Size-Dependent Surface Tension and Tolman's Length of Droplets

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A model for the size-dependent surface tension $\gamma_{lv}(D)$ of liquid droplets, free of any adjustable parameter, is presented in terms of the size-dependent surface energy $\gamma_{sv}(D)$. It is found that $\gamma_{lv}(D)$ drops monotonically with the size of the droplet in the nanometer region. Modeling predictions agree with computer simulations for sodium, aluminum, and water droplets. Meanwhile, the Tolman's equation is found to be valid for small particles, and the Tolman's length is always positive and becomes longer when the droplet size is decreased.

1. Introduction

As a fundamental property of liquid droplets, the liquid–vapor interfacial energy or surface tension γ_{lv} (subscripts l and v denote the liquid and gas, respectively) describes the reversible work to form a new liquid surface per unit area.[1] A method of dividing surface pioneered by Gibbs[1] defines that γ_{lv} with a given bulk value γ_{lv0} depends on the pressure P, temperature T, and composition of the two coexisting bulk phases. When the liquid–vapor interface is curved, γ_{lv} is a function of diameter D of the droplets, $\gamma_{lv}(D)$. Guggenheim suggested that $\gamma_{lv}(D)$ would change when D falls below 100 nm on the basis of statistical mechanical considerations.[2]

A half-century ago, Tolman extended the idea of Gibbs and showed that if the radius R_s of the surface of tension of the droplet did not coincide with the equimolar radius R_e, the surface tension must vary with droplet size.[3] Moreover, Tolman proposed that the two surfaces must, in general, be distinct from each other. Tolman estimated the Tolman's length δ, or the separation between the equimolar surface and the surface of tension, $\delta = R_e - R_s$.[4] He assumed that δ could be taken as a constant in the nanometer region and derived the equation[3]

$$\gamma_{lv}(D)/\gamma_{lv0} = 1/(1 + 4\delta/D) \qquad (1)$$

Kirkwood and Buff developed a general theory based on statistical mechanics for the interfacial phenomena and confirmed the validity of Tolman's approach.[5] For a sufficiently large droplet, eq 1 may be expanded into power series. Neglecting all the terms above the first order, the asymptotic form was obtained, which is the same as the equation derived by Buff,[6]

$$\gamma_{lv}(D)/\gamma_{lv0} \approx 1 - 4\delta/D + ... \qquad (2)$$

Values for $\gamma_{lv}(D)/\gamma_{lv0}$ determined by these two equations are close to each other at $D/\delta \geq 20$.

Tolman predicted that $\gamma_{lv}(D)$ should decrease with decreasing particle size,[3] indicating the positive δ. The

asymptotic Tolman's length in the limit of $D \rightarrow \infty$, δ_∞, is independent of the choice of the dividing surface,[7] and $\delta_\infty = h$ with h being the atomic diameter.[3] However, δ was also predicted to be negative by a rigorous thermodynamic derivation,[8] which would lead to an increase of $\gamma_{lv}(D)$ when the solid size is decreased. It is generally assumed that $\delta > 0$ for spherical droplets and $\delta < 0$ for bubbles in a liquid.[9-11] This consideration can also be simply translated as that the δ is always positive while D may be positive for the droplets but negative for the bubbles. In addition to the uncertainty in the sign of δ, the validity of eq 1 is considered to be questionable for very small particles.[12]

In this contribution, we extend the recent model for the size-dependent surface energy $\gamma_{sv}(D)$ to determine the $\gamma_{lv}(D)$ function of spherical droplets because the structure and energy differences between solid and liquid are very small in comparison with those between solid and gas or between liquid and gas. Agreement between the model predictions for $\gamma_{lv}(D)$ and the results of computer simulations for sodium, aluminum, and water droplets has been reached.

2. Model

For a planar interface at the melting point, $\gamma_{sv0}/\gamma_{lv0} = k$ for metallic elements with $k = 1.18 \pm 0.03$.[14] Note that in the derivation of $\gamma_{sv}(D)$, it is assumed that the nanocrystal has the same structure as that of the corresponding bulk.[13] Because the structure and energy differences between solid and liquid are small in comparison with those between solid and gas or between liquid and gas, the above expression for the bulk may be extended to nanometer size with the same form,

$$\gamma_{lv}(D)/\gamma_{sv}(D) = k \qquad (3)$$

$\gamma_{sv}(D)/\gamma_{sv0}$ can be determined by[13]

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$$\frac{\gamma_{sv}(D)}{\gamma_{sv0}} = \left[1 - \frac{1}{2D/h - 1}\right]\exp\left(-\frac{2S_b}{3R}\frac{1}{2D/h - 1}\right) \quad (4)$$

where $S_b = E_0/T_b$ is the solid−vapor transition entropy of crystals with E_0 and T_b being the bulk solid−vapor transition enthalpy and temperature, respectively. R is the ideal gas constant. Combining eqs 3 and 4 as well as the expression for the bulk, there is

$$\frac{\gamma_{lv}(D)}{\gamma_{lv0}} = \left[1 - \frac{1}{2D/h - 1}\right]\exp\left(-\frac{2S_b}{3R}\frac{1}{2D/h - 1}\right) \quad (5)$$

3. Results and Discussion

In terms of eq 5, comparisons of $\gamma_{lv}(D)/\gamma_{lv0}$ for Na and Al droplets between the model predictions and the computer simulation results[16] are shown in Figures 1 and 2, and the parameters involved in eq 5 are listed in Table 1. It is evident that the model predictions are in agreement with the computer simulation results for Na and Al. This agreement in return confirms the validity of the assumption in eq 3. As a comparison, the predictions of eq 1 with $\delta = \delta_\infty = h$ are also shown in these two figures.

Although eq 5 is deduced in light of the relation between γ_{sv0} and the broken bond number of surface atoms for metals,[13] this relation should be also applicable to other types of materials. Figure 3 shows the $\gamma_{lv}(D)$ function of water droplets in terms of eq 5. The model prediction also corresponds well to the computer simulation results.[19] Note that the definition for h in this case is defined as the O−H bond length.[17] At the same time, the prediction of eq 1 with $\delta = h$ is also shown in Figure 3.

As shown in Figures 1−3, $\gamma_{lv}(D)$ decreases with size, following the trend of $\gamma_{sv}(D)$.[13] This is because $\gamma_{lv}(D)$ as an energetic difference between the surface molecules and the interior molecules of the droplets decreases as the energetic state of the interior molecules increases more quickly than that of the surface molecules. Note that the prediction based on eq 5 provides the same or better accuracy than eq 1.

Although δ is assumed to be constant as required by the derivation of eqs 1 and 2, several applications of statistical thermodynamics have indicated that δ depends strongly on D.[11,20,21] Because the results of these treatments are based on rather complex numerical calculations, it would be helpful to express $\delta(D)$ analytically. Fortunately, eq 5 can be used to satisfy this requirement. Substituting eq 5 into eq 1 rather than eq 2 because the latter is an approximation of eq 1 and leads to error when $D/\delta \leq 10$,

$$\delta(D) = \frac{D}{4}\left[\exp\left(\frac{2S_b}{3R}\frac{1}{2D/h - 1}\right)\Big/\left(1 - \frac{1}{2D/h - 1}\right) - 1\right] \quad (6)$$

$\delta(D)/h$ determined by eq 6 for Na, Al, and water droplets is shown as a function of D/h in Figure 4. It is observed that the Tolman's length is positive for these droplets and decreases when the size is increased, being consistent with statistical thermodynamics,[11,20,21] computer simulations,[22,23]
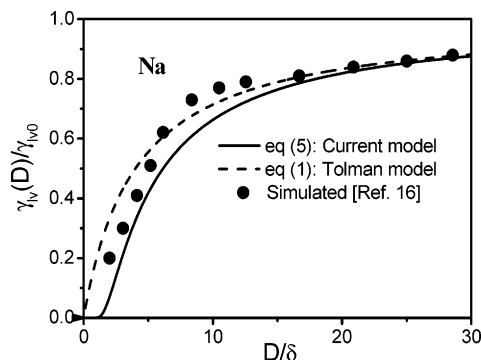

Figure 1. Comparison of the D/δ ($\delta = h$) dependence of $\gamma_{lv}(D)/\gamma_{lv0}$ described by various models and computational results for Na.[16]
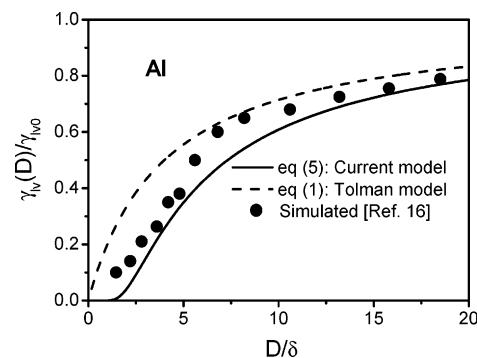

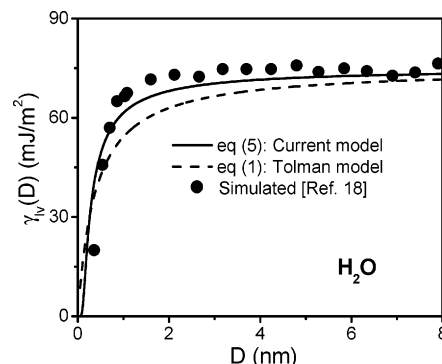**Figure 2.** D/δ ($\delta = h$) dependence of $\gamma_{lv}(D)/\gamma_{lv0}$ for Al.[16]

Figure 3. D dependence of $\gamma_{lv}(D)$ with $\delta = h$ for water.[18]

Table 1. Several Necessary Parameters Used in the Equations

	h (nm)	γ_{lv0} (mJ/m²)	E_0 (kJ/mol)	T_b (K)	$S_b = E_0/T_b$ [J/(mol·K)]
Na	0.372[15]		97.7[15]	1156[15]	84.5
Al	0.286[15]		293[15]	2792[15]	105
H₂O	0.096[17]	75[18]	13.6[19]	373[19]	36.5

and other approaches[24] for Lennard-Jones fluids. However, there is an obvious difference between our model predictions and others; namely, $\delta(D)$ remains positive among the whole size range in this model while it will decrease to a negative limiting value for the planar interface in the others.

The value of δ in eq 6 is on the verge of infinite when D reaches its lower limit h.[13] When D is sufficiently large, considering the mathematical relation of $\exp(-x) \approx 1 -$

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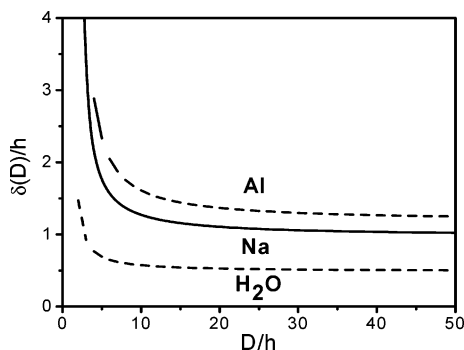(24) Bartell, L. S. *J. Phys. Chem. B* **2001**, *105*, 11615.

Figure 4. $\delta(D)/h$ as a function of D/h in terms of eq 6 for Na, Al, and water droplets. Parameters are given in Table 1.

x when x is small enough (e.g., $x < 0.1$), the minimal value δ_{min} in terms of eq 6 can be written as $\delta_{min} = \delta_{\infty} = hS_b/(12R)$ or

$$hS_b/(12R) < \delta \qquad (7)$$

$S_b \approx 12R$ for metallic elements as shown in Table 1 leads to $\delta_{\infty} \approx h$ for Na and Al as indicated by Tolman[3] while $\delta_{\infty}' \approx 3h/8$ for water due to $S_b \approx 9R/2$. This is the reason that the differences between the model prediction in terms of eq 1 and that in terms of eq 5 appear at D/h

≤ 10 for Na and Al while they appear at $D/h \geq 20$ for water. Thus, the size dependence of $\delta(D)$ strongly depends on the value of S_b. Equation 7 also implies that the decrease of the bond strength leads to the diffusion of the liquid−vapor interface. The corresponding physical picture is that the energetic difference of the molecule on the liquid surface and that in the vapor decreases as the bond strength weakens. Thus, the liquid−vapor interface transition zone becomes narrow.

4. Conclusions

In summary, a simple model for the $\gamma_{lv}(D)$ function has been developed on the basis of the model for the size-dependent surface energy $\gamma_{sv}(D)$. Reasonable agreements between the model predictions and those of computer simulations for Na, Al, and H_2O droplets have been found. Moreover, the Tolman's equation is applicable for very small particles where the Tolman's lengths δ for these liquid droplets are found to be always positive and increase when the solid size is decreased.