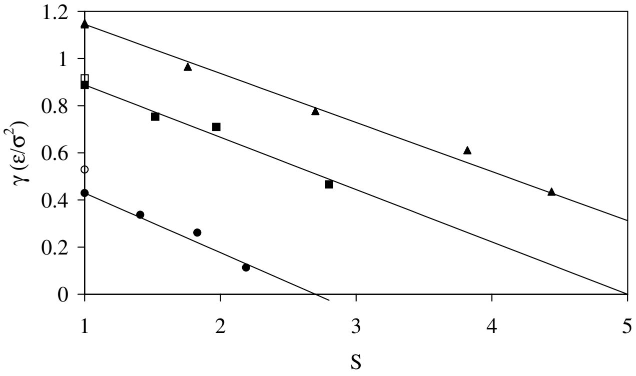

FIG. 1. Monte Carlo ghost interface simulations of the planar surface tension of a Lennard-Jones fluid (ϵ is the well depth and σ is the diameter), as a function of the supersaturation ratio of the vapor phase. The triangles, squares, and circles represent $T = 0.7\epsilon/k_B$, $0.8\epsilon/k_B$, and $1.0\epsilon/k_B$, respectively. The open symbols represent the coexistence surface tension $\gamma^\dagger$ simulated using the standard Kirkwood-Buff approach [9] (obscured for $T = 0.7\epsilon/k_B$), and the straight lines are fits using Eq. (8), with $S^0 = 2.7$, 5, and 6.5, and $\gamma^\dagger = 0.43\epsilon/\sigma^2$, $0.89\epsilon/\sigma^2$, and $1.15\epsilon/\sigma^2$, from highest to lowest temperature, respectively.

Using the fitted Eq. (8), the local supersaturation ratio has been calculated as a function of droplet radius, Eq. (5), and the surface tension of the droplet is displayed in Fig. 2. As can be seen there is a significant decrease in the surface tension for small droplets due to the high local supersaturation, and one can anticipate that the barrier to nucleation will be greatly reduced by the effect.

Conventional molecular dynamics simulations for a droplet contain inseparably the geometric and thermodynamic curvature effects. It can be seen in Fig. 2 that conventional results [7] are nevertheless in relatively good agreement with the present thermodynamic results for large droplet radii. These conventional simulations rely upon Tolman's equation to estimate the surface tension, and so they are not expected to be valid beyond leading order in $1/R$. Likewise, application of the present results obtained for planar supersaturated interfaces to very small droplets may be questioned, although one might expect that the effects of supersaturation ought simply to be added to the geometric effects of curvature since the effects of supersaturation on the surface tension do not disappear just because the interface is curved. The geometric effects have been previously calculated by cavity simulations [11] and would act to decrease further the surface tension at these temperatures.

Tolman's equation for the curvature correction, $\gamma(R) = \gamma^\dagger[1 - 2\delta/R]$, fitted to the data at large R in Fig. 2 yields a value of Tolman's length of $\delta = 0.38\sigma$, with higher order terms clearly entering at small R. Asymptotic analysis of Eqs. (5) and (8) yields an explicit expression for Tolman's length,

$$\delta = \frac{\gamma^\dagger}{(k_B T \rho_l - p^\dagger)(S^0 - 1)}. \tag{9}$$

This gives a value of $\delta = 0.35\sigma$ for the parameters of $T = 0.8\epsilon/k_B$. This thermodynamic contribution to Tolman's length can be compared to the geometric contribution obtained for cavities, 0.15 [11] and to the total for droplets, 0.4–0.6 [7]. This analytic expression for Tolman's length should be generally applicable.

Figure 3 compares the nucleation free energy of the droplet given by the classical theory using $\gamma^\dagger$ with two versions of the present nonclassical theory that take into account the effect of supersaturation: one using $\gamma(S^{\mathrm{local}}(R))$, and one using the fixed value, $\gamma(S)$. These two nonclassical theories correspond to the two extremes of the physical situation, namely, either the gas above the droplet is in equilibrium with the droplet, or else it is in equilibrium with the gas reservoir, with the former

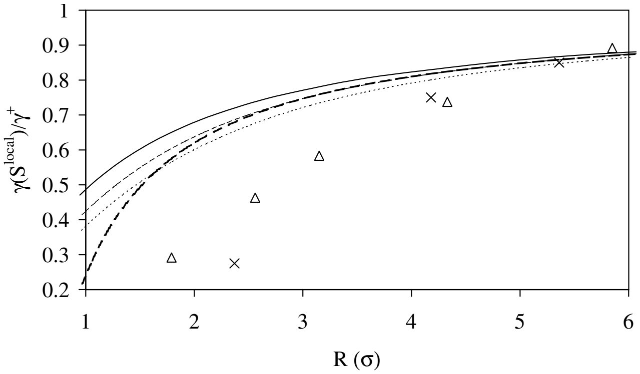

FIG. 2. Relative surface tension as a function of droplet radius, Eqs. (5) and (8). The dotted, dashed, and solid lines are for $T = 0.7\epsilon/k_B$, $0.8\epsilon/k_B$, and $1.0\epsilon/k_B$, respectively. The bold dashed curve is the fitted Tolman's equation, $\gamma(R)/\gamma^\dagger = 1 - 2\delta/R$, with $\delta = 0.38\sigma$. The triangles ($T = 0.71$) and crosses ($T = 0.80$) are results from simulations of a droplet [7], which uses the thermodynamic route and Tolman's equation.

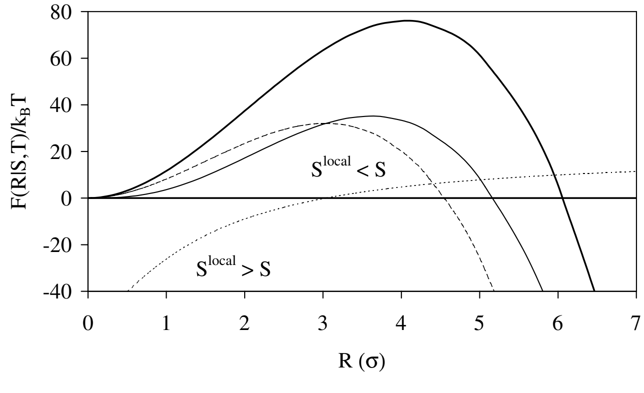

FIG. 3. Constrained free energy of a growing droplet for $T = 0.8\epsilon/k_B$ and $S = 2$. The solid curve uses $\gamma(S^{\mathrm{local}}(R))$, the dashed curve uses fixed $\gamma(S)$, and the bold curve is the classical theory using the planar coexistence surface tension, $\gamma^\dagger$. The dotted curve is $20[S - S^{\mathrm{local}}]$.

probably being the closest to reality. The two theories that invoke a supersaturated surface tension greatly lower the free energy barrier to droplet formation compared to the classical theory that uses the fixed coexistence value.

In the case of Fig. 3 the change in barrier height is about $40k_BT$, which is quite significant. [There is a small difference in the height of the maximum between the two nonclassical theories, with the one for fixed $\gamma(S)$ being the lower and occurring at a smaller radius.] Most kinetic theories invoke a rate constant that is proportional to a Boltzmann factor of the barrier height, in which case the present theories predict that the rate of droplet formation would be a factor of 10^{17} faster than predicted by the classical prediction. Such large adjustments to nucleation rate constants are not unknown in comparing nucleation theory and experiment and in modifying classical nucleation theory [2,13].

Figure 3 also shows the difference between the local and the global supersaturation ratios. When the local supersaturation ratio is larger than the bulk (negative regions of the dotted curve at small radii, and $\gamma(S^{\text{local}}) < \gamma(S)$), vapor diffuses from the droplet to the bulk due to the chemical potential gradient and the droplet shrinks. Conversely, for large droplet radii the local supersaturation is less than in the bulk [and $\gamma(S^{\text{local}}) > \gamma(S)$], and vapor diffuses toward the droplet causing it to grow. When $S^{\text{local}} = S$ an unstable equilibrium exists. In the case of Fig. 3 this occurs at $R = 3\sigma$, which is in agreement with the critical radius of the present theory using fixed $\gamma(S)$, and which may be compared to the critical radius of $R = 3.5\sigma$ for the present theory using $\gamma(S^{\text{local}}(R))$. The reasonable agreement between these supports the physical validity of the present theory.

In summary, a new simulation method has been developed and applied to a supersaturated liquid-vapor interface. It was shown that the surface tension varied approximately linearly with the supersaturation ratio and vanished approaching the vapor spinodal. An expression for the local supersaturation of the vapor above a droplet of finite radius was given, which was used to predict a novel curvature dependence in the surface tension and to obtain an analytic expression for Tolman's length. It was found that the reduction of the surface tension by vapor supersaturation substantially decreased the height of the energy barrier to droplet formation, and it was concluded that droplets form at a much greater rate than is predicted by classical homogeneous nucleation theory. The theory presented here should be applicable as well to bubble formation and to more general nucleation phenomena.

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