

Reversible work of formation of an embryo of a new phase within a uniform macroscopic mother phase

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A thermodynamically consistent formalism is derived for calculating the reversible work needed to form a small amount of a new phase (embryo) within a uniform macroscopic mother phase. The treatment goes beyond the classic work of Gibbs, who solved the problem for the particular case in which the embryo is in equilibrium with the mother phase, constituting a so-called critical nucleus. The formalism results in a new expression for the reversible work of embryo formation, the extrema conditions for which yield the correct conditions of equilibrium between the critical nucleus and the mother phase, as well as Gibbs' result for the reversible work needed to form the critical nucleus. The new expression for the work of embryo formation differs from the one commonly used in the nucleation literature. In order to extend the Gibbsian formalism to noncritical nuclei, it is necessary to introduce a constraint that prevents the free transfer of matter between the embryo and the mother phase. The present approach is valid in the limit in which curvature contributions to the interfacial energy can be neglected. © 1998 American Institute of Physics. [S0021-9606(98)50513-2]

I. INTRODUCTION

The reversible work of formation of a small fragment (embryo) of a new phase is of primary interest in the field of nucleation, where it can represent the initial free energy barrier that a metastable system must surmount in passing from a local to a global minimum in a coarse-grained phase space. In a fully molecular theory this initial process would involve the formation of some appropriate molecular cluster that later develops into a recognizable piece of the new phase. However, such molecular theories are not generally available, so that workers have been forced to rely on quasiphenomenological theories¹⁻⁵ in which the initial fragment is treated as though it were *already* a piece of the stable phase, appropriate allowance being made for surface effects. Under these circumstances, methods that are purely thermodynamic can be used for the evaluation of the free energy change involved in its formation.

In spite of the widespread interest in the problem, few thermodynamically rigorous treatments exist. Gibbs^{6,7} considered only that fragment of the new phase that served as the "nucleus" for the phase transition (i.e., a fragment that would be at least in *unstable* equilibrium with the mother phase). Nishioka and Kusaka⁸ extended Gibbs' treatment to embryos of arbitrary size, but without properly accounting for the constraint that, as we show below, must be introduced in order to consider this situation. Recently, the thermodynamically rigorous extension of the Gibbsian approach to arbitrarily sized embryos of the new phase has been derived.⁹ However, this derivation appears as an appendix to a mono-

graph and is therefore rather condensed and not well-suited to the discussion of the many subtleties of the problem. Such a detailed analysis is the objective of this work.

This paper is organized as follows. In Sec. II, which is didactic in nature, we review the central role played by constraints in the rigorous treatment of equilibrium criteria. Section III revisits the Gibbsian treatment of fluid interfaces. In Sec. IV we extend the Gibbsian treatment to the general case of arbitrarily sized embryos that are not in equilibrium with the mother phase. In Sec. V we derive the reversible work of formation of an embryo of a new phase within a homogeneous mother phase. Conclusions are presented in Sec. VI.

II. CONSTRAINTS

Constraints play an overwhelming but usually *hidden* role in thermodynamics¹⁰⁻¹³ and they are particularly important in the problem before us. To facilitate discussion, it is therefore worthwhile to consider the role of constraints and their relation to both work and thermodynamic potentials. It is convenient to begin with the following expression that combines the first and second laws of thermodynamics,

$$\Delta U - \int T dS + W_0 + W_1 = 0. \quad (1)$$

In this expression ΔU represents the change in the internal energy of a *closed* system that accompanies a particular *change* of state, while T is the temperature and S represents the entropy of the system. The change of state is here considered to be accomplished by means of a reversible *process* so that the integral in Eq. (1) is the heat absorbed by the system during this process. W_0 and W_1 denote reversible work performed *by* the system (positive when the system

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performs work *on* its environment) during the process. To illustrate the meaning of W_0 and W_1 , suppose that we are interested in describing the state of equilibrium of a system that is set up (constrained) to perform work only of type 0, i.e., W_0 . It is then convenient to write Eq. (1) as

$$\Delta\Psi = \Delta U - \int T dS + W_0 = -W_1, \quad (2)$$

where $\Delta\Psi$ is only a symbol for the collection of terms constituting the middle expression on the right (i.e., is not meant to represent a change in a quantity Ψ). In order to make things more concrete, assume that W_0 is volume work. Then Eq. (2) may be written as

$$\Delta\Psi = \Delta U - \int T dS + \int P dV = -W_1, \quad (3)$$

where P is the equilibrium pressure of the system and V is its volume. Suppose now that the system has achieved a state of equilibrium subject to constraints that allow it to perform only volume work. Since the system is in equilibrium subject to those constraints, it can only be driven away from the given equilibrium state into other equilibrium states through the application of another constraint, and this constraint must obviously perform work on the system while driving it away. We can assume that the constraint utilizes a reversible process for this purpose, and then the work that it performs *on* the system can be represented by $-W_1$ in Eqs. (2) and (3). Since work is being performed *on* the system, W_1 is negative and $-W_1$ must be positive. Thus however the system is driven away from the state in which it can only perform volume work (whatever additional constraint is applied) $\Delta\Psi$ for the change of state must be positive. The additional constraint is accompanied by an additional independent variable and the reversible path defined by the constraint is a sequence of equilibrium states characterized by one more variable than the initial state. Thus the variation may be thought of as one that carries the system from an equilibrium controlled by say n variables to one controlled by $n+1$ variables. Since $-W_1$ is always positive, provided that none of the original constraints are removed, it should be clear that the quantity $\Delta\Psi$ is minimized at the initial state.

To summarize, then, W_1 is the reversible work performed by the system on the environment during the reversible removal of a constraint (i.e., work performed against the constraint) that drove the system away from its initial equilibrium state. W_0 differs from W_1 in that, in the absence of the constraint, the system can perform only work of type 0. Equation (2), as written, includes only two kinds of work, but it could include additional types. *The kinds of work depend on how the system is set up.* This is the key point that we wish to emphasize. An equilibrium state of the system is subject to certain constraints. These can be varied in such a manner that the system either performs reversible work against a constraint (i.e., *on* its environment) or such that the constraint performs reversible work on the system during a process leading to a change of state. The constraints determine the kinds of work of which the system is capable. They

also determine the number of independent variables that describe the system. The addition of a constraint amounts to the addition of a variable.

Thus far our argument has concentrated on *stable* equilibrium. For *unstable* equilibrium a similar argument can be used for the properties of $\Delta\Psi$, but then one must consider reversible paths that are generated by the reversible *removal* of a constraint such that $-W_1$ is negative rather than positive, i.e., the system does work *against* the constraint. In both cases *thermodynamic potentials* (functions of state whose variations imitate $\Delta\Psi$) exhibit extrema in the initial state of equilibrium. However, there are cases that we discuss below in which a saddle point rather than an extremum is involved. Then both situations are possible, depending on the path of the variation.

Our interest is in the properties of the initial equilibrium, and not in the equilibrium states generated by the constraint, so it is unnecessary to specify the detailed nature of the additional constraint. Different constraints will however generate different paths of displacement from the initial equilibrium, and in the usual strategy, the path rather than the constraint is specified. That strategy is the following. One constructs a thermodynamic function of state whose change *imitates* $\Delta\Psi$ on the particular path generated by the constraint. Then, *on that path*, the function of state must be minimized in the initial state since $\Delta\Psi$ is minimum on any path at that state. Such a function of state serves as a thermodynamic potential for the system in question. Many thermodynamic potentials for the same system and for the same equilibrium state can be constructed by imitating $\Delta\Psi$. If the system in its original equilibrium state is allowed to perform other kinds of work, additional to volume work, then the constructed thermodynamic potential and/or the path of displacement will have to contain terms and features that reflect this fact.

An important use of the thermodynamic potential is the provision of a differential equation useful for the description of the internal equilibrium of the system subject to the initial constraints. For example, in a closed system and along a path of constant T and P , the Gibbs energy can serve as a thermodynamic potential. Thus for a system constrained to perform only volume work, the Gibbs energy is minimized in the initial equilibrium state along a path of constant T and P , and we can write (for that state)

$$(\delta G)_{T,P} = 0. \quad (4a)$$

If we choose a path of constant S and V , the energy serves as a thermodynamic potential and we can write

$$(\delta U)_{S,V} = 0. \quad (4b)$$

In the case of a saddle point, an extremum of the thermodynamic potential is not involved, but Eqs. (4a) and (4b) and similar equations for other thermodynamic potentials still apply. Thus we achieve a description of internal features of the equilibrium system so constrained that only volume work is possible for the system.

III. PRELIMINARIES TO THE DERIVATION OF THE WORK OF FORMATION OF AN EMBRYO OF THE NEW PHASE

The preceding section, didactic in nature and possibly repetitious of ideas familiar to many readers, is useful in emphasizing conceptual material that tends to be hidden even though it forms the foundation of a rigorous derivation of the work of formation of an embryo of a new phase. Furthermore, before advancing to the derivation itself, it is convenient to list some of the most important definitions and relations of the conventional Gibbsian approach to the thermodynamics of interfaces.^{6,7,9}

Most readers should be familiar with the concept of the *Gibbs dividing surface*, a mathematical construct whose contour conforms to that of the physical transition zone within which the properties of one phase change continuously to those of the contiguous phase. The position of this dividing surface along the local normal to the physical contour can be chosen arbitrarily, but in practice it is convenient to limit the choices. Having made a choice, one treats the inhomogeneous system formally as though the densities of various extensive properties in the coexisting bulk phases remain uniform up to the dividing surface. An accounting of the total amounts of the various extensive properties in the system, on this basis, will then be in error. For a given extensive quantity, the difference between the actual total amount and the “spurious” amount calculated assuming uniformity of intensive properties up to the dividing surface is defined as the *surface excess*. For example, consider a not necessarily closed system consisting of two coexisting phases, one denoted by a single prime and the other by a double prime. If the volumes (defined by the dividing surface) of the two phases are V' and V'' , respectively, and the uniform densities of say the internal energies are denoted by u' and u'' , then the surface excess of internal energy is prescribed by

$$U^\sigma = U - u'V' - u''V'', \quad (5)$$

where U is the actual total internal energy in the system and the superscript σ denotes a surface excess quantity (σ will also be used to denote the surface tension). By considering the usual thermodynamic expressions for the differentials of the various extensive variables for the imagined primed phases as well as for the actual total system and choosing reversible paths for the associated differential changes of state, it is a straightforward matter of “balancing the books” to show^{6,7,9} that, for changes that do not alter V' and V'' or the shape and extent of the interface between the phases,

$$dU^\sigma = T dS^\sigma + \sum_i \mu_i dN_i^\sigma, \quad (6)$$

where μ_i is the chemical potential of the i th species, and it is assumed that the constraints on the system allow that species to be freely transferred to the interface. Equation (6) and similar relations between excess quantities are obtained by default as a result of “balancing the books.” They allow us to consider an “excess” system whose thermodynamic variables are connected by relations that satisfy the requirements of thermodynamics.

The derivation of Eq. (6) involves an additional consideration. It is allowable to define V' and V'' so that each is bounded, not only at the interface but everywhere, by a mathematical surface itself immersed in the bulk phase. In this way it is not only easy to maintain the volumes fixed, but also to avoid the introduction of other physical surfaces besides the interface and the additional surface properties that would then have to appear in relations such as Eq. (6).

If the shape and extent of the interface is allowed to vary, then the quantities that describe these variations, namely the interfacial area and the local principal curvatures, enter the picture as additional thermodynamic variables. However, Gibbs showed how the differentials of curvature could be eliminated from explicit consideration (provided that the local radii of curvature were large compared to the physical thickness of the interfacial transition zone) through the choice of a particular dividing surface. In particular, choice of this dividing surface yields as a condition of mechanical equilibrium the well-known Laplace relation between the pressures on the convex and concave sides of the surface, namely,

$$\Delta P = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right), \quad (7)$$

where r_1 and r_2 are the principal radii of curvature. For a curved interface the surface tension σ depends, in general, on the choice of dividing surface and σ appearing in Eq. (7) refers to the dividing surface in question which is itself referred to as the “surface of tension.” The variation of surface tension with choice of dividing surface is nonphysical to the extent that it is a consequence of this choice, and the corresponding derivative of surface tension is therefore often referred to as a “notional” derivative. However, it should be indicated that for a plane surface (zero principal curvature) the surface tension is independent of the choice of dividing surface, a result that is closely connected to the fact that, for a flat surface, the pressures on opposite sides of the interface are equal, and implies that the surface tensions corresponding to all choices of dividing surface converge to one value for the case of a flat surface. In any event, the important result that can be demonstrated^{6,7,9} for the surface of tension is

$$dU^\sigma = T dS^\sigma + \sum_i \mu_i dN_i^\sigma + \sigma dF, \quad (8)$$

where F denotes the area of the interface, and the surface tension σ is in essence defined by its position in this equation. The term σdF clearly represents surface work, and Eq. (8) gives the changes in energy associated with reversible variations about a particular initial equilibrium state, said variations allowing for changes in the shape of the interface. It is understood that the dividing surface is chosen as the surface of tension, so that changes of curvature do not contribute additional work terms. Integrating Eq. (8) along the interface while maintaining the intensive variables, T , μ_i , and σ constant, we find

$$U^\sigma = TS^\sigma + \sigma F + \sum_i \mu_i N_i^\sigma. \quad (9)$$

Taking the differential of U^σ and substituting Eq. (8) yields

$$S^\sigma dT + F d\sigma + \sum_i N_i^\sigma d\mu_i = 0, \quad (10)$$

and dividing by F we get

$$s^\sigma dT + d\sigma + \sum_i \Gamma_i d\mu_i = 0, \quad (11)$$

with

$$s^\sigma = S^\sigma/F; \quad \Gamma_i = N_i^\sigma/F, \quad (12)$$

where Γ_i is the ‘‘superficial density’’ of component i .

Dividing Eq. (9) by F , taking the differential of the result, and substituting Eq. (11) yields, with $u^\sigma = U^\sigma/F$

$$du^\sigma = T ds^\sigma + \sum_i \mu_i d\Gamma_i. \quad (13)$$

We reiterate that Eq. (9) is valid for the surface of tension and for the case where the various components are freely transferable between the two phases and the interface coexisting in equilibrium. Thus for example, if one phase is a small liquid drop and the other phase the corresponding vapor, the pressure of the vapor should be equal to the vapor pressure of the drop. This equilibrium is generally unstable,⁹ but it *is* an equilibrium.

IV. EXTENSION TO PHASES NOT IN EQUILIBRIUM

We now extend the previous treatment to the case where the two phases are not in equilibrium, or, equivalently, to arbitrarily sized embryos. For example, we may wish to consider the case of a droplet surrounded by a vapor in which the pressure of the vapor does not equal the vapor pressure of the droplet. In order to apply thermodynamic reasoning to this situation we require the imposition of a *constraint* that prevents the free transfer of matter between the vapor phase and the inhomogeneous system consisting of the droplet and the transition zone where the intensive properties change continuously from their values in the droplet to those in the vapor. This extension to the nonequilibrium case¹⁴ is essential in order to place the entire discussion of the energetics of embryo formation on sound and thermodynamically consistent footing. This is so because the so-called critical nucleus, being in equilibrium with the mother phase, corresponds to an extremum or saddle point of the more general expression for the reversible work of embryo formation, and to give meaning to this saddle point we must be able to consider reversible variations about it.

Figure 1(a) illustrates the relevant geometry. To the right of surface a we have a homogeneous vapor, and to the left of b the homogeneous droplet. The region between a and b is the physical interface. The constraint will be imagined as a field that acts only on the droplet and the transition zone (i.e., to the left of surface a). As explained in Sec. II, the exact nature of the constraint need not be specified, although we will find it convenient in the derivations that follow to do so for purely didactic reasons. We first derive the conditions of constrained equilibrium for the system defined in Fig. 1(a). For this purpose we find it convenient to define a new sur-

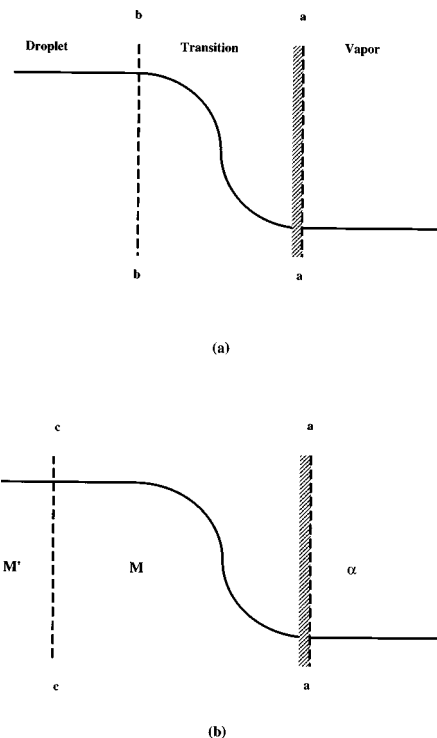


FIG. 1. Definitions of mathematical surfaces used in the derivation of the work of embryo formation. The phases are homogeneous to the right of a and to the left of b . The field acts to the left of a .

face, c in Fig. 1(b), lying entirely within the homogeneous droplet. As explained in Sec. III, we imagine the system to be bounded not only at the interface, but everywhere, by a mathematical surface immersed in the bulk phases. For variations about equilibrium that do not involve movements of the boundaries, changes of volume, or exchange of matter across the mathematical surface (closed system), we can use the energy as a thermodynamic potential provided that variations are conducted along a path of constant entropy [see Eq. (4b)]. Thus it is necessary and sufficient for the stability of the constrained equilibrium that

$$\delta U + \delta\Phi + \delta U' + \delta U^\alpha \geq 0, \quad (14)$$

$$\delta S + \delta S' + \delta S^\alpha = 0, \quad (15)$$

$$\delta N_i + \delta N'_i = 0; \quad \delta N_i^\alpha = 0 \quad (i=1, \dots, n), \quad (16)$$

where primes refer to the homogeneous interior of the droplet; unprimed quantities denote the system M , composed of the interface as well as a portion of the homogeneous interior of the droplet [Fig. 1(b)]; superscript α denotes the homogeneous vapor; and Φ denotes the energy associated with the field. As an example, Φ could be a ‘‘gravitational’’ field,

$$\Phi = g \sum_i m_i \int z dN_i, \quad (17)$$

where z is the distance measured in the direction normal to the interface, $i(1, \dots, n)$ identifies the various components in the mixture, and m_i is the molecular weight of component i . In order to make the discussion more general, we can write

$$\Phi = \sum_i \Psi_i \int f(z) dN_i, \quad (18)$$

where $f(z)$ generalizes Eq. (17) to the case in which the dependence on z may be nonlinear, and Ψ_i generalizes mg_i . Ψ_i and $f(z)$, in other words, are generalized forces and generalized displacements, respectively. For example, $f(z)$ can be chosen to vanish within the vapor phase as we have effectively done, since our field acts only within the droplet and the interface. In the presence of the field, the variations Eq. (16) should be interpreted as follows,

$$\delta \int dN_i(z) + \delta \int dN'_i(z) = \int \delta dN_i(z) + \int \delta dN'_i(z) = 0, \quad (19)$$

where the integrals are over slices of given z .¹¹ Substituting Eqs. (15), (16), and (18) in (14),

$$(T - T^\alpha) \delta S + (T' - T^\alpha) \delta S' + \sum_i \left\{ \int [\mu_i + \psi_i f(z)] \delta dN_i + \int \mu'_i \delta dN'_i \right\} \geq 0, \quad (20)$$

from which it follows that the necessary and sufficient conditions of equilibrium are

$$T = T' = T^\alpha, \quad (21)$$

$$\mu'_i = \mu_i + \psi_i f(z) = c_i, \quad (22)$$

where c_i is independent of position. Thus the constrained equilibrium is one in which the temperature and the generalized chemical potentials $\mu_i + \psi_i f(z)$ are constant throughout $(M + M')$. The field, in other words, stabilizes the interface and establishes equilibrium within the inhomogeneous droplet.

We now derive the fundamental equations corresponding to differential variations about the constrained equilibrium. To this end, we denote by β the droplet and its hypothetical homogeneous continuation up to the mathematical surface a . For variations about equilibrium subject to the same conditions used in deriving Eqs. (21) and (22), we must have

$$\delta U^\beta = T \delta S^\beta + \sum_i \int \mu_i^\beta \delta dN_i^\beta, \quad (23)$$

$$\delta U = T \delta S + \sum_i \int \mu_i \delta dN_i, \quad (24)$$

$$\delta \Phi = \sum_i \psi_i \int f(z) \delta dN_i, \quad (25)$$

and, therefore,

$$\delta(U + \Phi - U^\beta) = T \delta(S - S^\beta) + \sum_i \int [\mu_i + \psi_i f(z)] \times \delta dN_i - \sum_i \int \mu_i^\beta \delta dN_i, \quad (26)$$

in which the reference level for the potential $f(z)$ is taken as zero within the homogeneous core of the droplet. We can write, equivalently,

$$\delta U^\sigma = T \delta S^\sigma + \sum_i \int \tilde{\mu}_i \delta dN_i^\sigma. \quad (27)$$

For variations in which the system remains at equilibrium, we can write^{6,7}

$$dU^\sigma = T dS^\sigma + \sum_i \tilde{\mu}_i dN_i^\sigma, \quad (28)$$

where $\tilde{\mu}_i$ denotes the position-independent potential, $\mu_i + \psi_i f(z)$; superscript σ denotes the excess of an extensive quantity due to the presence of the interface, over and above the amount of that extensive quantity associated with the droplet and its hypothetical homogeneous continuation up to surface a . In the case of the energy, this includes the contribution of the field. Also, we have used the simplified notation

$$\delta \int dN_i^\sigma = \delta N_i^\sigma. \quad (29)$$

Integrating along the interface,

$$U^\sigma = TS^\sigma + \sum_i \tilde{\mu}_i N_i^\sigma. \quad (30)$$

If the variations include changes in the interface area, Eqs. (28) and (30) become

$$dU^\sigma = T dS^\sigma + \sum_i \tilde{\mu}_i dN_i^\sigma + \sigma dF, \quad (31)$$

$$U^\sigma = TS^\sigma + \sum_i \tilde{\mu}_i N_i^\sigma + \sigma F. \quad (32)$$

Equations (31) and (32) are formally identical to Eqs. (8) and (9). However, there are important differences:

- (1) Equations (8) and (9) apply to an interface across which matter is freely transferable, the phases on either side of which are in equilibrium;
- (2) In contrast, Eqs. (31) and (32) apply to a constrained inhomogeneous system, with matter freely transferable on one side of the interface only;
- (3) Equations (8) and (9) apply in the absence of a field, and the μ_i are ordinary chemical potentials;
- (4) Equations (31) and (32) apply in the presence of a field, and the $\tilde{\mu}_i$ are quantities incorporating the influence of the field;
- (5) Equations (8) and (9) apply to the dividing surface, which is defined so that curvature contributions vanish identically;
- (6) Equations (31) and (32) apply to the boundary of the interface (surface a in Fig. 1), where we have not introduced the equivalent of a surface of tension. They are therefore strictly valid only in the limit when curvature contributions are small. In practice, this means that the radii of curvature are large with respect to molecular dimensions;
- (7) In Eqs. (8) and (9), surface excess quantities, denoted by the superscript σ , are defined to be the difference between the actual amount of an extensive quantity present in the entire inhomogeneous system and that which

would exist if the two homogeneous phases maintained their intensive properties unchanged up to the dividing surface;

- (8) In Eqs. (31) and (32), surface excess quantities, denoted by superscript σ , are defined to be only the difference between the actual amount of an extensive quantity present in the inhomogeneous system, and that which would exist if the phase with which mass exchange is allowed by the bounding surface a (Fig. 1) maintained its intensive properties unchanged up to the bounding surface.

V. DERIVATION OF THE WORK OF FORMATION

Consider a homogeneous fluid mass α in contact with a thermal reservoir τ and a work reservoir π which, respectively, impose on α a temperature T and a pressure P . The boundary between the work reservoir and α is adiabatic while that with the thermal reservoir must, of course, be diathermal. For simplicity we first treat the single component case. Let an embryo of a second phase β be formed entirely within α . The entropy, volume, and mass of the composite (system plus reservoirs) is chosen to be constant. In the final state, once β has been formed, we will use α and β to denote uniform phases having the intensive properties of the bulk phases in their imagined continuation up to the dividing surface (e.g., a in Fig. 1). Then with subscripts o and f denoting initial and final states, the change in internal energy of the composite system due to the formation of phase β is given by

$$\Delta U = \Delta U^\tau + \Delta U^\pi + U_f^\alpha - U_o^\alpha + U^\beta + U^\sigma, \quad (33)$$

where U_o^α , U_f^α , and U^β all refer to uniform phases, imagined or otherwise, and U^σ refers to the excess quantity associated with the interface that appears in the final state. Since the temperature reservoir does not perform work and the work reservoir cannot communicate heat to the remainder of the system (and T and P are maintained constant) we have

$$\Delta U^\tau = T\Delta S^\tau = -T(S^\beta + S^\sigma + S_f^\alpha - S_o^\alpha), \quad (34)$$

$$\Delta U^\pi = -P\Delta V^\pi = P(V^\beta + V_f^\alpha - V_o^\alpha), \quad (35)$$

while the first degree homogeneous nature of the extensive quantities requires

$$U_f^\alpha = TS_f^\alpha - PV_f^\alpha + \mu^\alpha N_f^\alpha, \quad (36)$$

$$U_o^\alpha = TS_o^\alpha - PV_o^\alpha + \mu^\alpha N_o^\alpha, \quad (37)$$

$$U^\beta = TS^\beta - P^\beta V^\beta + \mu^\beta N^\beta. \quad (38)$$

Proper accounting of the actual amount of extensive quantities is restored via the single-component analog of Eq. (32),

$$U^\sigma = TS^\sigma + \sigma F + \tilde{\mu} N^\sigma. \quad (39)$$

In Eqs. (36) and (37) we have used the fact that μ^α remains unchanged because T and P are constant in α . Furthermore, by introducing P^β , we have allowed for the possibility, discussed in the previous section, that the pressures in the two phases may be different. We emphasize again that

$\tilde{\mu}$ is a generalized potential that includes the action of the field, and U^σ includes the contribution of the ‘‘potential’’ energy [see Eq. (26)].

Conservation of mass imposes the constraint

$$N_o^\alpha = N_f^\alpha + N^\beta + N^\sigma. \quad (40)$$

Substituting Eqs. (34)–(40) into Eq. (33) yields

$$\begin{aligned} \Delta U = & (P - P^\beta)V^\beta + \sigma F + [\mu^\beta(P^\beta) - \mu^\alpha(P)]N^\beta \\ & + [\tilde{\mu} - \mu^\alpha(P)]N^\sigma. \end{aligned} \quad (41)$$

The assumption is often made that $\tilde{\mu} = \mu^\alpha$. This implies that the bulk phase α imposes its chemical potential on the interface σ though not in general on the new phase β , except at equilibrium. Equation (41) then simplifies to

$$\Delta U = (P - P^\beta)V^\beta + \sigma F + [\mu^\beta(P^\beta) - \mu^\alpha(P)]N^\beta. \quad (42)$$

We point out that this situation is possible, but that it also implies the application of a field (constraint) that will cause $\tilde{\mu} = \mu^\alpha$. Since the ΔU in Eq. (42) refers (see its introduction at the beginning of this section) to a change of state in which both the entropy and volume are maintained constant, it is clearly equal to the $-W_1$ of Eq. (3), i.e., to the reversible work, in excess of volume work, performed on the system. It is thus the reversible work of formation of the embryo, and if $\tilde{\mu} = \mu^\alpha$ it may include work exchanged with the field. We note that Eq. (41) is more general than Eq. (42).

Using identical arguments, the reversible work of forming a bubble or a droplet β within an existing phase α for an n -component mixture ($i = 1, \dots, n$) is

$$\begin{aligned} W_{\text{rev}} = & (P - P^\beta)V^\beta + \sigma F + \sum_i [\mu_i^\beta(P^\beta) - \mu_i^\alpha(P)]N_i^\beta \\ & + \sum_i [\tilde{\mu}_i - \mu_i^\alpha(P)]N_i^\sigma. \end{aligned} \quad (43)$$

In deriving this equation it is assumed that the formation of the embryo β does not change the composition of the mother phase α . In other words, the embryo is small compared to the mother phase.

When the embryo is incompressible, as is approximately true for a small droplet, we can write

$$\mu_i^\beta(P^\beta) = \mu_i^\beta(P) + \bar{v}_i^\beta(P^\beta - P), \quad (44)$$

where \bar{v}_i^β is the partial molar volume of component i in phase β . Then the work of formation simplifies to

$$\begin{aligned} W_{\text{rev}} = & \sigma F + \sum_i [\mu_i^\beta(P) - \mu_i^\alpha(P)]N_i^\beta \\ & + \sum_i [\tilde{\mu}_i - \mu_i^\alpha(P)]N_i^\sigma. \end{aligned} \quad (45)$$

The last summation in this equation is often incorrectly omitted in the nucleation literature.

The reversible work of formation of an embryo that is not a nucleus is given by Eqs. (43) or (45), and in this sense the argument has gone beyond the point where Gibbs left it. However, the characteristics of this embryo, in particular σ and $\tilde{\mu}_i$ depend on the particular constraint used to maintain

the equilibrium. The constraint can be interpreted as a field. Exactly what model, that is to say what field, needs to be introduced is then an open question. The need to employ this constraint is a nontrivial problem because the path of displacement from the initial state of equilibrium must be a reversible one (i.e., a sequence of equilibrium states) if the use and variation of a thermodynamic potential is to have any meaning. Thus constrained equilibrium states adjacent to that of the nucleus must be involved in this path, and in the nucleation case these states must represent embryos that are not nuclei. Fortunately, as explained in Sec. II, in the variation of the thermodynamic potential about the state of the system containing the nucleus, the constraints defining the reversible path do not have to be specified in detail (they may remain “hidden”) as long as we are only interested in the properties of the nucleus itself, and, as a result, we need not concern ourselves about the “model” as long as our interest remains concentrated on the properties of the nucleus itself.

We now consider the determination of the critical nucleus. The composition of the critical nucleus follows from applying to Eq. (45) the conditions ($i=1,\dots,n$)

$$\frac{\partial W_{\text{rev}}}{\partial N_i^\beta} = 0, \quad (46)$$

$$\frac{\partial W_{\text{rev}}}{\partial N_i^\sigma} = 0. \quad (47)$$

In Eq. (46) N_j^β ($j \neq i$) and all N_i^σ are kept constant. In Eq. (47) N_j^σ ($j \neq i$) and all N_i^β are kept constant. Equation (46) yields

$$\begin{aligned} \frac{\partial W_{\text{rev}}}{\partial N_j^\beta} = & \sigma \frac{\partial F}{\partial N_j^\beta} + \Delta \mu_j + F \frac{\partial \sigma}{\partial N_j^\beta} + \sum_i N_i^\sigma \frac{\partial \tilde{\mu}_i}{\partial N_j^\beta} \\ & + \sum_i N_i^\beta \frac{\partial \mu_i^\beta}{\partial N_j^\beta}, \end{aligned} \quad (48)$$

and Eq. (47) yields

$$\begin{aligned} \frac{\partial W_{\text{rev}}}{\partial N_j^\sigma} = & \sigma \frac{\partial F}{\partial N_j^\sigma} + \Delta \tilde{\mu}_j + F \frac{\partial \sigma}{\partial N_j^\sigma} + \sum_i N_i^\sigma \frac{\partial \tilde{\mu}_i}{\partial N_j^\sigma} \\ & + \sum_i N_i^\beta \frac{\partial \mu_i^\beta}{\partial N_j^\sigma}, \end{aligned} \quad (49)$$

where

$$\Delta \mu_j = \mu_j^\beta(P) - \mu_j^\alpha(P), \quad (50)$$

$$\Delta \tilde{\mu}_j = \tilde{\mu}_j - \mu_j^\alpha(P). \quad (51)$$

The sum of the third and fourth terms on the right hand side in both Eqs. (48) and (49) vanishes because of (32). The fifth terms cancel because of the Gibbs–Duhem equation. Finally,

$$F = 4\pi r^2 = 4\pi \left[\frac{3}{4\pi} \left(\sum_i \bar{v}_i N_i^\beta \right) \right]^{2/3}, \quad (52)$$

$$\frac{\partial F}{\partial N_j^\beta} = \frac{2\bar{v}_j^\beta}{r}, \quad (53)$$

$$\frac{\partial F}{\partial N_j^\sigma} = 0. \quad (54)$$

Using Eq. (53) in (48) and (54) in (49) yields the conditions of equilibrium

$$\Delta \mu_j + \sigma \frac{\partial F}{\partial N_j^\beta} = 0 \Rightarrow \mu_j^\beta(P^\beta) = \mu_j^\alpha(P), \quad (55)$$

$$\Delta \tilde{\mu}_j = 0 \Rightarrow \tilde{\mu}_j = \mu_j^\alpha(P). \quad (56)$$

Equations (55) and (56) imply that the chemical potentials of each component are uniform throughout the entire system. Thus for the critical nucleus, the constraint vanishes identically. As shown elsewhere,⁹ the critical nucleus is in unstable equilibrium with the mother phase.

Returning now to Eq. (41), if phase β is in equilibrium with α , the reversible work becomes

$$\delta U \equiv W_{\text{rev}} = \sigma F + (P - P^\beta) V^\beta. \quad (57)$$

If the new phase is spherical, we invoke Eq. (7), Laplace’s equation, to obtain^{6,7}

$$W_{\text{rev}} = \frac{4\pi r^2 \sigma}{3} = \frac{2\pi r^3 (P^\beta - P)}{3} = \frac{16\pi \sigma^3}{3(P^\beta - P)^2}. \quad (58)$$

Equation (58) gives the reversible work of forming a spherical critical nucleus. It is completely general, and does not depend on any assumptions as to the nucleus’ incompressibility.

In order to calculate the nucleation rate, it is necessary to determine the critical nucleus’ size and composition. The nucleus, in classical theory, is assumed homogeneous. However, because real nuclei are not uniform, the proper, thermodynamically consistent way of determining the nucleus size and composition within the classical theory is an important problem. It is often referred to as the surface enrichment problem in the nucleation literature.^{15,16}

We consider as an illustration the condensation of a binary vapor mixture. Treating the liquidlike embryos as incompressible, the thermodynamically consistent set of equations needed to calculate the composition, size, and work of formation of the critical nucleus are

$$\mu_1^\beta(P) + (P^\beta - P) \bar{v}_1^\beta = \mu_1^\alpha(P), \quad (59)$$

$$\mu_2^\beta(P) + (P^\beta - P) \bar{v}_2^\beta = \mu_2^\alpha(P), \quad (60)$$

$$r^* = \frac{2\sigma}{(P^\beta - P)}, \quad (61)$$

$$W_{\text{rev}}^* = \frac{4\pi}{3} \sigma (r^*)^2, \quad (62)$$

where superscript * denotes the critical nucleus, β denotes the liquid, and α the vapor. Equations (59) and (60) are used to solve for P^β and x_1^β (mole fraction of component 1). Then, with σ evaluated at the calculated composition, the size and work of formation of the critical nucleus are obtained from Eqs. (61) and (62). The above equations are in one-to-one correspondence with Eqs. (55), (7), and (58). The key point here is that the starting point, Eq. (45), is correct and thermodynamically consistent. If, as is usually done in the nucle-

ation literature, one starts instead from the incorrect equation by truncating Eq. (45) through removal of the surface terms, erroneous conditions of equilibrium are obtained instead of Eq. (55).^{17,18}

These inconsistencies were noted by Wilemski,^{15,16} who argued that the correct equations to be used in the calculation of the size and composition of the critical nucleus are Eq. (55), which indeed they are. Interestingly, Wilemski started with the incorrect equation, namely the truncated version of Eq. (45), but he arrived at the correct result by partitioning the embryo into bulk and surface portions.

VI. DISCUSSION

In this work we have extended the Gibbsian treatment of interfacial thermodynamics in order to properly consider the energetics of forming a small embryo of a new phase within a uniform macroscopic mother phase. Whereas Gibbs considered the particular case in which the embryo is in unstable equilibrium with the mother phase, we have treated the general case in which the embryo and the mother phase are not in equilibrium. This extension is necessary in order to provide a rigorous and thermodynamically consistent expression for the reversible work of embryo formation, from which the work of formation of the critical nucleus follows as an extremum condition. The important result from the present work is an expression for the reversible work of embryo formation, from which the equilibrium conditions between embryo and mother phase, as well as the Gibbs expression for the reversible work of nucleus formation, are obtained naturally as extremum conditions. The new expression derived here differs from the one usually used in the nucleation literature.

In order to apply thermodynamic reasoning to a composite system that is not in equilibrium, it is necessary to introduce a constraint that prevents the free exchange of matter between embryo and mother phase. The resulting constrained system is amenable to thermodynamic analysis, the approach thus serving to illustrate the crucial but often neglected role of constraints in thermodynamics. The constraint imposes internal equilibrium throughout the inhomogeneous system consisting of the embryo and the interface between the embryo and the mother phase. This fixes the location of the mathematical surface of discontinuity between the embryo and the mother phase. In the absence of a constraint, the location of this surface is specified by the identical vanishing of the curvature contribution to the interfacial energy. The constraint, however, removes this degree of freedom by fixing *a priori* the location of the surface of discontinuity. The present treatment is therefore strictly applicable only in the limit in which the radii of curvature are large with respect to molecular dimensions, or, in other words, when the interface can be considered locally planar.

Our work is closely related to that of Nishioka and Kusaka,⁸ who also extended interfacial thermodynamics to

noncritical clusters. However, these authors did not treat the constraint explicitly, and hence arrived at a different expression for the work of embryo formation.

Although for most purposes of nucleation theory it is only the extremum (single-component systems) or saddle point (multicomponent mixtures) of the expression derived here that matters, the present generalization provides the proper and thermodynamically consistent formalism for discussing the energetics of embryo formation. Among the benefits resulting from this rigorous approach is the unambiguous resolution of a long-standing controversy in the nucleation literature^{15–18} about whether the size and composition dependence of the interfacial tension should be included in taking the extremum condition of the reversible work of embryo formation in binary mixtures. Finally, the density functional approach to nucleation theory (e.g., Ref. 19) is limited in its rigorous applications to the nucleus alone, so that a plausibility argument must be used to incorporate the effects of embryos that are not nuclei.²⁰ The present development may be helpful in eliminating the need for a plausibility argument.

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