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Thermodynamics of a liquid microcluster

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A theory of surface tension is formulated for liquid microclusters which are so small that the homogeneous properties of the bulk liquid are not attained even at the center. The choice of the equimolecular dividing surface is made possible by employing a reference bulk liquid which possesses a different chemical potential from that of the real system. Cluster-size dependence of the surface tension is formulated in such a manner that the results of computer simulations for microclusters and for the bulk liquid may be employed, and it is found that for the size range relevant in nucleation the value of surface tension is appreciably greater than the bulk surface tension. The formalism is extended to noncritical microclusters, and the Gibbs-Thomson equation is derived in the present formalism to provide the size of a critical nucleus under a given supersaturation.

I. INTRODUCTION

Liquid microclusters relevant in nucleation from vapor are usually extremely small in size so that the homogeneous properties of the bulk liquid are probably not attained even at the center. Gibbs' theory of surface tension[1] is, in principle, applicable to those microclusters as well, but the location of the dividing surface at the surface of tension limits its practical applicability because of the difficulty involved in calculating the position of the surface of tension.[2-6] Employment of the equimolecular dividing surface, on the other hand, involves the curvature term in the fundamental equation,[1,6-11] which causes much inconvenience in practical applications.

An alternative formalism for liquid microclusters was provided by Hill[12] as an application of the method of small-system thermodynamics.[13] Hill's formalism does not invoke the concept of either the dividing surface or the surface tension, and is more general than the Gibbs method in this respect. However, in view of practical applications, Gibbs' method is superior to Hill's in that the former intends to represent the thermodynamic quantities of microclusters in terms of the measurable quantities of the macroscopic system. It is desirable, therefore, to develop a convenient alternative formalism of surface tension for liquid microclusters; this is intended in the present paper. In the following development we follow closely the idea behind the theory of surface tension by Gibbs.[1]

The value of surface tension for microclusters will be appreciably different from that obtainable from surface-tension measurements such as the capillary-rise experiment. Thus, in order for the thermodynamics of a microcluster in Gibbs' method to be useful in practical applications, formulation of the theory of size dependence of the surface tension is inevitable. This problem was already investigated by Tolman,[14] but his theory is not applicable to such extremely small clusters as those investigated here. In addition, in Tolman's theory the cluster-size dependence is expressed in terms of the distance Δ between the surface of tension and the equimolecular dividing surface which is difficult to calculate.[2-6] Therefore, a new theory for the size dependence of surface tension is formulated in such a manner that the results of computer simulations for microclusters[15,16] and for the bulk liquid[17,18] may be employed instead of the knowledge of the value of Δ. To complete the present formalism of surface tension, noncritical microclusters are studied and the Gibbs-Thomson equation is derived to relate the size of the critical nucleus to the pressure of a supersaturated vapor under a given temperature. Problems relating to the translation and rotation of a microcluster in vapor[19-21] are neglected here, which will be the subject of a future investigation.

II. THEORY FOR A CRITICAL NUCLEUS

Consider a liquid microcluster in a supersaturated vapor, which consists of a pure substance and is in thermodynamic equilibrium. The microcluster is assumed to be spherical. Suppose there is a mathematical boundary of the spherical shape within the vapor whose center coincides with the center of the microcluster, as shown in Fig. 1. The radius R_g of the boundary is taken to be so large that it passes through the homogeneous vapor phase. Imagine another mathematical boundary which, together with the spherical boundary, encloses a conical domain having a solid angle ω, and consider its thermodynamic properties.

Since the system under consideration is small, the interaction between the molecules inside and

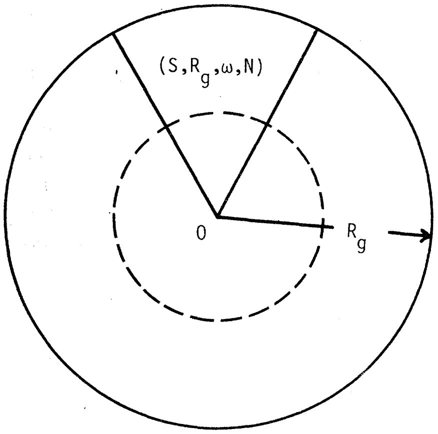

FIG. 1. Liquid microcluster-supersaturated vapor system.

outside the boundary must be taken into account. Thermodynamic properties are homogeneous along the direction perpendicular to the boundary, so that internal energy and entropy may be considered as shared equally between the molecules on both sides of the boundary at R_g; hence the values of those "extensive" variables for the entire sphere are well defined. We define the values of those extensive variables for the system of a conical shape as $\omega/4\pi$ times those for the entire sphere. The number of molecules within the domain fluctuates, but only the average value is treated in thermodynamics. The thermodynamic state of the conical domain is determined by S, R_g, ω, and N, in which N denotes the number of molecules. The fundamental equation in differential form is given by

$$dE = T\,dS - P_g \omega R_g^2\, dR_g + \sigma\, d\omega + \mu\, dN, \tag{1}$$

where T denotes the temperature, P_g the pressure of the gas, μ the chemical potential, and σ is defined by

$$\sigma = \left(\frac{\partial E}{\partial \omega}\right)_{S,R_g,N}. \tag{2}$$

Upon integration of Eq. (1) by keeping R_g and the nature of the system invariant, one obtains

$$E = TS + \sigma\omega + \mu N. \tag{3}$$

Note that all the thermodynamic properties are supposed to be kept uniform along the direction perpendicular to the boundary when we consider a differential change in the state of the system. For example, $(\partial E/\partial S)_{R_g,\omega,N}$ actually means the value $(\partial E_{4\pi}/\partial S_{4\pi})_{R_g,N_{4\pi}}$, where the subscript 4π denotes the values for the entire sphere. This enables us to identify the quantity $(\partial E/\partial S)_{R_g,\omega,N}$ with temperature T of the vapor. The same is true for both P_g and μ. The reason for considering a conical domain instead of the entire sphere as a system is to obtain Eq. (3) from Eq. (1), i.e., to make E a homogeneous function of the first degree in terms of S, ω, and N under a fixed value of R_g.

σ represents the complex effect due to the existence of the interface between the microcluster and the vapor. However, the value of σ cannot be measured in practice; hence we must represent the term $\sigma\, d\omega$ in terms of experimentally measurable quantities. Consider a reference bulk liquid having temperature T and pressure P_l, within which we define a hypothetical microcluster as a spherical domain enclosed by a mathematical boundary. The pressure P_l will be determined later. Introduce a hypothetical system by replacing the real microcluster by the hypothetical one and by filling the space outside the hypothetical microcluster with the homogeneous vapor of T and P_g, as shown schematically in Fig. 2. Density profiles for the real and the hypothetical systems are schematically shown in Fig. 3. Note that both the hypothetical microcluster and the surrounding vapor possess the properties of the bulk phases and that the interface does not exist in the hypothetical system. The radius R of the hypothetical microcluster is to be determined in accordance with a chosen dividing surface condition, which will be specified later. Once the reference bulk liquid and the dividing surface condition are specified, the hypothetical system is defined unambiguously. The following equations hold for the hypothetical microcluster and the hypothetical vapor within the conical domain of Fig. 1:

$$dE_l = T\,dS_l - P_l\, dV_l + \mu_l^0\, dN_l, \tag{4}$$

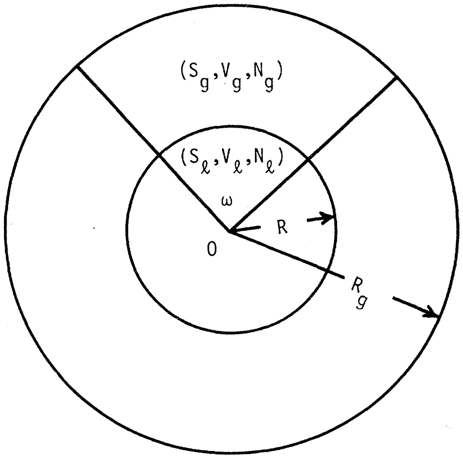

FIG. 2. Hypothetical system with a dividing surface at R.

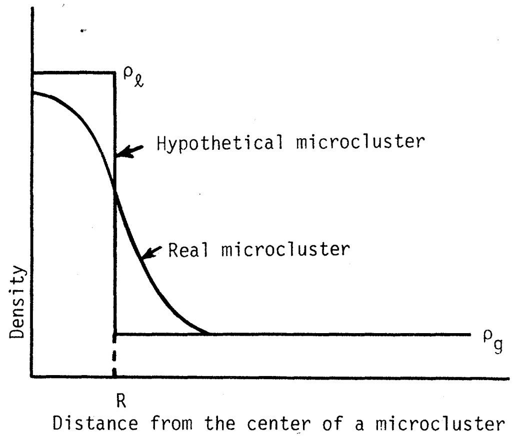

FIG. 3. Density distribution in the real and the hypothetical microcluster. ρ_l and ρ_g denote the densities of the reference bulk liquid and the supersaturated vapor, respectively.

$$dE_g = T\,dS_g - P_g\,dV_g + \mu\,dN_g, \tag{5}$$

where the subscripts l and g refer to the hypothetical microcluster and the hypothetical vapor, respectively. A superscript is used in μ_l^0 to distinguish it from the value of the real microcluster which appears in Sec. IV. The following equations hold from the geometry:

$$V_l = \tfrac{1}{3}\,\omega R^3\ , \tag{6}$$

$$V_g = \tfrac{1}{3}\,\omega(R_g^3 - R^3)\ , \tag{7}$$

$$A = \omega R^2, \tag{8}$$

where A denotes the area of the dividing surface.

We introduce the term $\gamma\,dA$, in which γ denotes the surface tension, as the difference between $\sigma\,d\omega$ and the corresponding work terms of the hypothetical system, i.e.,

$$\gamma\,dA = \sigma\,d\omega + P_l\,dV_l + P_g\,dV_g', \tag{9}$$

where dV_g' denotes the volume change of the hypothetical vapor with R_g kept constant. Equation (9) merely replaces the unknown quantity σ by another unknown quantity γ at this stage, but γ will be related later to the macroscopically measurable value of surface tension so that σ may be expressed in terms of known quantities. Eliminating the term $\sigma\,d\omega$ from Eqs. (1) and (9), we obtain

$$dE = T\,dS + \gamma\,dA - P_l\,dV_l - P_g\,dV_g + \mu\,dN. \tag{10}$$

Differentials dA, dV_l, dV_g', and dV_g in Eqs. (9) and (10) represent the changes in the state of the hypothetical system corresponding to changes dS, $d\omega$, dR_g, and dN of the real system. The value of R changes, under a given dividing surface condition, in accordance with a change in the state of the real system; hence dA represents the change in area due to changes in both ω and R. In particular, Eqs. (9) and (10) remain meaningful even for the cases where $d\omega = 0$, which will be utilized later in the derivation of the size dependence of surface tension. Note that V_l and A are not independent, and the number of independent variables in Eq. (10) is four as in Eq. (1). Since the system is in equilibrium, $dE = 0$ under S, N and the boundary of the conical domain kept invariant. It follows therefore that

$$P_l - P_g = 2\gamma/R. \tag{11}$$

Integrating Eq. (10) by keeping R_g and the nature of the system invariant, we obtain

$$E = TS + \gamma A - P_l V_l - P_g V_g + \mu N. \tag{12}$$

This result is also obtainable by integrating Eq. (9) and employing Eq. (3).

Eliminating γ from Eqs. (11) and (12), one obtains

$$R^3 = \frac{6(E - TS - \mu N + \frac{1}{3} P_g \omega R_g^3)}{\omega(P_l - P_g)}\ . \tag{13}$$

This equation determines the relation between R and P_l under a given state of the real system. When the reference bulk liquid is specified, R is determined by Eq. (13), which in turn means that the dividing surface condition is specified. Considering that $\gamma\,dA$ is introduced in Eq. (9) as the difference in the reversible work between the systems with and without the interface, a natural choice of the reference bulk liquid would be the one which possesses the same μ and T as those of the real system. R is the radius of the surface of tension in this case, as will be discussed later, which causes much inconvenience in practical applications due to the difficulty involved in calculating its position. Hence, we take the view that Eq. (13) determines the reference bulk liquid under a chosen dividing surface condition. As long as we take the view that the concept of surface tension is a method to represent the unmeasurable work term $\sigma\,d\omega$ in Eq. (1) in terms of the experimentally measurable quantities, the choice of the reference bulk liquid is completely arbitrary. Let us take the equimolecular dividing surface which is defined by the following condition:

$$N_l + N_g = N. \tag{14}$$

Equation (14) is practically equivalent to

$$\tfrac{4}{3}\,\pi R^3 = n v_l, \tag{15}$$

where n denotes the number of molecules in a cluster and v_l the molecular volume of the reference bulk liquid. Since bulk liquid is nearly incompressible, Eq. (15) determines R in practice without an explicit knowledge of P_l.

Introducing the excess internal energy E^{ex} and the excess entropy S^{ex} as

$$E^{ex}=E-E_l-E_g, \quad S^{ex}=S-S_l-S_g, \tag{16}$$

γA may be expressed as follows:

$$\gamma A=E^{ex}-TS^{ex}-(\mu-\mu_l^0)N_l. \tag{17}$$

μ_l^0 in Eq. (17) is given by

$$\mu_l^0 \simeq \mu_e+v_l(P_l-P_e), \tag{18}$$

where P_e denotes the equilibrium vapor pressure and μ_e the chemical potential in equilibrium. In Eq. (17), γA may be interpreted as the reversible work associated with a thought process that the real system with the interface is formed from the hypothetical system without the interface. Note that γA is not the excess Helmholtz free energy. It follows from Eqs. (4), (5), and (10) that

$$dE^{ex}=T\,dS^{ex}+\gamma\,dA+(\mu-\mu_l^0)\,dN_l. \tag{19}$$

This is the fundamental equation for the "surface system." Differentiating Eq. (17) and combining the result with Eq. (19), we obtain the Gibbs-Duhem relation as follows:

$$A\,d\gamma=-S^{ex}dT-N_l\,d(\mu-\mu_l^0). \tag{20}$$

This equation plays the principal role in a development of the cluster-size dependence of the surface tension. The reversible work required to form a critical nucleus from a large amount of its vapor is given by the difference in the internal energy under entropy, number of molecules, and total volume kept invariant. The internal energy at the final state is given by Eq. (12) with $\omega=4\pi$. The internal energy E_o at the initial state of a uniform vapor is given by the following when the total volume V is sufficiently large as compared with[6] V_l:

$$E_o=TS-P_gV+\mu N. \tag{21}$$

Hence, the reversible work W is given by

$$W=E-E_o=\gamma A-(P_l-P_g)V_l. \tag{22}$$

Substituting Eq. (11) into Eq. (22), we obtain

$$W=\tfrac{4}{3}\pi R^2\gamma\ . \tag{23}$$

This result is formally identical with that of Gibbs[1]; however the meanings of R and γ are of course different.

III. CLUSTER-SIZE DEPENDENCE OF THE SURFACE TENSION

The Gibbs-Duhem relation for the surface system under a constant temperature is given by

$$A\,d\gamma=-n\,d(\mu-\mu_l^0), \tag{24}$$

where ω is taken as 4π, and N_l in Eq. (20) is replaced by n. The Gibbs-Duhem relations for the bulk phases are

$$d\mu=v_g\,dP_g, \quad d\mu_l^0=v_l\,dP_l, \tag{25}$$

in which v_g denotes the molecular volume in a supersaturated vapor. It follows from Eqs. (11), (24), and (25) that

$$d\gamma=R(1-v_g/v_l)\,dP_g-(2\gamma/R)\,dR. \tag{26}$$

When P_g is altered under a constant T, the size of the critical nucleus changes accordingly and γ in turn changes due to the size dependence of the surface tension. Equation (26) provides the relation among those quantities. To proceed further we need a relationship between dP_g and dR. Assuming that the vapor phase is approximated to be ideal, we have

$$\mu=\mu_e+kT\ln(P_g/P_e). \tag{27}$$

It follows from Eqs. (11), (12), and (27) that

$$\tfrac{1}{3}\gamma A=(E-TS)-(E_g-TS_g)+\tfrac{4}{3}\pi R^3P_g$$
$$-n\mu_e-nkT\ln(P_g/P_e). \tag{28}$$

$(E-TS)-(E_g-TS_g)$ in this equation may be considered as the Helmholtz free energy of a cluster, which we denote as $F(n)$, because the interaction between a cluster and the surrounding vapor is usually negligible, i.e.,

$$F(n)=(E-TS)-(E_g-TS_g). \tag{29}$$

Using Eq. (29) in Eq. (28) and taking the differential of the result, one obtains

$$\frac{v_l}{R}\,d\gamma-\frac{\gamma v_l}{R^2}\,dR=\frac{\partial[F(n)/n]}{\partial n}\,\frac{4\pi R^2}{v_l}\,dR+(v_l-v_g)\,dP_g. \tag{30}$$

Elimination of dP_g from Eqs. (26) and (30) leads to

$$\left(\frac{\gamma v_l}{R}+n\frac{\partial[F(n)/n]}{\partial n}\right)dR=0. \tag{31}$$

Thus, the size dependence of the surface tension is obtained as

$$\gamma(n)=-\frac{Rn}{v_l}\,\frac{\partial[F(n)/n]}{\partial n}. \tag{32}$$

Calculation of $\gamma(n)$ in Eq. (32) depends on the knowledge of the cluster free energy $F(n)$, which is not known in reality. However, $F(n)$ was recently computed for argon under the Lennard-Jones potential through a Monte Carlo simulation[15,16]; hence it is possible to calculate $\gamma(n)$ for this case. It is hoped that the result will indicate a general feature for the size dependence of surface tension.

An important problem arises in the course of the calculation due to translation and rotation of a cluster in vapor because they are not properly taken into consideration in the present formalism. Let us leave this problem to a future investigation and proceed by replacing $F(n)$ in Eq. (32) with the internal free energy $F^{\text{int}}(n)$. Lee *et al.*[15,16] actually computed the free energy of clusters with the center of mass fixed in space. We use here the values of $F^{\text{int}}(n)$ which were obtained[15] by subtracting the rotational free energy further. Since $\gamma(n)$ is determined by the slope of $F^{\text{int}}(n)/n$, it is desired to represent the simulation data by an explicit function. The condition that $\gamma(n)$ must approach a constant value γ_∞ as $n\to\infty$ requires $F^{\text{int}}(n)/n$ to approach the form $f_\infty + C_1 n^{-1/3}$, where C_1 is a constant and f_∞ denotes the molecular Helmholtz free energy of the bulk liquid. Let us employ the following function to represent the data:

$$F^{\text{int}}(n)/n = f_\infty + C_1 n^{-1/3} + C_2 n^{-2/3} + C_3 n^{-1}, \tag{33}$$

where C_2 and C_3 are constants. The value of C_1 is related to γ_∞ by

$$\gamma_\infty = [4\pi(3v_l)^2]^{-1/3} C_1 . \tag{34}$$

To evaluate the constants in Eq. (33) we employ, in addition to the simulation data for liquid microclusters, the simulation data for the bulk liquid[17,18] which were obtained for argon under the same potential as that used by Lee *et al.*[15,16] Thus, the following functions are obtained through least-squares fitting of Eq. (33) to the simulation data[15-18]:

at 84 °K,

$$F^{\text{int}}(n)/n = -1.567\times10^{-13} + 1.1\times10^{-13} n^{-1/3} - 3.6\times10^{-14} n^{-2/3} + 2.1\times10^{-13} n^{-1} \text{ (erg)}; \tag{35}$$

at 80 °K,

$$F^{\text{int}}(n)/n = -1.533\times10^{-13} + 1.2\times10^{-13} n^{-1/3} - 5.2\times10^{-14} n^{-2/3} + 2.1\times10^{-13} n^{-1} \text{ (erg)}; \tag{36}$$

at 70 °K,

$$F^{\text{int}}(n)/n = -1.452\times10^{-13} + 1.4\times10^{-13} n^{-1/3} - 7.3\times10^{-14} n^{-2/3} + 1.9\times10^{-13} n^{-1} \text{ (erg)}. \tag{37}$$

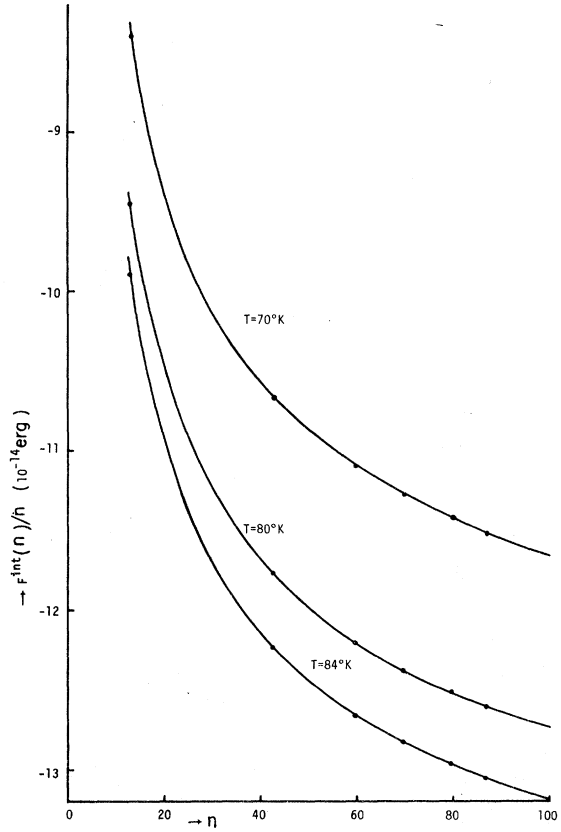

FIG. 4. Monte Carlo simulation data for the internal Helmholtz free energy per atom for argon microclusters. (Refs. 15 and 16).

The results are illustrated in Fig. 4 together with the simulation data. Substitution of those results into Eq. (32) results in

at 84 °K,

$$\gamma(n) = 1.8\times10 - 1.2\times10 n^{-1/3} + 1.0\times10^2 n^{-2/3} \text{ (dyn/cm)}; \tag{38}$$

at 80 °K,

$$\gamma(n) = 2.0\times10 - 1.7\times10 n^{-1/3} + 1.0\times10^2 n^{-2/3} \text{ (dyn/cm)}; \tag{39}$$

at 70 °K,

$$\gamma(n) = 2.3\times10 - 2.4\times10 n^{-1/3} + 9.5\times10 n^{-2/3} \text{ (dyn/cm)}, \tag{40}$$

which are illustrated in Fig. 5. Numerical precision of the results will be discussed later.

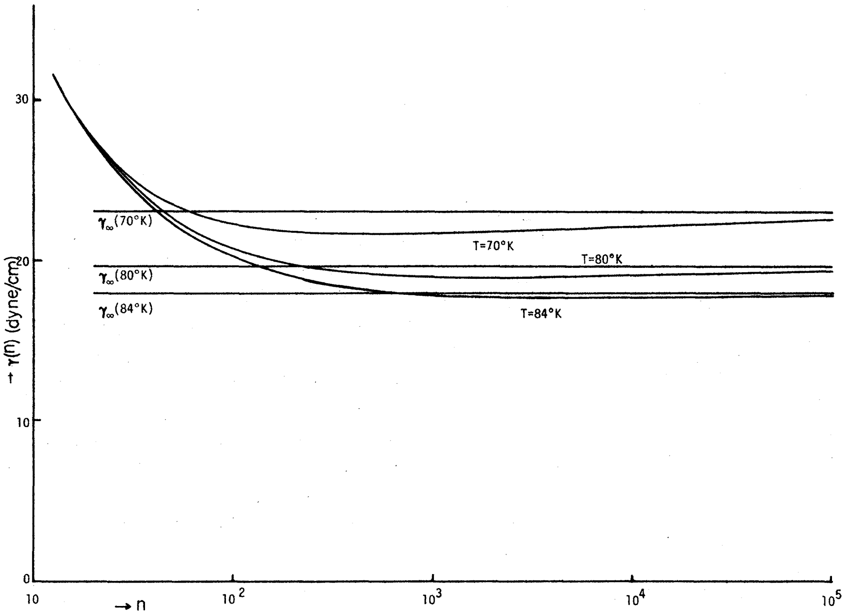

FIG. 5. Cluster size dependence of the surface tension for argon.

IV. EXTENSION TO NONCRITICAL MICROCLUSTERS AND THE GIBBS-THOMSON EQUATION

Once $\gamma(n)$ is known, we can calculate from Eq. (23) the reversible work to form a critical nucleus. However, for this to be useful in practice the Gibbs-Thomson equation must be derived in the present formalism to provide the size of the critical nucleus for a given supersaturation. This may be done by extending the formalism to noncritical microclusters.

Consider a spherical liquid microcluster which is not in equilibrium with the surrounding supersaturated vapor. Suppose that the temperature is uniform throughout the system and assume also that the chemical potential μ_l of a molecule in the cluster is well defined. Consider a conical domain as in Fig. 1. The thermodynamical state of the domain is determined by S, R_g, ω, N_l, and N_g, and the fundamental equation is given by

$$dE = T\,dS - P_g \omega R_g^2\,dR_g + \sigma\,d\omega + \mu_l\,dN_l + \mu\,dN_g, \tag{41}$$

where N_l and N_g denote the number of molecules in the microcluster and in the vapor, respectively. We use here the same notation N_l and N_g as those for the hypothetical system by anticipating the choice of the equimolecular dividing surface. μ denotes the chemical potential of the vapor, and σ is defined by

$$\sigma = \left(\frac{\partial E}{\partial \omega}\right)_{S, R_g, N_l, N_g}. \tag{42}$$

Let us introduce a reference bulk liquid and a hypothetical system as in Sec. II and define the surface tension γ by Eq. (9). From Eqs. (9) and (41) one obtains

$$dE = T\,dS + \gamma\,dA - P_l\,dV_l - P_g\,dV_g + \mu_l\,dN_l + \mu\,dN_g. \tag{43}$$

The differential dA represents the change in area due to changes in both ω and R. Although μ_l may be different from μ in the present consideration, the system is otherwise in equilibrium. This condition may be expressed as

$$(dE - \mu_l\,dN_l - \mu_g\,dN_g)_{S,\omega,R_g,N_l+N_g} = 0, \tag{44}$$

which results in Eq. (11). Integrating Eq. (43) by keeping R_g and the nature of the system invariant, we obtain

$$E = TS + \gamma A - P_l V_l - P_g V_g + \mu_l N_l + \mu N_g. \tag{45}$$

Elimination of γ from Eqs. (11) and (45) leads to

$$R^3 = \frac{6(E - TS - \mu_l N_l - \mu N_g + \frac{1}{3}\omega R_g^3 P_g)}{\omega(P_l - P_g)}. \tag{46}$$

This equation determines the pressure of the reference bulk liquid if we employ the equimolecular dividing surface as the dividing surface condition. Note that the number of independent variables in Eq. (43) is five as in Eq. (41) because V_l and N_l are interdependent. Introducing excess quantities as in Sec. II, γA may be expressed as

$$\gamma A = E^{\text{ex}} - TS^{\text{ex}} - (\mu_l - \mu_l^0)N_l. \tag{47}$$

The fundamental equation for the "surface system" follows from Eqs. (4), (5), and (43) as

$$dE^{\mathrm{ex}} = T\,dS^{\mathrm{ex}} + \gamma\, dA + (\mu_l - \mu_l^0)\, dN_l, \tag{48}$$

and the Gibbs-Duhem relation is given by

$$A\, d\gamma = -S^{\mathrm{ex}} dT - N_l\, d(\mu_l - \mu_l^0). \tag{49}$$

The reversible work to form a microcluster containing n molecules from a large amount of its vapor is found to be

$$W = \tfrac{4}{3}\pi R^2 \gamma + n(\mu_l - \mu). \tag{50}$$

For a microcluster of a given size the surface tension is now introduced through two distinct equations, (17) and (47). The difference between the two rests on the difference in the pressure of the surrounding vapor. One expects the difference in γ due to the difference of P_g to be negligible at low temperatures, but some care need be given because μ_l^0 in Eqs. (17) and (47) may depend on P_g through Eqs. (13) and (46) which determine the pressure P_l of the reference bulk liquid. The effect of P_g on γ may be studied through the following equation which follows from Eqs. (11) and (45):

$$\tfrac{1}{3}\gamma A = E - TS + P_g(V_l + V_g) - \mu_l N_l - \mu N_g. \tag{51}$$

Since the interaction between the cluster and the surrounding vapor is negligible, Eq. (51) may be rewritten, for $\omega = 4\pi$, as

$$\tfrac{1}{3}\gamma A = F(n) - n\mu_l + P_g V_l. \tag{52}$$

Introducing the bulk liquid with the chemical potential μ_l, which must be distinguished from the reference bulk liquid having μ_l^0, $n\mu_l$ in Eq. (52) may be expressed as

$$n\mu_l = n f_\infty(\mu_l) + P_l(\mu_l) V_l, \tag{53}$$

where $f_\infty(\mu_l)$ and $P_l(\mu_l)$ denote the molecular Helmholtz free energy and the pressure, respectively, of the bulk liquid introduced here. Substituting Eq. (53) into Eq. (52), one obtains

$$\tfrac{1}{3}\gamma A = F(n) - n f_\infty(\mu_l) - [P_l(\mu_l) - P_g] V_l. \tag{54}$$

$P_l(\mu_l)$ must be distinguished from P_l which appears, for example, in Eq. (11). It is seen as follows that P_g may be neglected in Eq. (54). For the case where $\mu = \mu_l$, $P_l(\mu_l)$ and P_g are related by

$$P_l(\mu_l) = P_e + (v_g/v_l) P_g \ln(P_g/P_e). \tag{55}$$

Since $v_g \gg v_l$ and $\ln(P_g/P_e) = O(1)$, Eq. (55) shows that $P_l(\mu_l) \gg P_g$. This result remains valid when P_g is changed under a fixed size of the cluster as long as $\ln(P_g/P_e) = O(1)$. When $\ln(P_g/P_e) = O(1)$ and the inequality $P_l(\mu_l) \gg P_g$ fails, the relevant size of clusters becomes large and γ approaches a unique value irrespective of the choice of both the reference bulk liquid and the dividing surface condition, which will be discussed later. Thus it is concluded that the value of γ in the present formalism does not depend on the pressure of the surrounding vapor but is determined unambiguously by the size of the cluster.

Let us proceed to the Gibbs-Thomson equation. The critical nucleus is characterized by the condition $\mu_l = \mu$, which may be rewritten as

$$(\mu_l - \mu_l^0) + (\mu_l^0 - \mu_e) + (\mu_e - \mu) = 0. \tag{56}$$

This is equivalent to the condition that the reversible work of formation given by Eq. (50) takes the maximum value under a given value of P_g. Employing the Gibbs-Duhem relation (25) and Eq. (11), the last two terms in Eq. (56) may be expressed as follows:

$$\mu_e - \mu = -kT \ln(P_g/P_e), \tag{57}$$

$$\mu_l^0 - \mu_e = v_l(2\gamma/R + P_g - P_e). \tag{58}$$

To represent the first term in Eq. (56) in terms of known quantities, we employ the Gibbs-Duhem relation (49) to obtain

$$\frac{\partial(\mu_l - \mu_l^0)}{\partial R} = -\frac{3v_l}{R}\frac{\partial\gamma}{\partial R}\,. \tag{59}$$

Integration of Eq. (59) from infinity to R results in

$$\mu_l - \mu_l^0 = -3v_l\left(\frac{\gamma}{R} - \int_R^\infty \frac{\gamma}{R^2}\, dR\right). \tag{60}$$

It follows from Eqs. (56), (57), (58), and (60) that

$$\frac{kT}{v_l}\ln\left(\frac{P_g}{P_e}\right) = 3\int_R^\infty \frac{\gamma}{R^2}\, dR - \frac{\gamma}{R} + (P_g - P_e), \tag{61}$$

which provides the Gibbs-Thomson equation in the present formalism. When the dependence of γ on R is negligible in $[R, \infty)$, Eq. (61) may be approximated by the following familiar form:

$$(kT/v_l)\ln(P_g/P_e) = 2\gamma R + (P_g - P_e). \tag{62}$$

V. DISCUSSION

Let us first consider the numerical accuracy concerning the results obtained in Sec. III. For this purpose we employ the results of a recent Monte Carlo simulation for γ_∞ at 83.86 °K and its extrapolation to the other temperatures which were obtained by Miyazaki *et al.*[22,23] for argon under the same potential as that used for the microcluster simulation by Lee *et al.*[15,16] The values of γ_∞ obtained from Eq. (34) in the present formalism are compared with the results due to Miyazaki *et al.*[22,23] in Table I. It is observed that the values coincide to the accuracy of two significant digits at 84 and 80 °K, and almost two at

TABLE I. Values of the macroscopic surface tension γ_∞ resulting from the present theory and those obtained by Miyazaki *et al.*[22,23]

Work \ T (°K)	84	80	70
Present theory	18.01	19.66	23.06
Miyazaki *et al.*	18.16	19.14	21.60

TABLE II. Asymptotic behavior of the surface tension for three temperatures.

n \ T (°K)	84	80	70
10^5	17.81	19.35	22.59
10^7	17.96	19.58	22.95
10^{10}	18.00	19.65	23.05
$\rightarrow\infty$	18.01	19.66	23.06

70 °K. This strongly suggests that the values of the constant C_1 obtained by the least-squares fitting possess the accuracy of two significant digits. Detailed analysis of the least-squares fitting procedure discloses that the accuracy of two significant digits for C_1 corresponds to the accuracy of at least one significant digit for C_2, two for C_3, and four for f_∞. Thus the cluster-size dependence of surface tension illustrated in Fig. 5 possesses, at least to some extent, quantitative significance.

The present results on the size dependence of surface tension indicate that γ first decreases according to $n^{-1/3}$, which is in agreement with Tolman's.[14] However, Tolman's result quantitatively shows somewhat stronger dependence. Tolman's result[14] gives, for example,

$$\gamma_s/\gamma_\infty = 0.98 \text{ at } \Delta/R_s = 0.01,$$

$$\gamma_s/\gamma_\infty = 0.91 \text{ at } \Delta/R_s = 0.05,$$

where γ_s and R_s denote those values with the surface of tension as the dividing surface, and Δ is defined by

$$\Delta = R - R_s. \tag{63}$$

The value of Δ was estimated to be about 3 Å for argon[4,5]; hence γ_s diminishes about 2% at $n \simeq 10^6$ and 9% at $n \simeq 10^4$. Although the physical content in γ_s is different from that in the surface tension in the present formalism, the discrepancy between the present results and Tolman's is significant because the work of formation of a critical nucleus must be independent of the formalism; i.e.,

$$\tfrac{4}{3}\pi R^2 \gamma = \tfrac{4}{3}\pi R_s^2 \gamma_s \tag{64}$$

must hold. The origin of this discrepancy may be due to both the difficulty involved in calculating Δ and the error involved in obtaining the constants for Eq. (33) from the simulation data. Employment of $F^{\text{int}}(n)$ in the present formalism may have also contributed to the discrepancy, because in Tolman's theory a cluster with $3n$ degrees of freedom was treated as if it were stationary. We must extend the formalism by taking the translation and rotation into consideration consistently in order to establish a complete theory for the size dependence of surface tension.

As n becomes smaller, γ increases again with decrease of n due to the term proportional to $n^{-2/3}$. Note that $\gamma(n)$ is appreciably greater than γ_∞ for $n \lesssim 10^2$, which corresponds to the size range being relevant in nucleation. The origin of this increase in $\gamma(n)$ may be understood from Eq. (17) as that the difference in the thermodynamic properties between the microcluster and the reference bulk liquid is entirely absorbed in the concept of surface tension; and the smaller the cluster, the larger the difference becomes.

Asymptotic behavior of the surface tension for larger n is shown in Table II. It is seen that the macroscopic value is attained at $n = 10^7 \sim 10^{10}$, i.e., $R = 500$ Å ~ 5000 Å. This is in agreement with the result of Lee *et al.*[24] They studied the size dependence of surface tension for crystalline clusters under the generalized Einstein model[25,26] and found that the surface tension becomes convergent at $n = 10^7 \sim 10^8$. However, contrary to the present result for liquid, the surface tension for crystallites shows, on the whole, monotonically increasing behavior with decrease in size.

Let us next consider the dependence of the value of surface tension on the choice of the dividing surface. It follows from Eqs. (11) and (13) that

$$\delta\gamma/\gamma = -2\,\delta R/R, \tag{65}$$

where δR and $\delta\gamma$ denote the changes in those values due to a change in the choice of the dividing surface with the state of the system kept invariant. Equation (65) indicates that the value of surface tension in the present formalism must be smaller than γ_s by $2\gamma_s\Delta/R_s$. Since Δ is of the order of the interatomic spacing in the bulk liquid,[2-5] γ is to be smaller than γ_s by about 1% at $n \simeq 10^6$. As $n \rightarrow \infty$, the radius of a cluster, the pressure of the reference bulk liquid, and the surface tension all approach unique values. In this limit Eq. (11) approaches the condition of mechanical equilibrium which is employed in the surface-tension measurement. Hence, Eq. (32) relates the surface tension of a microcluster to the experimentally measurable quantity γ_∞.

Let us lastly discuss the interrelation between the present formalism and the previous ones. In the theories by Hill[8,9] and by Ono and Kondo[6] the size of a cluster was assumed to be sufficiently large so that the central part possesses the homogeneous property of a bulk liquid. This enabled them, in a conical domain as that in Fig. 1, to define an additional spherical boundary with the radius R_l which passes through the central homogeneous part of the cluster. Denoting the pressure at the central homogeneous part as P_l, the fundamental equation was given by

$$dE = T\,dS + \sigma\,d\omega - P_g \omega R_g\,dR_g + P_l \omega R_l^2\,dR_l + \mu\,dN. \tag{66}$$

The boundary of the system was taken to be a physical wall instead of a hypothetical boundary employed in the present formalism. The reference bulk liquid was chosen to have the same property as that of the homogeneous liquid phase at the central part of the cluster. The surface tension γ was introduced by

$$\gamma\,dA + C\,dR = \sigma\,d\omega + P_l\,dV_l' + P_g\,dV_g', \tag{67}$$

where the term $C\,dR$ represents the work term associated with a change in the curvature of the dividing surface under a fixed dividing surface condition. This term was originally introduced by Gibbs.[1] It follows from Eqs. (66) and (67) that

$$dE = T\,dS + \gamma\,dA + C\,dR - P_g\,dV_g - P_l\,dV_l + \mu\,dN. \tag{68}$$

The reason for necessity of the curvature term $C\,dR$ may be understood as an extra "independent variable" to fix the dividing surface condition.[11] If the term $C\,dR$ is not introduced in Eq. (67), the dividing surface is to be determined through the following relation:

$$R^3 = \frac{6(E - TS - \mu N + \frac{1}{3}P_g \omega R_g^3 - \frac{1}{3}P_l \omega R_l^3)}{\omega (P_l - P_g)}, \tag{69}$$

and we cannot choose the dividing surface condition at will. The dividing surface determined by Eq. (69) is called the surface of tension. Note that Eq. (13) in the present formalism is identical to Eq. (69) with $R_l = 0$. This means that the dividing surface determined by Eq. (13) in the present formalism corresponds to the surface of tension in the previous theories[1-11,14] if the reference bulk liquid is chosen to possess the same chemical potential as that of the real system. However, the boundary of the system in the previous theories must be reinterpreted as the hypothetical boundary in this case. It is not possible in the present formalism to introduce the curvature term in the same way as in Eq. (67). This may be seen from Eqs. (6)-(8) by noting that V_l, V_g, and A determine R as well as ω and R_g.

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