

# Liquid-drop formalism and free-energy surfaces in binary homogeneous nucleation theory

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Three different derivations of the classical binary nucleation theory are considered in detail. It is shown that the derivation originally presented by Wilemski [J. Chem. Phys. **80**, 1370 (1984)] is consistent with more extensive derivations [Oxtoby and Kashchiev, J. Chem. Phys. **100**, 7665 (1994)]; Debenedetti, *Metastable Liquids: Concepts and Principles* (Princeton University Press, Princeton, 1996) if and only if the assumption is made that the surface of tension of the binary nucleus coincides with the dividing surface specified by the surface condition  $\sum n_{s,i} v_{li} = 0$ , where the  $n_{s,i}$  denote surface excess numbers of molecules of species  $i$ , and the  $v$ 's are partial molecular volumes. From this condition, it follows that (1) the surface tension is curvature independent and (2) that the nucleus volume is  $V = \sum n_{li} v_{li} = \sum g_i v_{li}$ , where the  $n_{li}$  are the numbers of molecules in the uniform liquid phase of the droplet model encompassed by the surface of tension, and the  $g_i$  are the total molecular occupation numbers contained by the nucleus. We show, furthermore, that the above surface condition leads to explicit formulas for the surface excess numbers  $n_{s,i}$  in the nucleus. Computations for the ethanol–water system show that the surface number for water molecules ( $n_{s,H_2O}$ ) causes the negative occupation numbers ( $g_{H_2O}$ ) obtained earlier using the classical nucleation theory. The unphysical behavior produced by the classical theory for surface active systems is thus a direct consequence of the assumption of curvature independence of surface tension. Based on the explicit formulas for  $n_{s,i}$ , we calculate the full free-energy surfaces for binary nucleation in the revised classical theory and compare these with the free-energy surfaces in the Doyle (unrevised classical) theory. Significant differences in nucleus size and composition are found between these models and they are related to surface excess density. It is shown that only for the revised classical theory is the nucleus composition consistent with the Gibbs dividing surface model. © 1999 American Institute of Physics. [S0021-9606(99)51029-5]

## I. INTRODUCTION

The classical binary nucleation theory is still today the only working theory that can be applied for calculation of nucleation rates in nonideal molecular systems such as sulfuric acid/water, which is thought to be important in atmospheric particle formation. Despite the simple appearance of the equations of the theory, their derivation contains puzzles that have not been solved so far. For example, Debenedetti<sup>1,2</sup> has noted that the derivation presented by Wilemski<sup>3</sup> starts off with an incorrect equation, but “interestingly” the resulting equations are correct. Furthermore, it is known that with surface active systems such as ethanol/water, the theory sometimes produces unphysical predictions (negative occupation numbers of water molecules in critical nuclei), but the specific reasons for this behavior are somewhat unclear. Below, we will examine closely three different derivations of the theory, namely, a derivation extended from the work of Oxtoby and Kashchiev,<sup>4</sup> a derivation by Debenedetti<sup>1</sup> and a derivation by Wilemski,<sup>3</sup> and show that the last one is con-

sistent with the others if (and only if) a certain dividing surface is assumed to coincide with the surface of tension of the critical nucleus. We will also show that the unphysical predictions are due to the same assumption, which, on the other hand, has to be made in order to justify the application of curvature-independent surface tension in the calculations. We will also compare the various derivations with those given by Nishioka and Kusaka.<sup>5</sup> We then go on to consider the numerical consequences of our findings.

## II. THEORY

### A. Oxtoby–Kashchiev derivation

Consider a two-component spherical cluster that has a volume  $V$  and contains  $g_1$  and  $g_2$  molecules of each component, respectively. The cluster reference state is modeled as a spherical liquid drop that has a sharp boundary (Gibbs dividing surface) between the liquid and vapor phases. Differences between the true cluster and the reference state in the

Gibbs dividing surface model are collected in the surface excess quantities. Thus the total number of each species in the cluster (excess number of molecules over the uniform vapor phase) is independent of choice of dividing surface and can be written as

$$g_i = n_{li} - n_{vi} + n_{si}, \quad (1)$$

where  $n_{li} = V\rho_{li}$  and  $n_{vi} = V\rho_{vi}$  with  $\rho_{li}$  and  $\rho_{vi}$  densities of species  $i$  in the uniform liquid and vapor phases, respectively, and  $n_{si}$  is the surface excess number of molecules of species  $i$  that corrects for the difference between the numbers of molecules that are obtained by integrating over the step profiles and over the actual interfacial density profiles, respectively.

The free-energy change to create the cluster can now be expressed as<sup>4</sup>

$$\begin{aligned} \Delta G = & (P_v - P_l)V + \sum_i (\mu_{li} - \mu_{vi})n_{li} \\ & + \sum_i (\mu_{si} - \mu_{vi})n_{si} + \Phi(g_1, g_2, V). \end{aligned} \quad (2)$$

Here the  $P$ 's are the pressures and the  $\mu_i$ 's the chemical potentials of the uniform liquid and vapor phases (taken at the pressure and composition of the respective phase), and  $\Phi$  is an excess energy term dependent on both  $V$  and  $g_i$ . The critical nucleus is in unstable equilibrium with the environment. Thus we can set the partial derivatives of  $\Delta G$  with respect to  $V$ ,  $n_{li}$ , and  $n_{si}$  equal to zero and obtain the following conditions:

$$\mu_{li}^* = \mu_{si}^* = \mu_{vi}, \quad (3)$$

$$\Delta P^* = P_l^* - P_v = [\partial\Phi^*/\partial V^*], \quad (4)$$

where the asterisk denotes critical cluster, and the derivative in square brackets is associated with a mathematical displacement of the dividing surface keeping all the physical quantities of the system unaltered. The work of nucleus formation then takes the form

$$W^* = \Delta G^* = -\Delta P^* V^* + \Phi^*. \quad (5)$$

The subject of the paper of Oxtoby and Kashchiev<sup>4</sup> is thermodynamic derivation of the nucleation theorem, and they do not go any further in treating the pressure difference and the nucleation work. However, producing the usual equations of the classical nucleation theory from Eqs. (4) and (5) is rather simple. Assume that the excess energy term can be written as

$$\Phi^* = A^* \sigma, \quad (6)$$

where  $\sigma$  denotes surface tension, and the surface area and the volume are

$$A^* = 4\pi R^{*2}, \quad (7)$$

$$V^* = (4\pi/3)R^{*3} = \sum n_{li} v_{li}, \quad (8)$$

where  $v_{li} \equiv (\partial V/\partial n_{li})|_{T, P_l, n_{lj}(j \neq i)}$  the partial molecular volume of species  $i$ . Next, fix the volume of the droplet by requiring that  $[\partial\sigma(g^*, V^*)/\partial V^*] = 0$ . The special surface

$R_t^*$  at which this requirement holds is called the surface of tension, and we denote the surface tension at  $R_t^*$  (which is a function of  $g_1^*$  and  $g_2^*$  only) by  $\sigma_t$ . Thus,

$$\Delta P^* = 2\sigma_t/R_t^*, \quad (9)$$

$$W^* = -\Delta P^* V_t^* + A_t^* \sigma_t. \quad (10)$$

The differentials of chemical potential and total pressure in the liquid phase are related by

$$d\mu_{li} = v_{li} dP_l, \quad (11)$$

which holds for changes where temperature and composition of the liquid are kept constant. If the liquid phase is assumed incompressible, we can integrate this relation from  $P_v$  to  $P_l$  and use the equality of chemical potentials to write

$$\begin{aligned} v_{li} \Delta P &= \mu_{li}(P_l) - \mu_{li}(P_v) \\ &= \mu_{vi}(P_v) - \mu_{li}(P_v) = -\Delta\mu_i, \end{aligned} \quad (12)$$

to obtain the Kelvin equation

$$\Delta\mu_i^* = -2\sigma_t v_{li}/R_t^* \quad (13)$$

and the work of nucleus formation

$$W^* = \sum_i n_{li}^* \Delta\mu_i^* + A_t^* \sigma_t. \quad (14)$$

Finally, note that it follows already from Eq. (12) that

$$\Delta\mu_1^*/v_{l1} = \Delta\mu_2^*/v_{l2}. \quad (15)$$

This equation is used in the revised classical nucleation theory to determine the nucleus composition, and it is often assumed to be a consequence of the binary Kelvin equations. Importantly, however, incompressibility of the liquid phase is the only assumption needed in its derivation, and it is therefore more fundamental than the capillarity approximation, or the Kelvin equations, which contain surface tension.

## B. Debenedetti derivation

Debenedetti<sup>1</sup> gives the the work of formation of a droplet inside vapor phase in otherwise the same form as the free-energy change of Oxtoby and Kashchiev<sup>4</sup> [Eq. (2)], but the excess energy term is already fixed to be surface area times surface tension, and the dividing surface is taken to be the surface of tension. Debenedetti then goes on to use the incompressibility assumption, Eq. (12), to obtain

$$\begin{aligned} W &= \sum_i (\mu_{li}(P_v) - \mu_{vi}(P_v))n_{li} \\ &+ \sum_i (\mu_{si} - \mu_{vi}(P_v))n_{si} + A_t \sigma_t. \end{aligned} \quad (16)$$

The conditions  $(\partial W/\partial n_{li})|_{\{n_{si}, n_{lj \neq i}\}} = 0$  and  $(\partial W/\partial n_{si})|_{\{n_{li}, n_{sj \neq i}\}} = 0$  then lead to

$$\begin{aligned} \frac{\partial W}{\partial n_{lj}} &= \sigma_t \frac{\partial A_t}{\partial n_{lj}} + \Delta\mu_j + A_t \frac{\partial \sigma_t}{\partial n_{lj}} + \sum_i n_{si} \frac{\partial \mu_{si}}{\partial n_{lj}} \\ &+ \sum_i n_{li} \frac{\partial \mu_{li}}{\partial n_{lj}} = 0, \end{aligned} \quad (17)$$

$$\begin{aligned} \frac{\partial W}{\partial n_{sj}} &= \sigma_t \frac{\partial A_t}{\partial n_{sj}} + \Delta \mu'_j + A_t \frac{\partial \sigma_t}{\partial n_{sj}} \\ &+ \sum_i n_{si} \frac{\partial \mu_{si}}{\partial n_{sj}} + \sum_i n_{li} \frac{\partial \mu_{li}}{\partial n_{sj}} = 0, \end{aligned} \quad (18)$$

with  $\Delta \mu_j = \mu_{lj}(P_v) - \mu_{vj}(P_v)$  and  $\Delta \mu'_j = \mu_{sj} - \mu_{vj}(P_v)$ . The sum of the third and fourth terms on the right hand side of the first equalities in both Eqs. (17) and (18) vanishes because of the Gibbs adsorption isotherm

$$\sum_i n_{si} d\mu_{si} + A_t d\sigma_t = 0, \quad (19)$$

and the fifth terms cancel because of the Gibbs–Duhem equation at constant temperature and pressure,

$$\sum_i n_{li} d\mu_{li} = 0. \quad (20)$$

The surface area is

$$A_t = 4\pi R_t^2 = 4\pi \left( \frac{3}{4\pi} \sum_i (v_{li} n_{li}) \right)^{2/3} \quad (21)$$

and thus  $(\partial A_t / \partial n_{lj}) = (2 v_{lj} / R_t)$  and  $(\partial A_t / \partial n_{sj}) = 0$ . The equilibrium conditions are then

$$\Delta \mu_i^* + 2\sigma_t v_{li} / R_t^* = 0, \quad (22)$$

$$\Delta \mu'_j = 0, \quad (23)$$

and the work of droplet formation becomes the same as with Oxtoby and Kashchiev.<sup>4</sup>

### C. Surface tension

At this point we note that the Kelvin equations given in the form of Eq. (22) contain a surface tension  $\sigma_t$  which is not specified to be that of a flat interface,  $\gamma$ . In one component nucleation theory, the approximation  $\sigma_t = \gamma$  is equivalent to the assumption that the equimolar dividing surface coincides with the surface of tension,<sup>6</sup> or, equivalently, to the condition  $n_s = 0$ . For the binary and multicomponent cases this result can be generalized as follows: Consider the special dividing surface ( $K$ ) defined by the condition  $\sum_i n_{si}^K v_{li} = 0$ . We now follow Ono and Kondo<sup>7</sup> and show that curvature independence of surface tension is equivalent to the assumption that this special dividing surface ( $K$ ) coincides with the surface of tension.

The form of the adsorption isotherm given in Eq. (19) holds for the surface of tension only. Using the adsorption isotherm we can express the differential of the surface tension in terms of differentials of chemical potentials,

$$\begin{aligned} d\sigma_t &= - \sum_i (n_{si} / A_t^*) d\mu_{si} \\ &= - \sum_i (n_{si} / A_t^*) d\mu_{li} = - \sum_i (n_{si} / A_t^*) v_{li} dP_l, \end{aligned} \quad (24)$$

where we have used the phase equilibrium condition (3) and relation (11) to obtain the last two equalities. Equation (24)

holds for changes where the phase equilibrium is maintained and the temperature as well as the composition of the liquid phase ( $x$ ) are kept constant, whereas the pressures of both phases, the composition of the gas phase and the radius associated with the surface of tension are allowed to vary.

The expression for the derivative of surface tension with respect to the radius follows directly from Eq. (24),

$$\left( \frac{d\sigma_t}{dR_t^*} \right)_{x,T} = \left( \frac{dP_l}{dR_t^*} \right)_{x,T} \sum_i (n_{si} / A_t^*) v_{li}. \quad (25)$$

Since the liquid pressure is inevitably dependent on the radius  $R_t^*$  according to Eq. (9), the condition  $\sum_i n_{si} v_{li} = 0$  has to be satisfied at the surface of tension for the curvature dependence of the surface tension to vanish.

An alternative route to obtain this condition is presented below. Consider changes in the surface tension defined at the surface of tension, and evaluate these changes at constant nucleus composition ( $x$ ). These variations can only be produced by variations in gas-phase chemical potentials, thus

$$\left( \frac{\partial \sigma_t}{\partial R_t^*} \right)_{x,T} = \sum_i \left( \frac{\partial \sigma_t}{\partial \mu_{vi}} \right)_{x,T} \left( \frac{\partial \mu_{vi}}{\partial R_t^*} \right)_{x,T}. \quad (26)$$

We now seek the condition that the left-hand side, giving the curvature dependence of  $\sigma_t$ , is zero. Consider, first, the first terms on the right-hand side of Eq. (26). For simplicity, subscript  $T$  is dropped, although all the derivatives are taken at constant temperature. Using the chain rule we obtain

$$\left( \frac{\partial \sigma_t}{\partial \mu_{vi}} \right)_x = \left( \frac{\partial \sigma_t}{\partial \mu_{vi}} \right)_{\mu_{vj}} + \left( \frac{\partial \sigma_t}{\partial \mu_{vj}} \right)_{\mu_{vi}} \frac{v_{lj}}{v_{li}} = \frac{-n_{si}}{A_t} - \frac{n_{sj}}{A_t} \frac{v_{lj}}{v_{li}}. \quad (27)$$

The first equality is obtained using Eq. (11) in the liquid phase and the equality of chemical potentials in the gas and liquid phases, leading to  $d\mu_{vi} = v_{li} dP_l$ , and further to

$$\left( \frac{\partial \mu_{vj}}{\partial \mu_{vi}} \right)_x = \frac{v_{lj}}{v_{li}}. \quad (28)$$

The second equality in Eq. (27) follows from the Gibbs adsorption isotherm (19), which gives

$$\left( \frac{\partial \sigma_t}{\partial \mu_{vi}} \right)_{\mu_{vj}} = - \frac{n_{si}}{A_t}. \quad (29)$$

Inserting Eq. (27) for  $i=1,2$  to Eq. (26) we have

$$\begin{aligned} \left( \frac{\partial \sigma_t}{\partial R_t^*} \right)_x &= \left( \frac{-n_{s1} v_{l1} - n_{s2} v_{l2}}{A_t} \right) \\ &\times \left[ \left( \frac{\partial \mu_{v1}}{\partial R_t^*} \right)_x \frac{1}{v_{l1}} + \left( \frac{\partial \mu_{v2}}{\partial R_t^*} \right)_x \frac{1}{v_{l2}} \right]. \end{aligned} \quad (30)$$

Consider now the reciprocals of the second factors on the right-hand side of Eq. (26). By analysis similar to Eq. (27), we obtain

$$\begin{aligned} \left(\frac{\partial R_t^*}{\partial \mu_{vi}}\right)_x &= \left(\frac{\partial R_t^*}{\partial \mu_{vi}}\right)_{\mu_{vj}} + \left(\frac{\partial R_t^*}{\partial \mu_{vj}}\right)_{\mu_{vi}} \left(\frac{\partial \mu_{vj}}{\partial \mu_{vi}}\right)_x \\ &= \left(\frac{\partial R_t^*}{\partial \mu_{vi}}\right)_{\mu_{vj}} + \left(\frac{\partial R_t^*}{\partial \mu_{vj}}\right)_{\mu_{vi}} \frac{V_{lj}}{V_{li}}. \end{aligned} \quad (31)$$

Inserting Eq. (31) for  $i=1,2$  to Eq. (30) we end up with

$$\begin{aligned} \left(\frac{\partial \sigma_t}{\partial R_t^*}\right)_x &= \frac{-2}{A_t} (n_{s1} V_{l1} + n_{s2} V_{l2}) \\ &\quad \times \left[ V_{l1} \left(\frac{\partial R_t^*}{\partial \mu_{v1}}\right)_{\mu_{v2}} + V_{l2} \left(\frac{\partial R_t^*}{\partial \mu_{v2}}\right)_{\mu_{v1}} \right]^{-1}. \end{aligned} \quad (32)$$

Since the expression in the square brackets is obviously finite, the required condition that the surface tension is independent of curvature is

$$\sum_i n_{si} V_{li} = 0. \quad (33)$$

The “ $K$ ”-dividing surface was mentioned in a paper by Frank Buff<sup>8</sup> who noted that this surface “is conjugate to the surface of tension” in the sense that “the distance between these two dividing surfaces determines the curvature dependence of these two surface tensions.” Equation (33), giving the condition for vanishing curvature dependence of the surface tension, as defined at the surface of tension, is precisely the condition that the distance between these two surfaces vanishes as well. Thus it appears that our findings on this important point were long ago anticipated by Buff.

#### D. Wilemski derivation

Wilemski<sup>3</sup> assumes that the free-energy change to create a cluster can be written as

$$\Delta G = \sum_i (\mu_{li}(P_v) - \mu_{vi}(P_v)) g_i + A \gamma, \quad (34)$$

where  $\gamma$  is the surface tension of a flat interface. The volume of the cluster is taken to be  $V = g_1 V_{l1} + g_2 V_{l2}$ , and the radius and surface area are obtained from  $V = (4\pi/3)R^3$ ,  $A = 4\pi R^2$ . The critical cluster is then located by requiring that

$$\left(\frac{\partial \Delta G}{\partial g_i}\right)_{g_j} = 0. \quad (35)$$

Applying Eq. (1) and assuming that the vapor term  $n_{vi}$  is negligible, one has

$$\begin{aligned} \left(\Delta \mu_i^* + \frac{2\gamma V_{li}}{R^*}\right) dg_i + n_{l1} d\mu_{l1} + n_{l2} d\mu_{l2} \\ + n_{s1} d\mu_{s1} + n_{s2} d\mu_{s2} + A^* d\gamma = 0. \end{aligned} \quad (36)$$

The Gibbs–Duhem equation (20) and the Gibbs adsorption isotherm (19) (with  $\sigma_t = \gamma$ ) are then used to cancel terms from Eq. (36), leading to the Kelvin equations

$$\Delta \mu_i^* + \frac{2\gamma V_{li}}{R^*} = 0, \quad (37)$$

and the free energy change for the critical clusters reads

$$\Delta G^* = (4\pi/3)R^{*2}\gamma. \quad (38)$$

#### E. Relation between the different formalisms

The main difference between the Oxtoby–Kashchiev and Debenedetti derivations is clearly that in the former derivation the incompressibility assumption is used after the equilibrium conditions are evoked, whereas in the latter derivation the incompressibility assumption is applied first. Otherwise, both derivations start from the same work of formation (although the surface excess term is more general in the Oxtoby–Kashchiev derivation), and end up with the Kelvin equation and the same  $W^*$ . The curious thing here is the Wilemski derivation, which starts off with a different equation than do the others, but ends up with the same result.

The problem can be solved by noting that Eq. (16) reduces to Eq. (34) under the special circumstances that  $n_{s1} V_{l1} + n_{s2} V_{l2} = 0$  as will be shown below. Remember, first, that when the condition  $n_{s1} V_{l1} + n_{s2} V_{l2} = 0$  holds at the surface of tension,  $\sigma_t = \gamma$ . Furthermore, the volume is then  $V = \sum_i n_{li} V_{li} = \sum_i g_i V_{li}$ , so that the surface areas specified in Eqs. (16) and (34) are the same ( $A_t = A$ ), and the surface term in Eq. (16) is thus equal to  $A\gamma$ .

The first sum in Eq. (16) can be written as

$$\begin{aligned} \sum_i \Delta \mu_i n_{li} &= \sum_i \Delta \mu_i (g_i - n_{si}) \\ &= \sum_i \Delta \mu_i g_i - n_{s2} V_{l2} \left( -\frac{\Delta \mu_1}{V_{l1}} + \frac{\Delta \mu_2}{V_{l2}} \right) \\ &= \sum_i \Delta \mu_i g_i, \end{aligned} \quad (39)$$

where it has been assumed that the numbers of displaced vapor molecules,  $n_{vi}$ , are negligible, and the last equality follows from Eq. (15). Equation (16) then becomes

$$W = \sum_i \Delta \mu_i g_i + \sum_i \Delta \mu'_i n_{si} + A \gamma. \quad (40)$$

Applying the equilibrium condition  $(\partial W / \partial n_{si})|_{\{n_{li}, n_{sj \neq i}\}} = 0$  yields

$$\begin{aligned} \frac{\partial W}{\partial n_{sj}} &= \sigma_t \frac{\partial A_t}{\partial n_{sj}} + \Delta \mu'_j + A_t \frac{\partial \sigma_t}{\partial n_{sj}} + \sum_i n_{si} \frac{\partial \mu_{si}}{\partial n_{sj}} \\ &\quad + \sum_i g_i \frac{\partial \mu_{li}}{\partial n_{sj}} = 0. \end{aligned} \quad (41)$$

The first, third, and fourth terms cancel in the same way as with Eq. (18). The fifth term is

$$\sum_i g_i \frac{\partial \mu_{li}}{\partial n_{sj}} = \sum_i \left( n_{li} \frac{\partial \mu_{li}}{\partial n_{sj}} \right) + n_{s1} \frac{\partial \mu_{l1}}{\partial n_{sj}} + n_{s2} \frac{\partial \mu_{l2}}{\partial n_{sj}}. \quad (42)$$

The first term on the right-hand side of this equation vanishes because of Gibbs–Duhem relation, and the remaining terms can be written as

$$n_{s2} v_{l2} \left( -v_{l1}^{-1} \frac{\partial \mu_{l1}}{\partial n_{sj}} + v_{l2}^{-1} \frac{\partial \mu_{l2}}{\partial n_{sj}} \right), \quad (43)$$

which is zero, as can be seen by noting that since  $n_{li}$  are kept constant it follows from the relation  $d\mu_{li} = v_{li} dP_l$  [Eq. (11)] that  $d\mu_{l1}/v_{l1} - d\mu_{l2}/v_{l2} = dP_l - dP_l = 0$ . We thus have  $\Delta\mu' = 0$ , and substituting this into Eq. (40) gives us Wilemski's starting relation, Eq. (34).

Finally, we note that the second equilibrium condition,  $(\partial W/\partial n_{li})|_{\{n_{si}, n_{lj \neq i}\}} = 0$  can be replaced by  $(\partial W/\partial g_i)|_{\{g_j \neq i\}} = 0$  because  $g_i = n_{li} + n_{si}$ , and thus the rest of Wilemski's derivation is consistent.

### F. Comparison to work by Nishioka and Kusaka

The paper by Nishioka and Kusaka<sup>5</sup> (NK) is an extensive thermodynamic study aimed at clarifying the discrepancies of the binary nucleation theory. In this section, we summarize their key results, and highlight the relation of their work to the other papers considered.

NK start by presenting what they call the ‘‘Gibbs formula’’ for evaluating the reversible work of critical nucleus formation [Eqs. (1)–(3) of NK], which is practically equivalent to the Oxtoby–Kashchiev Eqs. (3), (9), and (10) above. They show that the incompressibility assumption can be used to derive an equation for the work of formation that contains  $\Delta\mu$  instead of  $\Delta P$  [Eq. (8) of NK].

NK then go on to consider the reversible work of formation of noncritical clusters, and show that it is given by an equation similar to Eq. (2) above with the slight differences that they have  $\Phi = A_t \sigma_t$  and assume  $\mu_{si} = \mu_{li}$  [Eq. (39) of NK]. Assuming incompressibility, they then obtain the counterpart of Eq. (16) [Eq. (45) of NK], from which they obtain the Kelvin equation [Eq. (48) of NK] using the extremity condition. They note that this equation may be employed to determine the composition and the radius of the critical nucleus.

Based on their thermodynamic considerations, NK criticize the ‘‘commonly used expression for the reversible work of formation for a cluster of general size and composition,’’ which they define as (in our notation)

$$W^{rev,g} = \sum_i n_{li} \Delta\mu_i + A_t \sigma_t. \quad (44)$$

NK correctly point out that, in order to obtain the proper equations for the critical nucleus from the extremity condition, the assumption has to be made that  $A_t d\sigma_t = 0$ , although ‘‘there is no logical justification to treat  $d\sigma_t$  as zero.’’

To summarize, NK presented correct equations for both noncritical and critical clusters, and the NK derivations, although not quite as straightforward, are thus consistent with the Oxtoby–Kashchiev and Debenedetti derivations (albeit slightly less general because of their assumption that the chemical potential of the cluster surface region equals that of the interior even with noncritical clusters). They also showed that the model for reversible work of noncritical cluster formation, Eq. (44), is not generally correct. However, it should be noted that although NK refer to Eq. (44) as an expression which is ‘‘generally used in literature,’’ it is not the same as Eq. (34) given by Wilemski.

## III. SURFACE COMPOSITION AND CURVATURE DEPENDENCE OF THE INTERFACIAL TENSION

### A. General

In the preceding section it was shown that the subclass of Gibbs droplets marked by the surface condition [Eq. (33)]  $n_{s1} v_{l1} + n_{s2} v_{l2} = 0$  where the  $n_{si}$  are defined with reference to surface of tension, has several important properties that are each equivalent to Eq. (33). These are first, the surface tension equality  $\sigma_t = \gamma$ , which holds independent of the curvature of the drop. Thus the surface tension is independent of the curvature of the drop. Second, the Wilemski free energy model [Eq. (34)] is valid, i.e., equivalent to the more complete forms given by Oxtoby and Kashchiev and Debenedetti, if and only if Eq. (33) applies. Finally, the volume of the nucleus is given by

$$V = g_{l1} v_{l1} + g_{l2} v_{l2} \quad (45)$$

if and only if Eq. (33) applies. In this section we obtain the molecular occupation numbers for the nucleus interior composition,  $n_{li}$ , and surface composition,  $n_{si}$ , under the condition that Eq. (33) applies.

The interior occupation numbers already follow from Eqs. (15) and (37). The surface numbers can then be obtained by subtracting the  $n_{li}$  from the  $g_i$ , which, in turn, are given by Eq. (45) and the Gibbs–Duhem relations (19) and (20) for the surface and interior phases, respectively, as shown by Laaksonen *et al.*<sup>9</sup> Substitutions using

$$x = \frac{n_{l2}}{n_{l1} + n_{l2}} \quad (46)$$

to denote the composition yield after algebraic reduction

$$n_{s1} = -A \left[ \frac{x v_{l2}}{(1-x) v_{l1} + x v_{l2}} \right] \left( \frac{d\mu_{l1}}{dx} \right)^{-1} \left( \frac{d\gamma}{dx} \right),$$

$$n_{s2} = -A \left[ \frac{(1-x) v_{l1}}{(1-x) v_{l1} + x v_{l2}} \right] \left( \frac{d\mu_{l2}}{dx} \right)^{-1} \left( \frac{d\gamma}{dx} \right), \quad (47)$$

where  $\mu_{li}$  are the chemical potentials of the two components in a bulk binary solution of composition  $x$ , under a flat interface, and  $\gamma$  is the surface tension of that solution. It is worth noting that in a recent paper on water–ethanol surface tension measurements, Aratono *et al.*<sup>10</sup> considered the special dividing surface (‘‘H’’) defined by the condition that  $n_{s1}^H + n_{s2}^H = 0$ . [Note the similarity of this condition to Eq. (33) for the case that the molecular volumes of the two components are equal.] The excess quantities  $n_{si}^H$  obtained by Aratono *et al.* are recovered from Eqs. (47) upon setting  $v_{l1} = v_{l2}$ .

### B. Calculations for ethanol–water droplets

To illustrate the results of this section, consider the critical nucleus for binary homogeneous nucleation of ethanol–water vapor in the Gibbs drop model. Neglecting the displaced vapor from Eq. (1), the total numbers of molecules in the critical nucleus are given as

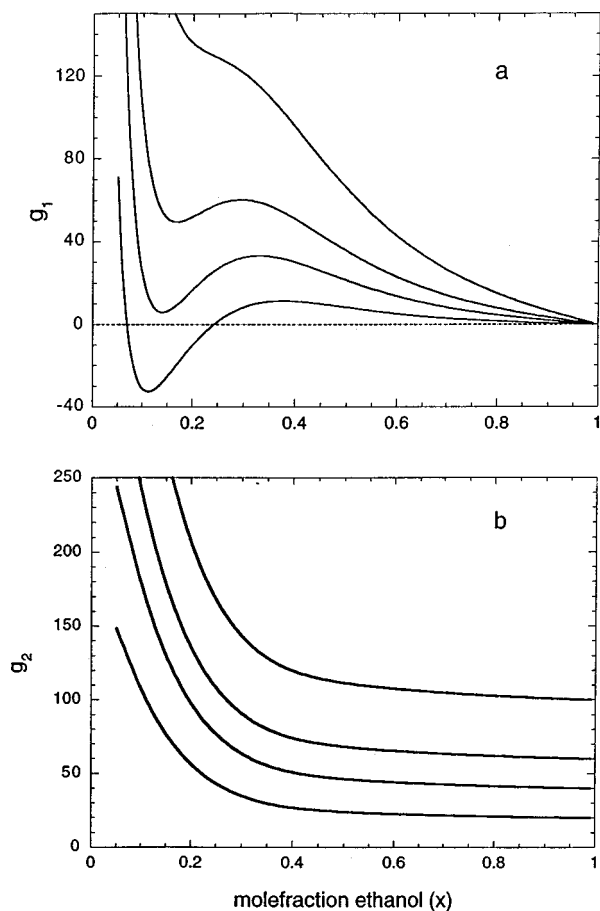


FIG. 1. (a) Total number of water molecules vs ethanol mole fraction in the core. Curves are for  $n_{l2}$  (number of ethanol molecules in the core region encompassed by the surface of tension)=20 (lowest curve), 40, 50, and 100 (highest curve).  $T=260$  K. (b) Total number of ethanol molecules vs ethanol mole fraction in the core. Curves are for  $n_{l2}=20$  (lowest curve), 40, 50, and 100 (highest curve).  $T=260$  K.

$$\begin{aligned} g_1 &= n_{l1} + n_{s1}, \\ g_2 &= n_{l2} + n_{s2}, \end{aligned} \quad (48)$$

where components 1 and 2 refer to water and ethanol, respectively. Each of the quantities on the right-hand side of Eqs. (48) is readily evaluated using Eqs. (15), (33), (37), and (47). The values of  $n_{l2}$  and  $x$  determine the area ( $A$ ) in Eqs. (47), the remaining quantities on the right-hand side of Eqs. (47) are functions of  $x$  and are available from bulk solution and interfacial tension measurements.

Figures 1(a) and 1(b) show, respectively, how the total numbers  $g_1$  and  $g_2$  vary as functions of  $x$  for several different values of  $n_{l2}$ . The unphysical negative values of  $g_1$  seen in Fig. 1(a) are especially interesting and coincide with the negative occupation numbers of molecules in the critical nucleus seen in calculations based on the revised nucleation theory. These negative occupation numbers show up as regions of positive slope,<sup>9</sup> (“the hump”) seen on plots of  $\mu_{v1}$  vs  $\mu_{v2}$  at constant nucleation rate ( $J$ ) for the ethanol–water system (and other surface active systems, such as propanol–water, as well). The connection between slope and occupation number is given by the nucleation theorem<sup>4,11</sup> which for a binary system takes the form<sup>12</sup>

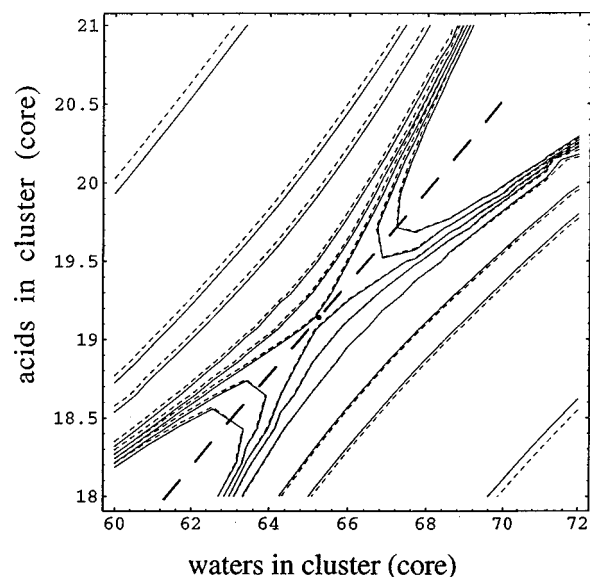


FIG. 2. Free energy surfaces for sulfuric acid/water. Saturation ratios are 0.5 for water and 0.00033 for sulfuric acid;  $T=298$  K. Figure shows the number of acid molecules in core region encompassed by surface of tension vs number of water molecules in the core. Solid contours indicate full surface, dashed contours indicate the constant surface tension model surface, the dashed straight line shows core composition, and the point shows core size and composition for the nucleus. Contours, reading from left to right in the bottom of the figure and from right to left in the top of the figure, correspond to energies 66.75, 66.76, 66.77, 66.78, 66.80, 66.90, 67, and 68 in units of  $kT$ .

$$\left( \frac{\partial \mu_{v1}}{\partial \mu_{v2}} \right)_J = - \frac{g_2}{g_1}. \quad (49)$$

Equation (49) indicates that the slope should always be negative for positive  $g_i$ . We have shown here that the occurrence of negative occupation numbers for the total number of molecules of a species ( $g_i$ ) in the critical nucleus is already a consequence of Eqs. (47), which as shown above are a consequence of the assumption of zero curvature dependence of the surface tension [Eq. (33)] used in the revised nucleation theory. The fact that the nucleation theorem gives negative values for the ratio ( $g_2/g_1$ ) is now seen to be simply a reflection of the fact that  $g_1$  is itself predicted to be negative [Fig. 1(a)] for some range of nucleus size and composition as a consequence of the zero curvature dependence assumption. Thus for surface active binary systems the assumption of zero curvature dependence can lead to unphysical, negative, occupation numbers in the nucleus and is therefore even more untenable as an approximation than it is in the case of single-component nucleation. Nevertheless, this assumption may be difficult to relinquish in practice due to the lack of any direct experimental measurements of curvature dependence for binary clusters in the critical nucleus size range.

#### IV. FREE-ENERGY SURFACE

In the preceding sections, a systematic method was presented for calculation of the composition of the core of the nucleus (volume enclosed by the surface of tension), generally, and of the surface excess quantities under the special condition [Eq. (33)] that the surface tension is curvature in-

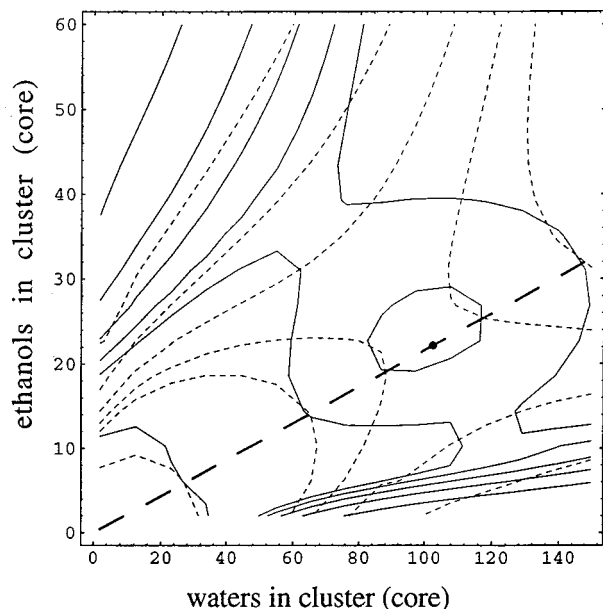


FIG. 3. As in Fig. 2, but for ethanol/water. Saturation ratios are 1.5 for both water and ethanol;  $T=260$  K. The dashed contours reading from left to right in the bottom of the figure and from right to left on top of the figure correspond to energies 30, 40, 42, 45, 50, and 60 in units of  $kT$ . The energies corresponding to the solid lines can be found out by noting that dashed and solid contours corresponding to same values cross along the core composition line.

dependent. These occupation numbers provide sufficient information for calculation of the full free-energy surface<sup>1</sup>

$$\Delta G_{\text{Gibbs}} = \sum_i (\mu_{li} - \mu_{vi})n_{li} + \sum_i (\mu_{si} - \mu_{vi})n_{si} + A\gamma \quad (50)$$

under the condition that  $\gamma$  is curvature independent and we can equate the chemical potentials of surface and bulk species ( $\mu_{li} = \mu_{si}$ ) within the drop. The latter is a reasonable assumption as the time scale for equilibration of species between the surface and interior of the drop is expected to be rapid compared to the time scale for vapor equilibration. This equality of surface and core chemical potentials can be handled formally in the Gibbs nucleus model through the application of constraints as described recently by Debenedetti and Reiss.<sup>2</sup>

Free-energy surfaces based on Eq. (50) have not apparently been presented previous to the present study. The results are shown in Figs. 2 and 3 (solid contours) for the two very different binary systems, sulfuric acid/water and ethanol/water, respectively. In these figures the thick dashed line gives the core composition obtained from Eq. (15) using bulk solution and volumetric properties (surface tension data is not required to obtain this line.) The indicated point along the line marks the composition and size of the critical nucleus, with the nucleus size determined from Eq. (13) using estimates of the surface tension for a bulk solution having the composition of the core.

The above prescription for obtaining the nucleus size is identical to the procedure previously used by Laaksonen *et al.*<sup>9</sup> to implement the revised classical theory of Wilemski.<sup>3</sup> From Fig. 2 it is seen that the location of the saddle point corresponds precisely to the location obtained

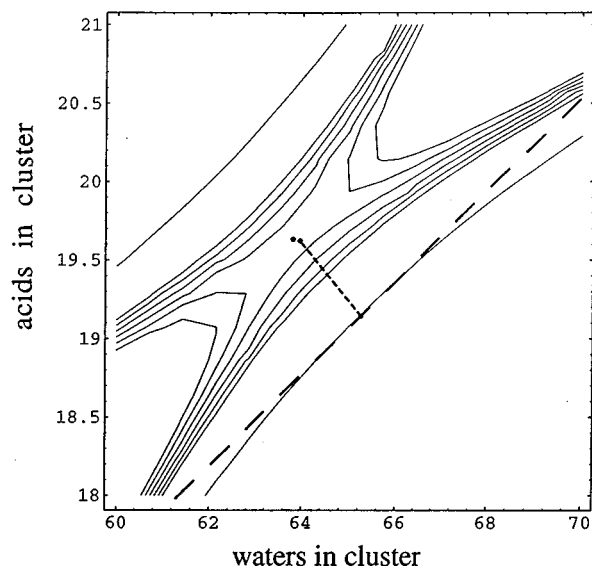


FIG. 4. Classical sulfuric acid–water free energy surface from Eq. (51). Saturation ratio is 0.5 for water and 0.00033 for sulfuric acid as in Fig. 2. Contours are presented in terms of the total numbers of waters ( $g_1$ ) and acids ( $g_2$ ) in the drop. Contours reading from left to right in the bottom of the figure and from right to left in the top of the figure are 66.60, 66.61, 66.62, 66.63, 66.64, 66.65, and 66.77 in units of  $kT$ . The highest contour level was chosen to be equal to the barrier height in the revised classical theory. See text for further description of points and lines.

from the revised classical theory. The free energy surface for ethanol–water, shown in Fig. 3, is more complicated but the location of the revised classical nucleus is nevertheless seen to lie on a local maximum of the surface where the derivatives of the free energy with respect to the occupation numbers of each component vanish. The height of this small local maximum is too small to be of consequence for the nucleation rate and one can still view this part of the surface as a broad saddle region. That the revised classical theory is able to correctly locate the saddle point of the free-energy surfaces given by Eq. (46) follows from the analysis present in Sec. II showing that the Wilemski free energy model [Eq. (34)] is equivalent to Eq. (50) if and only if condition (33) applies.

The saddle point of the classical free-energy surface as described by Doyle,<sup>13</sup> on the other hand, generally does not lie on the dashed line defining the core composition in the Gibbs dividing surface model. This is shown for the sulfuric acid–water binary system in Fig. 4, where contours are for the classical sulfuric acid–water free-energy surface,

$$\Delta G = \sum_{i=1}^2 [\mu_{li}(P_v) - \mu_{vi}(P_v)]g_i + A\gamma, \quad (51)$$

and the liquid-phase chemical potentials and the surface tension are calculated using the overall nucleus mole fraction,  $g_2/(g_1+g_2)$ . Component 1 is water and component 2 is acid and the conditions are the same as for Fig. 2. The long dashed line gives the core concentration bounded by the surface of tension in the Gibbs model and is the same as in Fig. 2. The short dashed line connects the core composition  $\{n_{11}=65.260, n_{12}=19.143\}$  and total nucleus com-

position  $\{n_{l1} + n_{s1}, n_{l2} + n_{s2}\}$  with the surface composition  $\{n_{s1} = -1.303, n_{s2} = 0.478\}$  obtained from Eqs. (43). The indicated saddle point marks the location of the saddle as obtained by partial differentiation of  $\Delta G$  following the Doyle prescription (i.e., the surface tension derivatives with respect to composition are included in the calculus of saddle location). It is seen that the Doyle saddle point location provides an excellent estimate for the *total* nucleus composition in this system. Nevertheless, the Doyle saddle point must be regarded as thermodynamically inconsistent with the Gibbs model of the nucleus. For example, one cannot realize a core pressure under which the chemical potentials for each species in the nucleus is equal to the chemical potential of the corresponding species in the vapor phase. This thermodynamic inconsistency was pointed out by Wilemski.<sup>14</sup> Indeed the long-dashed line in Fig. 4 gives the complete locus of such conditions for which equality of chemical potentials holds—and the saddle point of the classical surface clearly does not lie on this line. The free energy surfaces in Figs. 2–4 thus highlight a very important distinction between the Doyle nucleus and the Gibbs nucleus models. The latter provides a much more viable basis for extension of the thermodynamic properties of critical nuclei to multicomponent systems.<sup>15</sup>

We next present a simplified free-energy surface that, like the full surfaces shown by the solid contours in Figs. 2 and 3, is also consistent with the Gibbs thermodynamic model. Consider the Gibbs–Duhem equation,

$$\sum_i (n_{si} d\mu_{si}) = -A d\gamma, \quad (52)$$

where the summation is over all components in the nucleus (in the present case just two components are considered), and use this result to obtain an approximate expansion of the surface tension about the core surface tension  $\gamma_{\text{core}}$  for finite differences in composition

$$-\sum_i (\mu_{si} - \mu_{vi}) n_{si} - A(\gamma - \gamma_{\text{core}}) \approx 0. \quad (53)$$

Equation (53) is actually the integrated form of the Gibbs–Duhem equation above and is therefore valid only near the core composition where the differences in the parentheses are sufficiently small. Nevertheless, assume its validity locally for the moment and add together Eqs. (50) and (53) to obtain the approximate surface

$$\Delta G_{\text{approx}} = \sum_i (\mu_{li} - \mu_{vi}) n_{li} + A \gamma_{\text{core}}. \quad (54)$$

This model is virtually identical to the thermodynamic formula for the reversible work of forming a noncritical cluster by Nishioka and Mori<sup>16</sup> [their Eq. (12)]. For a curvature-independent surface tension, as assumed here, the models are indeed equivalent. We will refer to Eq. (54) as the  $\gamma_{\text{core}}$  model. A moments reflection reveals that Eq. (54) differs from the Doyle free-energy surface only in that the composition-dependent surface tension of the Doyle theory has been replaced with the constant core surface tension  $\gamma_{\text{core}}$ . In essence the surface tension composition depen-

dence has been eliminated, along with the corresponding surface excess quantities, through the cancellation of Eq. (53). The surface generated by Eq. (54) is shown as the dashed contours in Figs. 2 and 3. As in the case for the full surface of Eq. (50), the location of the nucleus in the  $\gamma_{\text{core}}$  model is consistent with the Gibbs thermodynamic model and with the revised classical theory. Furthermore it is seen that the two sets of surfaces, as expected, agree at the core composition.

## V. CONCLUSION

We have considered three different derivations of the classical nucleation theory within Gibbs dividing surface formalism. It was shown that two of the derivations, one extended from the work of Oxtoby and Kashchiev and the other originally presented by Debenedetti, are consistent with each other and are generally valid for the Gibbs model. In contrast, the third derivation by Wilemski is consistent with the other two if (and only if) the specific condition  $\sum_i n_{si} v_{li} = 0$  holds for the surface of tension. From this assumption it follows that (1) surface tension is curvature independent and (2) the nucleus volume is given by  $V = \sum_i g_i v_{li}$ , where the  $g$ 's are the total numbers of molecules contained in the nucleus. In practice the assumption  $\sum_i n_{si} v_{li} = 0$  is always made implicitly when applying the classical nucleation theory unless a specific curvature dependence is assumed for the surface tension.

From the assumption of a curvature-independent surface tension it was shown that the nucleus composition (both core and surface) is fully determined. For the case of the highly surface active system, ethanol–water, this assumption was found to result in the occurrence of unphysical negative occupation numbers of water in the nucleus. Previously deduced from the occurrence of positive slope regions (“the hump”) seen in plots of  $\mu_{v1}$  vs  $\mu_{v2}$  at constant nucleation rate, these negative occupation numbers have now been shown, through the results of Sec. III, to be a direct consequence of the assumption of curvature independence. In addition the assumption of curvature-independent surface tension was demonstrated to be sufficient for the generation of full free-energy surfaces for binary nucleation in the Gibbs nucleus model. The location of the saddle point on these surfaces was shown to coincide with the nucleus size and composition predicted by the revised classical theory. On the other hand the saddle point of the unrevised classical surface was found to be thermodynamically inconsistent with the Gibbs model. Finally, a simplified free-energy surface (the  $\gamma_{\text{core}}$  model) was presented that is also consistent with the Gibbs model and in exact agreement with the full surface from that model at the saddle point and along the core composition line obtained from the revised classical theory. Furthermore the  $\gamma_{\text{core}}$  surface is actually easier to calculate than the unrevised classical free-energy surface because the surface tension is required at only one solution composition, namely at the composition of the core. For systems that are not too strongly surface active, such as illustrated here for sulfuric acid–water mixtures, the  $\gamma_{\text{core}}$  surface was found to be in excellent agreement with the full surface even at significant distances away from the saddle region.



We also pointed out that the equation defining the core composition of the nucleus,  $\Delta\mu_1/v_{11} = \Delta\mu_2/v_{12}$ , is more general than the rest of the equations of the revised classical theory, because it relies only on the incompressibility assumption, and not on the capillarity approximation. Interestingly, a recent molecular dynamics<sup>17</sup> study found that in small ethanol–water clusters, practically all ethanol molecules are in the surface layer. Consistent with that observation, the above equation of the revised classical theory predicts almost zero ethanol core mole fractions for ethanol–water nuclei over a wide range of vapor-phase activities of both species.<sup>18</sup>

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