

Grand potential formalism of interfacial thermodynamics for critical nucleus

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ABSTRACT

In nucleation theories, the work of formation of a nucleus is often denoted by $W = \Delta G$. This convention misleads that the nucleation should be considered in the isothermal-isobaric system. However, the pressure in the system with a nucleus is no longer uniform due to Laplace's equation. Instead, the chemical potential is uniform throughout the system for the critical nucleus. Therefore, one can consider the nucleation in the grand ensemble properly. Accordingly, W is found to be the grand potential difference and the interfacial tension is also turned to be an interfacial excess grand potential. This treatment is not entirely new; however, to explicitly treat in the grand potential formalism is for the first time. We have successfully given an overwhelmingly clear description.

Keywords: Gibbs Interfacial Thermodynamics; Grad Potential; Interfacial Tension; Work of Nucleus Formation

1. INTRODUCTION

The work of formation of a nucleus is often written as ΔG . It leads one to understand the work of formation of the critical nucleus as a difference of the Gibbs energy. The meaning of the form of the work of formation of a critical nucleus (Equation (4) in the text) becomes, however, clear straightforwardly if we deal the system including a critical nucleus as an isothermal-isochoric open system. The treatment as an isothermal-isobaric closed system brings confusions. The concept of the Gibbs dividing surface is more clearly understood in the isothermal-isochoric open system. As will be stated in the text, the treatments of an isothermal-isochoric open system appeared in literatures already. In this paper, we will give

a clearer and direct statement in the grand potential formalism for nucleation, aiming at helping researchers who are not specialists in thermodynamics. In other words, by describing with definite terminologies we will put forward understandings—some terminologies will be for the first time used definitely in this paper.

Gibbs established the interfacial thermodynamic formula for the work of formation of a critical nucleus in 1870s [1]. Since then, this subject was sometimes revisited and developed and/or extended [2-21]. One of true developments may be descriptions for the curvature-dependence of the interfacial tension [4,22-31]; as shall be described in Section 1.2, the interfacial tension γ is assumed to be known prior to the calculation of the radius R of the nucleus in the Gibbs formula. In other words, Gibbs' treatment (Section 1.2) alone does work for evaluating the work of formation of the critical cluster if the interfacial tension is independent of the curvature of the interface. Later Tolman's treatment was extended to the binary system [32]. Clarifying the meaning of the Gibbs dividing surface as done previously [2,3,5,11] and shall be done in Section 1.3 is helpful for general readers to avoid confusions, but not entirely new. Also embodiment of the variation of area A by defining the conical system with the solid angle ω around the center of the nucleus, such as done previously [2, 3,5,9,11,21], is, indeed, very helpful for ones who need rigorous arguments, but also not entirely new.

Throughout this paper we restrict ourselves to the case of spherical interfaces for simplicity and for the sake of avoiding complexity for better understanding. For example, two principal curvatures appear in general; this may bring confusion. Also, for the same sake we limit ourselves to unary cases. Also, for the same sake we omit the structure of both two phases; if at least one of the co-existing phases is crystalline, the interfacial tension becomes, strictly speaking, crystallographic orientation dependent.

1.1. Issue

One of purposes of the thermodynamics of nucleation is to calculate the reversible work of formation of a critical nucleus of a stable phase in an undercooled parent phase [1]. Through this work, W , one can obtain the steady-state nucleation rate as $J_s = J_0 e^{-W/k_B T}$ with $k_B T$ being the temperature multiplied by Boltzmann's constant. Not only in textbooks [34-36] but also in advanced research papers [14,37-45] the following expression (or essentially equivalent one) is seen for the work of formation of a critical nucleus:

$$\Delta G = n\Delta\mu + \gamma A, \quad (1)$$

where $\Delta\mu \equiv \mu^\beta - \mu^\alpha (< 0)$ is the difference between the chemical potentials of the nucleating phase (β phase) and the parent phase (α phase). The direct interpretation of Equation (1) is as follows. Limiting ourselves to the case that the molecular volumes (volumes per molecule) of the α and β phases are equal¹, let us denote the molecular volume V_m . Hereafter, the subscript m indicates the molecular quantities. Then, the quantity n is defined as the number of molecule consisting the nucleus, which is equal to $4\pi R^3/3V_m = V^\beta/V_m$ with $V^\beta \equiv 4\pi R^3/3$ being the volume of the nucleus. The first term in Equation (1) is the volume term, which is the reversible work associated with the transformation from the α phase to the β phase of n molecules. The second term in Equation (1) is the surface term, which is the reversible work to form a surface of area $A = 4\pi R^2$. Here, R is the radius of the nucleus; the rigorous definition of R will be given later. Remembering that the chemical potential is equal to the molecular Gibbs energy, the expression of ΔG seems at apparent appropriate. The question arises whether the expression of Equation (1) is only valid for the case that no volume change is associated with the α - β phase transition or not. Exact expression for the reversible work W was already given and the approximation which reduces the exact expression to Equation (1) was derived [11]. Also the expression of ΔG makes one understood at apparent that the interfacial tension γ is defined as the superficial interfacial Gibbs energy; also exact expression for γ was already given [7,11]. Unfortunately, the previous derivations were not so transparent. A clearer interpretation will be given in this paper in a framework of the grand potential formalism. This paper aims at leading the readers to a clear understanding of the work of formation of a nucleus and solving the misunderstanding. The meaning of

¹A slight consideration reveals that we are not limited to the case that no volume change is associated with the phase transition. If there is a volume change, one should account for effect of the total volume change in ΔG . In the main text, it is written that this situation is somewhat confusing. Naively thinking may impede going forward and result in going around three positions (Equations (3)-(5) of [33]).

the interfacial free energy (or the interfacial tension) γ becomes also clear; the interfacial tension γ can be understood as the superficial grand potential [3-5,9,11,12].

1.2. Gibbs Interfacial Thermodynamics

To review the Gibbs' formalism for evaluating W is not only heuristic but also ingredient for understanding the thermodynamic "ensemble" appropriate for the system of nucleation. In other words, due to this one can find why the grand potential formalism is appropriate; that is, constant μVT condition is imposed. It is sufficient to limit ourselves to the unary case; formulation for the multi-component system is seen, for example, in a previous paper [46].

Consider a spherical nucleus of the β phase in an undercooled α phase of the chemical potential $\mu^\alpha = \mu$ at the temperature T . The chemical potential μ and temperature T are regarded as those of the reservoir. Along with the isothermal condition, for the critical nucleus one can regard a cluster of the β phase is in equilibrium with the α phase with respect to the material transport. One can select $\{T, V, \mu\}$ as independent variables specifying the total system with V being the volume of the total system. The following is the procedure of the calculation of the work of formation of a critical nucleus.

1) The pressure of the β phase is determined by the equilibrium equation with respect to the materials transport, *i.e.*

$$\mu^\beta(p^\beta, T) = \mu. \quad (2)$$

2) Presuming the interfacial tension γ as known, the radius R is determined by Laplace's equation,

$$p^\beta - p^\alpha = \frac{2\gamma}{R}, \quad (3)$$

where p^α is the pressure of the α phase corresponding to (T, μ) .

3) The work of formation of the critical nucleus of radius R is calculated by

$$W = -(p^\beta - p^\alpha)V^\beta + \gamma A. \quad (4)$$

We note that eliminating $p^\beta - p^\alpha$ using Laplace's equation (Equation (3)), Equation (4) is rewritten into

$$W = \frac{1}{3}\gamma A. \quad (5)$$

We should note that the work of formation of a critical nucleus consists of two terms; as has been mentioned the first term is the volume term and, in turn, the second term is the surface term. The first term in Equation (4) is the work to replace the α phase of volume V^β with the β phase. The second term, γA , is understood as the work associated with the formation of area A of the

surface free energy γ per unit area. In other words, in writing the work of formation of the critical nucleus we divide the process of nucleus formation into two. One is to form a hypothetical nucleus of the β phase possessing the bulk properties throughout the entire volume V^β in the parent α phase. The other is regarded to that to form a actual structure of the interface.

1.3. Gibbs Dividing Surface and Surface of Tension

For the first one of the two works of formation of a critical nucleus, the mathematical surface of radius R is a key concept. This surface is called the Gibbs dividing surface. Owing to introducing the dividing surface one can divide the work of formation of a nucleus into two. The volume term is the work of formation of a hypothetical cluster as illustrated in **Figure 1**. The surface term of the form of γA is, however, not very general; this form is valid only for the surface of tension, which will be explained later. The general form includes a curvature-dependent term [7]. There are varieties of choices of the dividing surface. Most straightforward one is the equimolar surface; the total numbers of molecules of the hypothetical system and the real one are the same thereby. The dividing surface introduced in Section 1.2 is called the surface of tension as mentioned there. By this choice, the coefficient γ appears in the surface term in the work of formation of a critical nucleus coincides with the interfacial tension. The definition of the surface of tension is implicit; the choice so that the curvature-dependent term vanishes is the definition. For the choice of the surface of tension, Laplace's equation (Equation (3)) holds; Laplace's equation is the equation of the mechanical balance at the

order parameter

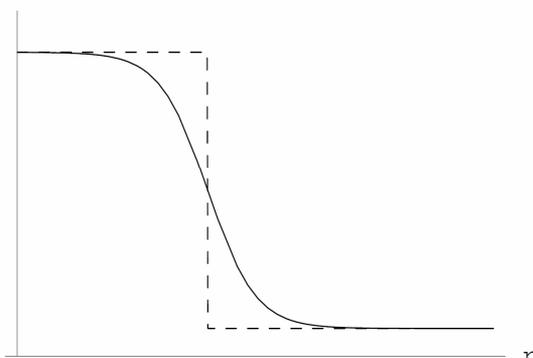


Figure 1. A schematic illustration of the profile of the order parameter (the density in, e.g., vapor-liquid case) with the horizontal axis indicating the distance from the center of the nucleus. In general, the order parameter varies between two bulk values gradually. Dashed lines indicate the hypothetical system, in which inside the dividing surface, indicated by a vertical dashed line, is occupied with a bulk β phase and outside with a bulk α phase.

curved interface possessing the mechanical tension γ . Therefore, the interfacial free energy γ is called the interfacial tension.

2. WORK OF FORMATION OF CRITICAL NUCLEUS

Sometimes very unnatural variables are specified [2,11]. That is, the internal energy E , the entropy S , and the amount of substances are selected as independent variable. The mass as well as the number of molecule can be employed as the amount of substances. Nevertheless, Nishioka [11,13] derived a correct conclusion that γ is equal to the superficial grand potential through an entangled argument.

As pointed in Section 1.2 the chemical potential throughout the system is uniform. Along with the fact that the system is considered as isothermal, it is appropriate to select the temperature T and the chemical potential μ as independent variables. In this case, because at least one extensive variable is necessary for complete description, the total system volume V must be, in general, selected as one of the independent variables. We note that the uniformity of the chemical potential was already pointed out [2]; the treatment there was, however, not fully satisfactory.

2.1. Isothermal-Isochoric Open System and Grand Potential

As mentioned above the temperature and the chemical potential are uniform throughout the system. One can regard that the system is exposed to the isobaric reservoir because if the chemical potential and the temperature are kept constant, the corresponding pressure, which is a function of T and μ , is also constant. In **Figure 2** we illustrate an isobaric closed system and an isochoric open system; whereas in the former the system size changes after the nucleation, in the latter the system size is unchanged thereafter. Therefore, we should take into

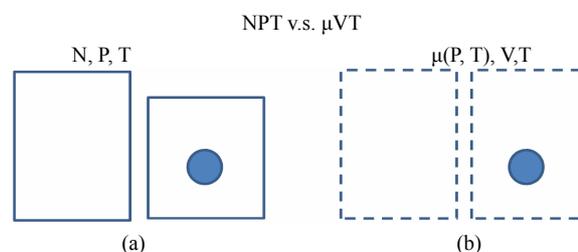


Figure 2. Comparison of the isobaric closed system and the isochoric open system before and after the nucleation. For clarity we assume that the nucleating phase is more condensed than the parent phase. In the isobaric case the total volume varies due to the nucleation. Accordingly, to figure out the work of formation of the nucleus in the isobaric system is somewhat complicated.

account the change of the total volume in calculation of the work of formation of a nucleus for the former case. This is somewhat complicated. Hence, it is convenient to treat the system as isothermal-isochoric open one. Of course, two ways of description are both correct. The reversible work calculated as the Gibbs energy difference should coincide to that calculated as the grand potential difference. Indeed, a consideration with confusions led to the correct answer [33]. Unfortunately, in [33] the volume term and the surface term had been intertwined with each other; the form of Equation (5) has been eventually obtained.

At least in Japan, a thermodynamics class does not teach the grand potential systematically. One can, however, obtain isochoric open system by Legendre transformation of the isothermal-isochoric closed system, *i.e.*, the independent variable is transformed from the amount of substances to the chemical potential to obtain this system [47]. The thermodynamic potential is obtained from the Helmholtz energy F by extracting $N\mu$ (remember that $\mu \equiv (\partial F / \partial N)_{T,V}$ is thermodynamic conjugate variable to N); that is,

$$\Omega = F - N\mu = F - G = -pV, \tag{6}$$

where $G = N\mu$ is the Gibbs energy. To reach to the last expression we have used the definition $G = F + pV$. One may be familiar with this form in the grand canonical ensemble (μVT ensemble) through the bridging relation in this ensemble [48]. The thermodynamic potential Ω is the grand potential. We note that the grand potential (or merely the symbol Ω) already appeared in a thermodynamic expression for the interface in literatures [20,25,28,31,42,49-51] and a textbook [48]. In addition, the grand potential Ω may be familiar in the fields of the density-functional theory.

By virtue of the last expression of Equation (6), we obtain the volume term of the work of formation of a critical nucleus, as the grand potential difference between the system including the hypothetical nucleus and the homogeneous α phase, as

$$\Delta\Omega = -(p^\beta - p^\alpha)V^\beta, \tag{7}$$

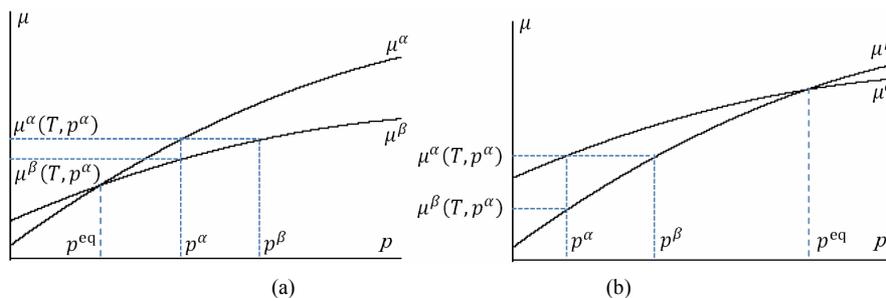


Figure 3. The μ - p relations are plotted for (a) a normal case ($V_m^\alpha > V_m^\beta$) and (b) an abnormal case ($V_m^\alpha < V_m^\beta$). Therefrom, one can confirm inequality $p^\beta > p^\alpha$.

where p^α and p^β are the pressures of respective bulk phases; even though there is no bulk part of the β phase in reality such as for a small nucleus, the pressure p^β is well defined (through Equation (2)). Due to the positive interfacial tension between the α and β phases, the pressure p^β of the phase inside the dividing surface is greater than p^α (thermodynamic derivation of this relation will be given in Section 2.2). In this way, we have the first term in Equation (4), which is negative and corresponding to the volume bulk term in Equation (1).

2.2. Work of Formation of Critical Nucleus

As argued up to now, we know that the work of formation of a critical nucleus is composed of the volume term, which is corresponding to the first term in Equation (1) and given by Equation (7), and the surface term, which is corresponding to the second term in Equation (1). If the equilibrium with respect to the materials transport holds between the parent phase and the nucleus, the pressure inside the nucleus, p^β , is obtained by solving

$$\mu^\alpha(T, p^\alpha) = \mu^\beta(T, p^\beta), \tag{8}$$

which corresponds to Equation (2) and consistent to the isothermal open system (μVT ensemble). Because the α phase is metastable and the β phase is the stable phase; that is,

$$\mu^\alpha(T, p^\alpha) > \mu^\beta(T, p^\alpha) \tag{9}$$

holds, one can derive $p^\beta > p^\alpha$. Recalling the Gibbs-Duhem relation $d\mu = -S_m dT + V_m dp$, we draw schematically the chemical potentials as functions of the pressure in **Figure 3**; the larger the slope is, the larger the molecular volume V_m is. In **Figure 3(a)**, we illustrate μ^α and μ^β for a normal case ($V_m^\alpha > V_m^\beta$). Because the α phase is metastable (Equation (9)), the location of p^α is in the side $p > p^{eq}$. Therefore, from Equation (8) one can find the location of p^β as illustrated in **Figure 3(a)**. An illustration for an abnormal case ($V_m^\alpha < V_m^\beta$) such as the case of water-ice phase transition is given in **Figure 3(b)**. The interpretation is logically the same.

In this way, the negativity of the volume term is understood. The criterion for the dividing surface has not been given yet. The surface term, in general, take a form [7,9,11]

$$\gamma(R)A + CdR. \quad (10)$$

Here, $\gamma(R)$ denotes that this coefficient depends on the criterion for the dividing surface. The surface of tension is defined by $C(R) = 0$. Only for this choice of R , the coefficient $\gamma(R)$ coincide with the interfacial tension. In other words, the surface term consist of, in general, the interfacial area dependent term and the curvature dependent term. The surface of tension is defined for which the curvature dependent term vanishes. We note that $\gamma(R)$ takes the minimum for the surface of tension [7].

In this way, we have obtained Equation (4) for the work of formation of a critical nucleus. We give a note here. The work for the formation of the critical nucleus takes, however, the same value if the physical condition is unchanged; that is, it is not dependent on the criterion of the dividing surface. Therefrom, one can derive the relation between the general $\gamma(R)$ and the interfacial tension. This was done by Kondo [7].

Noting $V^\beta = 4\pi R^3/3$ and $A = 4\pi R^2$, let us solve the equation that the derivative with respect to R of Equation (4) vanishes. By a simple calculation we have Laplace's equation (Equation (3)). This is a mechanical balance equation. Namely, in a case that two phases are co-existing via an interface of a curvature radius R with an interfacial tension γ , the force acting from the inside of the interface due to the pressure p^β balances with the composed force of the force due to the outside pressure p^α and that due to the interfacial tension (corresponding to $p^\alpha + 2\gamma/R$). The quantity γ defined as the interfacial free energy per unit area of the interface is, if one chooses the surface of tension as the dividing surface, coincides with the mechanical interfacial tension. Readers can readily confirm the coincidence between the unit of the energy per area and the tension.

Now, let us derive the form of the first term in Equation (1), following Nishioka and Kusaka [13]. We start with the relation

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m, \quad (11)$$

which is nothing other than the Gibbs-Duhem relation for the isothermal case. We consider a case that an incompressible β phase nucleus is nucleated in the α phase. Let us integrate Equation (11) for the β phase for p from p^α to p^β .

$$\mu^\beta(T, p^\beta) - \mu^\beta(T, p^\alpha) = \int_{p^\alpha}^{p^\beta} V_m^\beta dp = V_m^\beta (p^\beta - p^\alpha). \quad (12)$$

Eliminating $p^\beta - p^\alpha$ in Equation (4) using the equation derived by dividing Equation (12), we have an equation corresponding to Equation (1):

$$W = \frac{V^\beta}{V_m^\beta} \Delta \mu + \gamma A, \quad (13)$$

where

$$\begin{aligned} \Delta \mu &= \mu^\beta(T, p^\alpha) - \mu^\beta(T, p^\beta) \\ &= \mu^\beta(T, p^\alpha) - \mu^\alpha(T, p^\alpha). \end{aligned} \quad (14)$$

To reach to the last expression, Equation (8) has been used. One can integrate Equation (11) for the α phase to obtain the form of Equation (1) in a case that the α phase is incompressible. This is, however, not the present concern. It should be noted that for a case that no volume change is associated with the α - β phase transition, a form far from Equation (1) is obtained [52], although in this case one has intuitively $\Delta(n\mu) = n\Delta\mu$ with $n = V^\beta/V_m^\beta = V^\beta/V_m^\alpha$.

3. GIBBS ADSORPTION ISOTHERM

In this section, we derive the Gibbs adsorption isotherm

$$\left(\frac{\partial \gamma}{\partial \mu}\right)_T = -\Gamma, \quad (15)$$

where μ represents the chemical potential of the materials reservoir, which is equal to μ^α , and Γ is the superficial number density per unit area of the interface, sometimes referred to as the excess number density or the interfacial adsorption quantity. A rigorous definition of Γ will be given later.

3.1. Conical System and Superficial Quantities

We define the system as a spherical cone as illustrated in **Figure 4**. In this definition, there are two variables describing the extent of the system; through the solid angle ω we can apply Euler's theorem for the homogeneous equation. Unlike previous papers [9,11,13], we define the system as open with the chemical potential μ . In those papers, the arguments were started with selecting the entropy S , the number of molecule N , the radius R_0 , and the solid angle ω as independent variables. However, the argument becomes simplified with the selection of independent variables T and μ , instead of S and N . We note that R_0 is selected enough larger than R .

For the hypothetical system, because of the bulk properties, the following fundamental equations (Gibbs relations) hold for two parts of the system:

$$dE^{\alpha,\beta} = TdS^{\alpha,\beta} - p^{\alpha,\beta}dV^{\alpha,\beta} + \mu dN^{\alpha,\beta}. \quad (16)$$

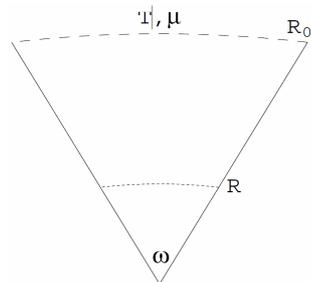


Figure 4. Conical system with the solid angle ω around the center of the nucleus. The system is defined as isochoric with the solid angle ω and the radius R_0 . The system is exposed to the reservoir of the temperature T and the chemical potential μ .

Here, according to a convention E is used to represent the internal energy. This equation is rewritten in terms of the grand potentials $\Omega^{\alpha,\beta} = E^{\alpha,\beta} - TS^{\alpha,\beta} - \mu N^{\alpha,\beta}$ as

$$d\Omega^{\alpha,\beta} = -p^{\alpha,\beta} dV^{\alpha,\beta} - V^{\alpha,\beta} dp^{\alpha,\beta} - S^{\alpha,\beta} dT - p^{\alpha,\beta} dV^{\alpha,\beta} - N^{\alpha,\beta} d\mu \tag{17}$$

Those equations hold for both systems with the solid angle ω , and the entire sphere ($\omega = 4\pi$). In those expressions

$$V^\beta = \omega R^3 / 3, \tag{18}$$

$$V^\alpha = \omega (R_0^3 - R^3) / 3, \tag{19}$$

and we should note that R_0 and ω are independent variables.

Let us denote quantities for the entire spherical system by symbols with a superscript 4π and those for the system with the solid angle ω by symbols without a superscript. For a while, let us consider again a general dividing surface. Denoting the contribution due to the nucleus by \dots , the fundamental equation

$$d\Omega^{4\pi} = -S^{4\pi} dT - p^\alpha dV^{4\pi} - N^{4\pi} d\mu^\alpha + \dots, \tag{20}$$

holds. Here, $V^{4\pi} = 4\pi R_0^3 / 3$ and because the R_0 is an independent variable, $dV^{4\pi} = 4\pi R_0^2 dR_0$. Let us rewrite Equation (20) using $S = (\omega/4\pi) S^{4\pi}$, $V = (\omega/4\pi) V^{4\pi}$, and $N = (\omega/4\pi) N^{4\pi}$. Because $dV = \omega R_0^2 dR_0 + (R_0^3/3) d\omega$ (from $V = \omega R_0^3 / 3$), we have

$$d\Omega = -SdT - p^\alpha [\omega R_0^2 dR_0 + (R_0^3/3) d\omega] - Nd\mu^\alpha = -SdT - p^\alpha \omega R_0^2 dR_0 - Nd\mu^\alpha + \sigma d\omega. \tag{21}$$

Here, we express the contribution of the nucleus by introducing the coefficient σ defined by

$$\sigma = (\partial\Omega/\partial\omega)_{T,R_0,\mu^\alpha} = (\partial E/\partial\omega)_{S,R_0,\mu^\alpha} \tag{22}$$

as previously done [2,3,5,9,11,13]. In those previous papers, the expression in the square brackets was given.

Differentiating $\Omega = (\omega/4\pi)\Omega^{4\pi}$ and using Equation (20), we have

$$d\Omega = (\omega/4\pi) d\Omega^{4\pi} + (\Omega^{4\pi}/4\pi) d\omega = -SdT - p^\alpha \omega R_0^2 dR_0 - Nd\mu^\alpha + (\Omega/\omega) d\omega. \tag{23}$$

By comparing Equations (21) and (23), we obtain

$$\sigma = \Omega/\omega \equiv (E - TS - \mu^\alpha N) / \omega. \tag{24}$$

In previous papers [2,3,5,9,11,13], the last expression was given, despite that the mid expression is conceptually meaningful. This equation is the equation obtained from the relation on the basis of the fact that when the solid angle is multiplied by λ , the grand potential $\Omega(T, R_0, \mu^\alpha; \omega)$ is transformed as

$$\Omega(T, R_0, \mu^\alpha; \lambda\omega) = \lambda\Omega(T, R_0, \mu^\alpha; \omega)$$

(Euler's theorem). We note that Nishioka [11] derived the same equation by applying Euler's theorem to E .

3.2. Interfacial Tension

In Equation (21), existence of $\sigma d\omega$ is due to the nucleus. Therefore, one can write

$$\sigma d\omega = -p^\alpha dV^\alpha - p^\beta dV^\beta + \gamma dA + CdR, \tag{25}$$

(pay attention on the independent variables). The first two terms are of the hypothetical system defined in Section 3.1. The last two terms are for forming interfacial structure after the formation of the hypothetical system. As mentioned above, we note that a term depending on the derivative of the curvature radius, dR , appears. This term, also as mentioned above, vanishes if the surface of tension is taken as the dividing surface.

Let us go forward the argument by taking the surface of tension as the dividing surface. Using the equation obtained by putting $C = 0$ in Equation (25), we rewrite Equation (21) into

$$d\Omega = -SdT - p^\alpha \omega R_0^2 dR_0 - Nd\mu^\alpha - p^\alpha dV^\alpha - p^\beta dV^\beta + \gamma dA. \tag{26}$$

The fundamental equation for the hypothetical system is just the addition of both of Equation (17):

$$d(\Omega^\alpha + \Omega^\beta) = -(S^\alpha + S^\beta) dT - p^\alpha dV^\alpha - p^\beta dV^\beta - (N^\alpha + N^\beta) d\mu. \tag{27}$$

Subtracting Equation (27) from Equation (26), we

have the fundamental equation for the superficial grand potential $\Omega^s = \Omega - (\Omega^\alpha + \Omega^\beta)$:

$$\begin{aligned} d\Omega^s &= -S^s dT - N^s d\mu^\alpha + \gamma dA \\ &= -S^s dT - N^s d\mu^\alpha + \gamma R^2 d\omega, \end{aligned} \quad (28)$$

where $S^s = S - (S^\alpha + S^\beta)$ and $N^s = N - (N^\alpha + N^\beta)$ are, respectively, the superficial entropy and the superficial number of molecules. In this equation $-p^\alpha \omega R_0^2 dR_0$ has been eliminated because the state of the interface is independent of the selection of R_0 ; in other words, R_0 has been fixed at the position $R_0 \gg R$.

Euler's relation obtained from the fact that Ω^s is transformed as $\Omega(T, \mu^\alpha; \lambda\omega) = \lambda\Omega(T, \mu^\alpha; \omega)$ when ω is multiplied by λ as $\omega \rightarrow \lambda\omega$ is

$$\gamma A = \Omega^s = E^s - TS^s - N^s \mu. \quad (29)$$

To derive this equation, one can use the same method to derive Equation (24). From Equation (29), the interfacial tension γ is revealed to be the superficial grand potential per unit area of the interface. Introducing the superficial quantities per unit area of the interface, $e^s = E^s/A$, $s^s = S^s/A$, and $\Gamma = N^s/A$, we have

$$\gamma = \Omega^s/A = e^s - Ts^s - \Gamma\mu. \quad (30)$$

The last expressions in Equations (29) and (30) have already been given in previous papers [3,4,5,9,11-13,15,20,21,31]. In those papers, except for [12,20,21,31]—Rusanov *et al.* [20] explicitly stated, however, the word of the superficial grand potential did not appear.

3.3. Gibbs-Duhem Relation for Interface

A general way to obtain the Gibbs-Duhem relation is to take differential of Euler's relation and subtract the fundamental equation. For the interface, the same procedure is possible; we can have the Gibbs-Duhem relation for the interface

$$d\gamma = -s^s dT - \Gamma d\mu^\alpha, \quad (31)$$

by taking differential of Equation (29) and subtract the first equation of Equation (28) and dividing by A . We can, also, obtain Equation (31) by direct differentiation of Equation (30) and using the fundamental equation for e^s . From Equation (31) we have Equation (15) or $d\gamma = -\Gamma d\mu$ ($T = \text{const.}$). This is the Gibbs adsorption isotherm.

4. SUMMARY

We have given a grand potential formalism for the interfacial thermodynamics. It is revealed that the work of formation of a critical nucleus is equal to the grand potential difference. This makes a point of view clearer overwhelmingly than regarding the work of formation of the nucleus as the Gibbs energy difference. Also, the

interfacial tension is revealed to be defined as the superficial grand potential per unit area of the interface. Although equivalent form was given previously [3-5,9,11,13], this paper has explicitly closed up the grand potential property for the first time.

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