

## Thermodynamic formalism for a liquid microcluster in vapor

Kazumi Nishioka

*Department of Precision Mechanics, The University of Tokushima, 2-1 Minamijosanjima, Tokushima 770, Japan*  
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A thermodynamic formalism is developed for a liquid microcluster which is so small that the homogeneous properties of the bulk liquid are not attained even at the center. The system is carefully defined by a mathematical boundary, and then the thermodynamic variables are introduced in such a manner that the interaction of molecules inside and outside the boundary is taken into consideration. It is shown that the variables may be classified into the extensive and the intensive ones and the Gibbs-Duhem relation may also be derived. It is clarified that both the surface tension in Nishioka's formalism with the equimolecular dividing surface and that in Gibbs's formalism with the surface of tension represent the reversible works of a very similar nature. Finally, complication due to translation and rotation of a microcluster in vapor is discussed, and the use of the internal free energy of a microcluster to get the cluster-size dependence of the surface tension in Nishioka's formalism is shown to be reasonable.

### I. INTRODUCTION

Liquid microclusters relevant in nucleation from the vapor are often extremely small in size so that the homogeneous properties of the bulk liquid are probably not attained even at the center. Following the idea behind the Gibbs theory of surface tension,<sup>1</sup> Nishioka<sup>2</sup> formulated a thermodynamic theory for those systems in such a manner that the results of computer simulations for microclusters<sup>3</sup> and for the bulk liquid<sup>4</sup> are employed to obtain the cluster-size dependence of the surface tension. The theory involves some subtle points due to an application of the concepts in macroscopic thermodynamics to such extremely small systems. The present article intends to clarify further the characteristic concepts invoked in the thermodynamic formalism of the theory. In addition, the nature of the reversible work associated with the surface tension in Nishioka's formalism is elucidated and is compared with that in the Gibbs theory. Complication due to translation and rotation of a microcluster in vapor is also discussed in relation to the estimated size dependence of the surface tension.

### II. THERMODYNAMIC FORMALISM

Consider a liquid microcluster with the spherical shape in a supersaturated vapor, which consists of a pure substance and is in thermodynamic equilibrium, i.e., the consideration will be limited to a critical nucleus. The first step in a thermodynamic consideration is to define the system, and it is defined here by a mathematical boundary having a conic shape intersected by a sphere as shown by the heavy solid line in Fig. 1. The center of the sphere coincides with the "center" of the microcluster which is indicated by the dashed line, and its radius  $R_v$  is taken to be so large that it passes through the homogeneous vapor phase. Complication due to translation and rotation of the microcluster will be discussed later.

Consider next the thermodynamic variables to define a state of the system. Since the system under consideration is small, interaction between the molecules inside and outside the boundary must be taken into account. The spherical boundary passes through the homogeneous vapor phase, hence the effect of the interaction on internal energy and entropy may be considered as shared equally between the molecules on both sides of the boundary at  $R_v$ . Thus, the internal energy  $E_{4\pi}$  and the entropy  $S_{4\pi}$  for the entire sphere are well defined, where the subscript  $4\pi$  indicates the solid angle for the entire sphere ( $4\pi$  sr). Since the thermodynamic properties are homogeneous along the direction perpendicular to the boundary defining the cone, the internal energy  $E$  and the entropy  $S$  of the system are given by

$$E = E_{4\pi}\omega/4\pi, \quad S = S_{4\pi}\omega/4\pi, \quad (1)$$

where  $\omega$  denotes the solid angle of the cone. The number of molecules within the system may fluctuate, but

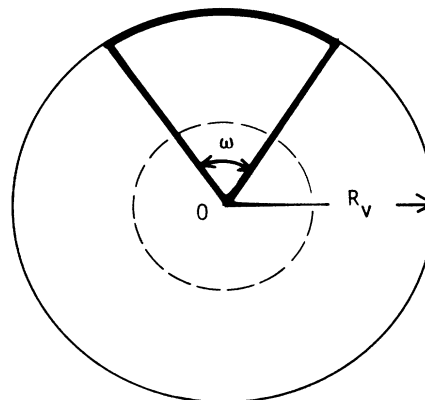


FIG. 1. System defined by a mathematical boundary.

only the average value is treated in thermodynamics. Thus,

$$N = N_{4\pi}\omega/4\pi, \quad (2)$$

where  $N$  and  $N_{4\pi}$  denote the number of molecules in the system and in the entire sphere, respectively.

The temperature  $T$  and the chemical potential  $\mu$  of a supersaturated vapor determine the state of the critical nucleus, such as its size and the density profile, as well as the intensive properties of the supersaturated vapor. Hence, the state of the entire sphere in Fig. 1, including its "extensive" properties, is determined by  $S_{4\pi}$ ,  $N_{4\pi}$ , and  $R_v$ ; thus the state of the system is determined by  $S$ ,  $N$ ,  $R_v$ , and  $\omega$ . The internal energy is a function of those variables, i.e.,

$$E = E(S, N, R_v, \omega), \quad (3)$$

which constitutes the fundamental equation for the system. Its differential form is given by

$$dE = (\partial E / \partial S) dS + (\partial E / \partial N) dN + (\partial E / \partial R_v) dR_v + (\partial E / \partial \omega) d\omega. \quad (4)$$

Implication of the differential coefficients in Eq. (4) is quite complex, and it is desirable to express them in terms of the more familiar quantities.

Eq. (3) may be rewritten as

$$E = E_{4\pi}(S_{4\pi}, N_{4\pi}, R_v)\omega/4\pi. \quad (5)$$

Employing the chain rule in differentiation, it follows that

$$\begin{aligned} (\partial E / \partial S)_{N, R_v, \omega} &= (\partial E_{4\pi} / \partial S_{4\pi})_{N_{4\pi}, R_v} (\partial S_{4\pi} / \partial S)_{\omega} \omega / 4\pi \\ &= (\partial E_{4\pi} / \partial S_{4\pi})_{N_{4\pi}, R_v}. \end{aligned} \quad (6)$$

Similarly, we get

$$\begin{aligned} (\partial E / \partial N)_{S, R_v, \omega} &= (\partial E_{4\pi} / \partial N_{4\pi})_{S_{4\pi}, R_v}, \\ (\partial E / \partial R_v)_{S, N, \omega} &= (\partial E_{4\pi} / \partial R_v)_{S_{4\pi}, N_{4\pi}} \omega / 4\pi, \\ (\partial E / \partial \omega)_{S, N, R_v} &= [(\partial E_{4\pi} / \partial S_{4\pi})_{N_{4\pi}, R_v} S / \omega \\ &\quad + (\partial E_{4\pi} / \partial N_{4\pi})_{S_{4\pi}, R_v} N / \omega] + E / \omega. \end{aligned} \quad (7)$$

Hence,

$$\begin{aligned} dE &= (\partial E_{4\pi} / \partial S_{4\pi}) dS + (\partial E_{4\pi} / \partial N_{4\pi}) dN \\ &\quad + (\omega / 4\pi) (\partial E_{4\pi} / \partial R_v) dR_v \\ &\quad + (1 / \omega) [E - (\partial E_{4\pi} / \partial S_{4\pi}) S - (\partial E_{4\pi} / \partial N_{4\pi}) N] d\omega. \end{aligned} \quad (8)$$

Note that the system is supposed to remain in equilibrium both before and after an infinitesimal change in state.

Equation (8) provides the differential form of the fundamental equation for the system in which the differential coefficients for the entire sphere are employed. Those differential coefficients are, strictly speaking, functions of the variables  $S$ ,  $N$ ,  $R_v$ , and  $\omega$  for the system, but they may be more directly considered as

functions of  $S_{4\pi}$ ,  $N_{4\pi}$ , and  $R_v$ , which in turn enables us to relate them to the intensive variables for the supersaturated vapor. Consider the supersystem in equilibrium as shown in Fig. 2 which consists of two regions, the entire sphere and the homogeneous supersaturated vapor surrounding it, separated by the mathematical boundary  $B$ . For an infinitesimal variation of the region of the homogeneous vapor, we have

$$\delta E_{\text{hv}} = T \delta S_{\text{hv}} - p \delta V_{\text{hv}} + \mu \delta N_{\text{hv}}, \quad (9)$$

where  $p$  denotes the pressure of the supersaturated vapor and the subscript hv indicates the quantities for the region of the homogeneous vapor. Similarly, for the entire sphere we have

$$\begin{aligned} \delta E_{4\pi} &= (\partial E_{4\pi} / \partial S_{4\pi}) \delta S_{4\pi} \\ &\quad + (\partial E_{4\pi} / \partial N_{4\pi}) \delta N_{4\pi} + (\partial E_{4\pi} / \partial R_v) \delta R_v. \end{aligned} \quad (10)$$

Individual variations in each region may cause infinitesimal discontinuity of state at the mathematical boundary  $B$ , but variations of internal energy and entropy in each region may be evaluated under the supposition that the varied state of each region extended beyond the boundary  $B$ .<sup>1,5</sup> Hence, the variations in Eqs. (9) and (10) are all well defined. Taking  $\delta S_{\text{hv}} = -\delta S_{4\pi}$  as variations in the two regions, it follows from the second law of thermodynamics that

$$(\delta E_{\text{su}})_{S_{\text{su}}, N_{\text{su}}, V_{\text{su}}} = (\partial E_{4\pi} / \partial S_{4\pi}) \delta S_{4\pi} - T \delta S_{4\pi} = 0, \quad (11)$$

hence,

$$(\partial E_{4\pi} / \partial S_{4\pi}) = T, \quad (12)$$

where the subscript "su" indicates the quantities for the supersystem. Similarly, we get

$$(\partial E_{4\pi} / \partial N_{4\pi}) = \mu, \quad (\partial E_{4\pi} / \partial R_v) = -p 4\pi R_v^2. \quad (13)$$

Substituting Eqs. (12) and (13) into Eq. (8), we get

$$dE = T dS + \mu dN - p \omega R_v^2 dR_v + \sigma d\omega, \quad (14)$$

where  $\sigma$  represents the following:

$$\sigma = (E - TS - \mu N) / \omega. \quad (15)$$

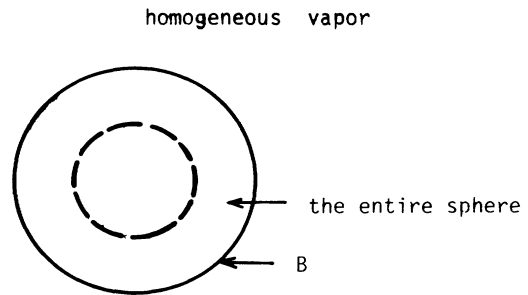


FIG. 2. Supersystem containing both the entire sphere and the homogeneous vapor surrounding it.  $B$  denotes the mathematical boundary between those two regions.

Thus, the differential coefficients in Eq. (4) are shown to be expressible in terms of the intensive variables  $T$ ,  $\mu$ , and  $p$  of the supersaturated vapor. It is instructive to compare Eq. (15) with the following equation for a bulk homogeneous system:

$$-p = (E - TS - \mu N) / V . \quad (16)$$

Let us consider the possibility of classifying the variables into extensive and intensive ones as done in the ordinary thermodynamic formalism. Suppose two systems both of which are specified by  $(S, N, R_v, \omega)$  and take them together to form a single system. The system thus formed is specified by  $(2S, 2N, R_v, 2\omega)$  due to Eqs. (1) and (2), and Eq. (5) leads to

$$E(2S, 2N, R_v, 2\omega) = 2E(S, N, R_v, \omega) . \quad (17)$$

Hence  $S$ ,  $N$ ,  $\omega$ , and  $E$  may be considered as extensive variables under a constant value for  $R_v$ , and  $E$  is a homogeneous function of the first degree in the variables  $S$ ,  $N$ , and  $\omega$ . It follows from Euler's theorem that

$$(\partial E / \partial S)S + (\partial E / \partial N)N + (\partial E / \partial \omega)\omega = E , \quad (18)$$

which is equivalent to Eq. (15) since  $(\partial E / \partial S)$  and  $(\partial E / \partial N)$  have been identified as  $T$  and  $\mu$  of the supersaturated vapor and  $(\partial E / \partial \omega)$  is denoted as  $\sigma$ . Under a constant value for  $R_v$ , the variables,  $T$ ,  $\mu$ , and  $\sigma$  are homogeneous functions of the zeroth degree in the variables  $S$ ,  $N$ , and  $\omega$ , hence they may be considered as intensive variables in the present formalism. Taking differential of Eq. (18) under a constant value for  $R_v$  and comparing the result with Eq. (14), we get the Gibbs-Duhem relation as

$$SdT + Nd\mu + \omega d\sigma = 0 . \quad (19)$$

When we change the values of  $S$ ,  $N$ , and  $\omega$  infinitesimally under a fixed  $R_v$ , the system will move to a new equilibrium state in which  $T$ ,  $\mu$ , and  $\sigma$  are modified. However, infinitesimal changes in those values will be mutually related through Eq. (19). The size of a liquid microcluster located at the center will also be altered. Equation (19) plays an indispensable role in obtaining the cluster-size dependence of the surface tension. Note that the present definition of the system having a conic shape is the clue in defining the Gibbs-Duhem relation (19). If we chose the entire sphere as the system, it would not be possible to classify the variables into the extensive and the intensive ones, hence Eq. (19) would not have been obtained.

### III. DIVIDING SURFACES AND THE SURFACE TENSION

It is shown in Sec. II that the thermodynamic formalism can be established even for an extremely small system containing a liquid microcluster and the vapor. However, for the practical usefulness of the formalism, thermodynamic variables must be either macroscopically observable or must be explicitly related to macroscopic variables.  $\sigma$  in Eq. (14) represents the complex effect due to the transition layer between the microcluster and the vapor, but it cannot be measured in practice and we

must represent the term  $\sigma d\omega$  in terms of experimentally measurable quantities.

Following Gibbs,<sup>1</sup> we employ a mathematical interface, called a dividing surface, within the transition layer under a chosen condition and introduce the hypothetical system<sup>2</sup> by filling each side of it with a reference bulk liquid and a bulk vapor. We call each part of the hypothetical system the hypothetical microcluster and the hypothetical vapor, respectively. As the reference bulk liquid and the reference bulk vapor, Gibbs<sup>1</sup> employed those which possess  $T$  and  $\mu$  of the real system, but we proceed for a while without committing a choice for the reference bulk liquid. For a given state of the system described by  $S$ ,  $N$ ,  $\omega$ , and  $R_v$ , the radius  $R$  and the area  $A$  of the dividing surface are determined once the dividing surface condition is specified. An infinitesimal change of the state described by  $dS$ ,  $dN$ ,  $d\omega$ , and  $dR_v$  accompanies an infinitesimal change in the size of the critical nucleus, and both  $dR$  and  $dA$  are determined accordingly. We introduce the concept of surface tension  $\gamma$  by

$$\sigma d\omega = -p_l dV_l - p dV'_v + \gamma dA + \rho dR , \quad (20)$$

where  $p_l$  and  $V_l$  denote the pressure and the volume of the hypothetical liquid phase and  $dV'_v$  denotes the volume change of the hypothetical vapor with  $R_v$  kept invariant. Equation (20) may be interpreted to find that the unmeasurable work term  $\sigma d\omega$  of the real system is represented by the work terms of the hypothetical system and that their difference is ascribed in the work terms  $\gamma dA + \rho dR$  associated with the dividing surface. Since a change in the curvature of the interface accompanies a modification of the molecular distribution within the interfacial region, necessity of the term  $\rho dR$  introduced by Gibbs<sup>1</sup> can be understood.<sup>6</sup> Eliminating the term  $\sigma d\omega$  from Eqs. (14) and (20), we obtain

$$dE = T dS + \mu dN - p_l dV_l - p dV_v + \gamma dA + \rho dR . \quad (21)$$

Observing that  $dV_l$  can be expressed in terms of  $dA$  and  $dR$ , there are five independent variables in Eq. (21) as compared with four in Eq. (14). One extra variable in Eq. (21) reflects the freedom to choose the dividing surface condition.<sup>7</sup> Note that Eqs. (20) and (21) remain meaningful even for the cases where  $d\omega = 0$ .

Integrating Eq. (20) by keeping  $R_v$  and the nature of the system invariant, we obtain

$$\sigma\omega = -p_l V_l - p V_v + \gamma A . \quad (22)$$

Substituting Eq. (22) into Eq. (18), one gets

$$E = TS + \mu N - p_l V_l - p V_v + \gamma A . \quad (23)$$

Differentiating Eq. (22) under a constant value for  $R_v$  and using Eq. (20), we obtain

$$\omega d\sigma = -V_l dP_l - V_v dp + A d\gamma - \rho dR . \quad (24)$$

Substituting Eq. (24) into Eq. (19) and manipulating the result, we get the following form for the Gibbs-Duhem relation:

$$S^{\text{ex}} dT + N^{\text{ex}} d\mu - N_l (d\mu^0 - d\mu) + A d\gamma - \rho dR = 0 , \quad (25)$$

where  $S^{\text{ex}}$  and  $N^{\text{ex}}$  denote the excess entropy and the excess number of molecules, respectively, and  $N_l$  the number of molecules in the hypothetical microcluster. Anticipating an extension of the Gibbs method, we allowed in Eq. (25) a possibility that the chemical potential  $\mu^0$  of a reference bulk liquid may be different from that of the real system, whereas temperature of the reference bulk liquid is taken to be the same as that of the real system. Equation (25) will be employed to get the cluster-size dependence of the surface tension.

It is intended<sup>2</sup> that the results of computer simulation<sup>3</sup> for liquid microclusters are utilized to derive the cluster-size dependence of the surface tension. For this purpose we need to employ the equimolecular dividing surface, which is specified by  $N^{\text{ex}}=0$ , because the simulation results are obtained in terms of the number of atoms contained in the clusters. However, the term  $\rho dR$  remains in Eq. (20) in this choice of the dividing surface, which causes much inconvenience in practical applications. The term  $\rho dR$  remains also in Eq. (25). To avoid this inconvenience, Nishioka<sup>2</sup> chose the pressure  $p_l^0$  for the reference bulk liquid so that  $\rho dR$  vanishes in Eq. (20). Chemical potential  $\mu^0$  of the reference bulk liquid will be different from that of the real system in this case. Under Nishioka's choice of the dividing surface and the reference bulk liquid, Eq. (25) becomes

$$S^{\text{ex}} dT - N_l(d\mu^0 - d\mu) + A d\gamma = 0. \quad (26)$$

Although it would be most natural to take the bulk liquid possessing  $T$  and  $\mu$  of the real system as the reference, the present choice is also allowable as long as we take the view that the concept of surface tension is a method to relate the unmeasurable work term  $\sigma d\omega$  in Eq. (14) to measurable quantities. It follows from the condition of thermodynamic equilibrium that

$$p_l^0 - p = 2\gamma / R. \quad (27)$$

Eliminating  $\gamma$  from Eqs. (23) and (27), one obtains

$$\omega(p_l^0 - p) = 6(E - TS - \mu N + p\omega R_v^3/3) / R^3. \quad (28)$$

The condition  $N^{\text{ex}}=0$  for the equimolecular dividing surface is practically equivalent to

$$4\pi R^3/3 = nv_l, \quad (29)$$

where  $n$  denotes the number of molecules contained in the cluster and  $v_l$  the molecular volume of the reference bulk liquid. For a given state of the system,  $R$  and  $p_l^0$  are determined by the simultaneous equations (28) and (29). However, since bulk liquid is nearly incompressible, pressure dependence of  $v_l$  may be neglected in practice and Eq. (29) alone determines  $R$ . Then,  $p_l^0$  is determined, in principle, by Eq. (28).

The surface tension  $\gamma$  is determined by Eq. (27) in the present formalism. As the cluster size becomes large,  $p_l^0$  approaches the actual pressure inside the cluster<sup>2</sup> and  $\gamma$  can be measured as the mechanical tension, whereas  $p_l^0$  may deviate from the pressure inside the cluster for smaller clusters. For extremely small clusters, the pressure inside the cluster may not be meaningful, but  $p_l^0$  is

still well defined as the pressure of the corresponding reference bulk liquid. However, it is not possible in practice to determine  $p_l^0$  and  $\gamma$  from Eqs. (27) and (28) in those cases. To obtain the general feature for the cluster-size dependence of the surface tension at constant temperatures, Eq. (26) and the results of computer simulation<sup>3,4</sup> were employed to get  $\gamma(n)$  for argon. This point will be discussed later in relation to the difficulty due to translation and rotation of a cluster in the vapor.

Let us consider the physical meaning of the surface tension introduced here and compare it with those due to Gibbs. For the entire sphere Eq. (23) may be rewritten as

$$\gamma A = E^{\text{ex}} - TS^{\text{ex}} - (\mu - \mu^0)n, \quad (30)$$

where  $E^{\text{ex}}$  denotes the excess internal energy. It is helpful for understanding the implication of Eq. (30) to consider the reversible work  $\Delta W^{\text{rev}}$  of forming a critical nucleus within the system of a supersaturated vapor which is maintained at constant  $T$  and  $p$ .  $\Delta W^{\text{rev}}$  is given by  $\Delta E - T\Delta S + p\Delta V$ , where  $\Delta E$ ,  $\Delta S$ , and  $\Delta V$  denote the changes for the system defined above upon forming a critical nucleus. After some manipulation,  $\Delta W^{\text{rev}}$  may be expressed as

$$\Delta W^{\text{rev}} = \gamma A - (p_l^0 - p)V_l, \quad (31)$$

where  $V_l$  represents  $4\pi R^3/3 = nv_l$ . To see the physical meaning of Eq. (31), we follow Gibbs<sup>1</sup> and consider a thought process to form a critical nucleus as shown in Figs. 3 and 4. Within the supersaturated vapor we imagine the reference bulk liquid with  $T$  and  $p_l^0$  which is enclosed by an envelope as illustrated in Fig. 3. Differences in the pressure and the chemical potential are maintained with the help of a reversible work source. Suppose that we transfer  $n$  molecules into the reference bulk liquid from the vapor. The reversible work  $\Delta W_1^{\text{rev}}$  in this process is given by

$$\Delta W_1^{\text{rev}} = n(\mu^0 - \mu) - (p_l^0 - p)V_l \quad (32)$$

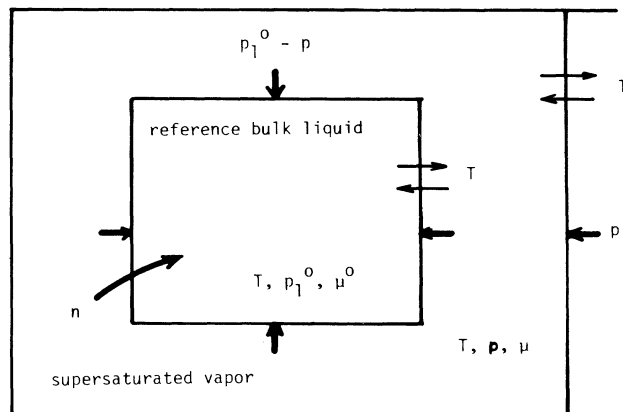


FIG. 3. Supersaturated vapor and the hypothetical reference bulk liquid.

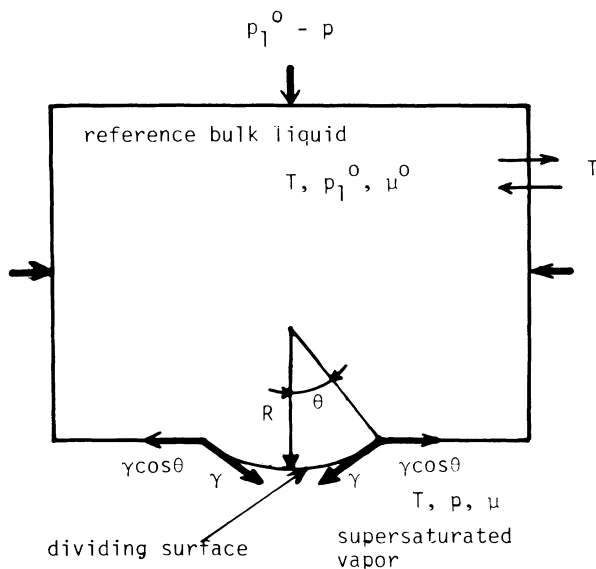


FIG. 4. Reversible thought process to form a liquid microcluster from the reference bulk liquid.

because the change in the outer area of the reference bulk liquid may be neglected. Consider next the process of forming a microcluster from the reference bulk liquid by following the procedure illustrated in Fig. 4. Suppose that a small aperture is opened and then closed in the envelope so as to extrude a liquid microcluster of  $n$  molecules into the vapor. Since the work term  $\sigma d\omega$  of the microcluster is represented by the work terms of the hypothetical system and the dividing surface, the reversible work  $\Delta W_2^{\text{rev}}$  for the extrusion process is given by

$$\Delta W_2^{\text{rev}} = \gamma A + (\mu - \mu^0)n, \quad (33)$$

in which the second term is needed to change the chemical potential from  $\mu^0$  to  $\mu$ . The first term  $\gamma A$  results from the following consideration. To keep the process reversible, we must provide the force  $\gamma \cos\theta$  at the edge of the aperture through the reversible work source as shown in Fig. 4. Amount of the work done at the edge of the aperture is given by

$$\int_0^R \gamma \cos\theta 2\pi R \sin\theta d(r \cos\theta) + \int_R^0 \gamma \sin\theta 2\pi R \cos\theta d(-r \cos\theta), \quad (34)$$

in which the first term represents the work done during the opening process and the second term during the closing process. Equation (34) results in  $4\pi R^2\gamma/3$ . In addition, the amount of the work  $4\pi R^3(p_l^0 - p)/3$ , which may be rewritten as  $8\pi R^2\gamma/3$  due to Eq. (27), is done to push the envelope inward during the extrusion process. Summation of those two amounts of the reversible work results in  $\gamma A$ , i.e., the first term of Eq. (33). Adding  $\Delta W_1^{\text{rev}}$  and  $\Delta W_2^{\text{rev}}$  together, we get  $\Delta W^{\text{rev}}$  given by Eq. (31). Since the volume of the system shown in Fig. 3 is invariant during the extrusion process,  $\Delta W_2^{\text{rev}}$  is given by  $E^{\text{ex}} - TS^{\text{ex}}$ , hence Eq. (33) is equivalent to Eq. (30) as it should be. Thus,  $\gamma A$  in the present formalism

represents the reversible work required in the extrusion process as shown in Fig. 4. Note, however, that the reversible work required to change the chemical potential is not contained in  $\gamma A$ .

Consider next the surface of tension due to Gibbs<sup>1</sup> as the dividing surface, where the reference bulk liquid is chosen to possess  $T$  and  $\mu$  of the real system. The term  $\rho dR$  is eliminated from Eqs. (20), (21), and (24) in this case also, and the following equation holds:

$$p_l - p = 2\gamma_s / R_s, \quad (35)$$

where the subscript  $s$  indicates the choice of the surface of tension.  $N_s^{\text{ex}}$  does not vanish and Eq. (25) becomes

$$S_s^{\text{ex}} dT + N_s^{\text{ex}} d\mu + A_s d\gamma_s = 0. \quad (36)$$

$p_l$  is determined by the requirement that the reference bulk liquid possesses  $T$  and  $\mu$  of the real system, and  $R_s$  is determined by

$$R_s^3 = 6(E - TS - \mu N + p\omega R_v^3/3) / \omega(p_l - p). \quad (37)$$

It follows from Eqs. (23) that

$$\gamma_s A_s = E_s^{\text{ex}} - TS_s^{\text{ex}} - \mu N_s^{\text{ex}}, \quad (38)$$

which determines  $\gamma_s$ . Consideration similar to that leading to Eq. (31) results in the following expression for the reversible work to form a critical nucleus:

$$\Delta W^{\text{rev}} = \gamma_s A_s - (p_l - p)V_{ls}. \quad (39)$$

Consider the thought process similar to those shown in Figs. 3 and 4. The reversible work to transfer the proper number of molecules into the reference bulk liquid from the vapor is given by  $-(p_l - p)V_{ls}$ . However, since the process in Fig. 3 may be interpreted as the formation of the hypothetical system from the initial state of the supersaturated vapor,  $N_s^{\text{ex}}$  molecules must be removed from the system by the reversible work source during the process. Hence,

$$\Delta W_{ls}^{\text{rev}} = -(p_l - p)V_{ls} - \mu N_s^{\text{ex}}. \quad (40)$$

During the extrusion process, the reversible work  $(p_l - p)V_{ls}$  is required to push in the envelope and  $4\pi R_s^2\gamma_s/3$  for opening and closing the aperture. In addition, the amount  $\mu N_s^{\text{ex}}$  is needed during the process because the process is equivalent to creating the real system from the hypothetical one. Thus,

$$\Delta W_{2s}^{\text{rev}} = \gamma_s A_s + \mu N_s^{\text{ex}}. \quad (41)$$

Summation of  $\Delta W_{1s}^{\text{rev}}$  and  $\Delta W_{2s}^{\text{rev}}$  results in  $\Delta W^{\text{rev}}$  as it should. Since the volume of the system in Fig. 3 is invariant during the process and the wall is restrictive with respect to the number of molecules,  $\Delta W_{2s}^{\text{rev}}$  is given by  $E^{\text{ex}} - TS^{\text{ex}}$ ; hence Eq. (41) is equivalent to Eq. (38) as it must.

Note that both of  $\gamma A$  in Nishioka's formalism and  $\gamma_s A_s$  in Gibbs's formalism with the surface of tension represent the mechanical part of the reversible work of the extrusion process which is done by pushing in the envelope and by opening and closing the aperture. Thus, both of  $\gamma A$  and  $\gamma_s A_s$  possess similar physical

meanings. Substituting Eqs. (27) and (35) into Eqs. (31) and (39), respectively, we get

$$\Delta W^{\text{rev}} = \gamma A / 3 = \gamma_s A_s / 3. \quad (42)$$

Since it is estimated<sup>8-10</sup> that  $R > R_s$ , it follows that  $\gamma < \gamma_s$ . Hence, Eqs. (27) and (35) lead to  $p_l^0 < p_l$ .

When the equimolecular dividing surface is employed under the choice of the reference bulk liquid having  $T$  and  $\mu$  of the real system, the term  $\rho dR$  remains in Eqs. (20), (21), (24), and (25). It follows that

$$p_l - p = 2\gamma_G / R + \rho / (\omega R^2), \quad (43)$$

where the subscript  $G$  denotes Gibb's choice of the reference bulk liquid employed here. Rigorously speaking,  $R$  also needs the subscript  $G$ , but it is neglected because the bulk liquid is nearly incompressible. Eliminating  $\gamma_G$  from Eqs. (23) and (43), we get

$$-2\pi\rho R / \omega = E - TS - \mu N + p_l V_l + p V_v - 2\pi R^3 (p_l - p). \quad (44)$$

This equation determines  $\rho$  and  $\gamma_G$  is then determined by Eq. (43). Neglecting the pressure dependence of the molecular volume for the reference bulk liquid, it follows from Eqs. (23), which holds irrespective of the choices for both the reference bulk liquid and the dividing surface condition, that

$$(\gamma - \gamma_G) A = (p_l^0 - p_l) V_l. \quad (45)$$

Since  $p_l^0 < p_l$ , it follows that  $\gamma < \gamma_G$ . We get from Eq. (23) that

$$\gamma_G A = E^{\text{ex}} - TS^{\text{ex}}. \quad (46)$$

The reversible work to form a critical nucleus from the vapor is found to be

$$\Delta W^{\text{rev}} = \gamma_G A - (p_l - p) V_l \quad (47)$$

in the present case. The second term in Eq. (47) may be interpreted in connection with Fig. 3 as in the preceding cases. However, it is not possible to interpret the first term as the mechanical work illustrated in Fig. 4, because  $\gamma_G$  cannot be interpreted as the mechanical tension due to the existence of the second term in Eq. (43). Substituting Eq. (43) into Eq. (47), we get

$$\Delta W^{\text{rev}} = \gamma_G A / 3 - \rho R / 3. \quad (48)$$

#### IV. DISCUSSION

The cluster-size dependence of the surface tension in Nishioka's formalism is governed by Eq. (26), and the

following expression was derived at a constant temperature:<sup>2</sup>

$$\gamma(n) = -(Rn/v_l) \{ \partial[F(n)/n] / \partial n \}, \quad (49)$$

where  $F(n)$  denotes the Helmholtz free energy of a liquid microcluster containing  $n$  molecules.  $\gamma(n)$  was computed for argon<sup>2</sup> by employing the results of computer simulation due to Lee *et al.*<sup>3</sup> Difficulty caused by translation and rotation of a microcluster in vapor was avoided by assigning the internal free energy  $F^{\text{int}}(n)$  to  $F(n)$ . Let us consider this point in the following a little further. However, the rigorous treatment of the problem is formidable,<sup>11</sup> and it is not attempted here.

Canonical partition function of a liquid microcluster in vapor may be separated into the translational, rotational, and internal parts by introducing the coordinate frame so that its origin coincides with the center of mass of the microcluster and there is no angular momentum relative to it.<sup>12</sup> Hence, the center of the sphere in Fig. 1 may be regarded as the center of mass of a microcluster, and the quantities  $E_{4\pi}$  and  $S_{4\pi}$  may be considered as the sum of the internal parts for the microcluster and the values for the surrounding vapor. Similarly, the center of the hypothetical microcluster may be considered as its center of mass, and its internal energy and entropy as their internal parts. Following these considerations, the translational and the rotational degrees of freedom are supposed to be excluded from both the hypothetical and the real microclusters in the extrusion process shown in Fig. 4. This view corresponds to the Loth-Pound theory,<sup>13-16</sup> and the further consideration of the theory is given in a review article.<sup>11</sup>

Thus,  $S^{\text{ex}}$  in Eq. (26) represents the difference in the internal parts of the entropies between the real and the hypothetical microclusters. In addition to Eq. (26), the following rewritten form of Eq. (23) is employed to derive Eq. (49),<sup>2</sup>

$$\gamma A / 3 = [(E - TS) - (E_v - TS_v)] + p V_l - n \mu. \quad (50)$$

The first term in Eq. (50) represents the Helmholtz free energy of the real microcluster, which is denoted as  $F(n)$  and appears in Eq. (49). It follows from the foregoing discussion that the first term in Eq. (50) actually represents the internal free energy  $F^{\text{int}}(n)$ , hence the assignment<sup>2</sup> of  $F^{\text{int}}(n)$  to  $F(n)$  in Eq. (49) is shown to be reasonable. Furthermore, both  $\gamma$  in Nishioka's formalism and  $\gamma_s$  in Gibb's formalism with the surface of tension represent the reversible works of a very similar nature as clarified in the present section. Thus, the cluster-size dependence of  $\gamma_s$  is expected to possess behavior similar to that of  $\gamma$  for argon investigated earlier.<sup>2</sup>

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