Chapter 6
Thermodynamics of Interfaces

Fundamental equations of thermodynamics are commonly written for homogeneous systems without explicitly accounting for effects of the container wall. Similarly, we treat a system consisting of multiple coexisting phases as if it is made of homogeneous parts separated by sharp interfaces. This is an acceptable practice provided that the number of molecules in the vicinity of the container wall or the interface is negligibly small compared with the number of the molecules in the bulk. The approach becomes inappropriate for microscopic systems in which the majority of molecules are near a wall or an interface. For example, inhomogeneity extends throughout the entire system of interest when a fluid is confined to a narrow pore of several atomic diameters. In this case, the phase behavior changes dramatically compared to that in the bulk. It is also possible that the phenomena of interest are dictated by the properties of the interface. Examples include formation of microemulsion, wetting of a solid surface, condensation of a vapor phase, and crystallization from a melt or a solution. In this chapter, we examine how thermodynamics can be extended to explicitly account for effects of interfaces.

6.1 Interfacial Region

When studying a system in two-phase coexistence, we usually ignore the microscopic details of the interface separating the phases. Instead, we simply think of the interface as a diathermal and movable wall that is permeable to all species. In Chap. 2, this led to the conditions of equilibrium expressed as

$$T^{\alpha} = T^{\beta} \,, \quad P^{\alpha} = P^{\beta} \,, \quad \text{and} \quad \mu_i^{\alpha} = \mu_i^{\beta} \,, \quad i = 1, \ldots, c \,, \tag{6.1}$$

where the superscripts α and β label the phases.

However, it is unrealistic to expect that the interface is sharply defined at the atomistic length scale. For example, the interface between liquid water and its saturated vapor is an inhomogeneous transition region over which the density changes

I. Kusaka, *Statistical Mechanics for Engineers*,
DOI 10.1007/978-3-319-13809-1_6

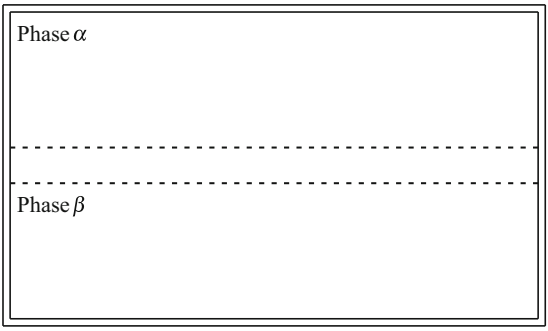

Fig. 6.1 The interfacial region is indicated by a pair of dashed lines and separates two coexisting bulk phases α and β.

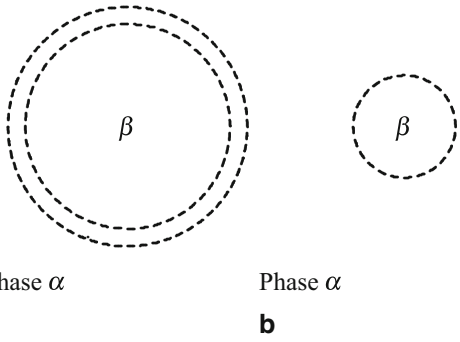

Fig. 6.2 A droplet (β) in equilibrium with a supersaturated vapor α. At a lower degree of supersaturation, the droplet attains bulk-like properties near its center, a situation we indicate with a pair of *dashed circles* in **a**. At a higher degree of supersaturation, however, it becomes inhomogeneous even at its center as indicated by a *single dashed circle* in **b**.

continuously from the bulk liquid value to that of the vapor. Typically, the thickness of this transition region is of the order of several atomic diameters. In the case of a multicomponent system, the density of certain species within the transition region may be significantly higher or lower than its values in the coexisting bulk phases. To emphasize the nonzero thickness of the transition region, we use a pair of dashed lines to indicate an interface between phases as shown in Fig. 6.1.

The equilibrium between two phases may involve a curved interface. A familiar example is meniscus formation where the interface meets the wall. As we shall see, a vapor phase can be compressed beyond its saturation pressure without undergoing a phase transition. This supersaturated vapor can coexist with a liquid droplet. Similarly, a bubble can coexists with superheated liquid phase. In these cases also, we have a transition region of nonzero thickness, which is again indicated by a pair of dashed circles as in Fig. 6.2a.

With the increasing degree of supersaturation, the droplet (in equilibrium with the supersaturated vapor) becomes smaller and eventually loses a bulk-like properties even at its center. The same applies for the bubble with an increasing degree of superheating. This will be indicated as in Fig. 6.2b using a single dashed circle, within which the state of the matter is inhomogeneous.

Following Ref. [12], we develop thermodynamics of interfaces for a system containing a spherical droplet. With the assumed spherical symmetry, our theory remains applicable even for extremely small droplets illustrated in Fig. 6.2b. No satisfactory extension of the theory has been developed to cope with the situation in Fig. 6.2b without the spherical symmetry. Our formulation carries over to the flat interface in Fig. 6.1 simply by increasing the characteristic radius of the interface indefinitely.

6.2 Defining a System

Let us consider an isolated macroscopic body that contains a small inhomogeneous region. For concreteness, we consider a microscopic liquid droplet floating in a supersaturated (metastable) vapor phase. We suppose that the droplet is spherically symmetric. As shown in Fig. 6.3, we take a spherical region of radius R_0 centered around the center of symmetry and mentally divide the body into two parts. The region inside the sphere will be called region I. The region outside the sphere is region II. Then, region I contains the droplet, some portion of the metastable vapor phase, and the interface between them. Region II contains only the remaining portion of the homogeneous vapor phase.

Because region I contains all that is interesting to us, it will be advantageous to take region I as the system,treating region II as the surroundings. But, we must first ask if thermodynamic quantities such as the internal energy U^I, entropy S^I, and the number N_i^I of molecules of species i are well defined for region I. This is because we are interested in effects of interfaces in this chapter and we cannot afford to simply ignore the interaction between I and II, which is mediated by molecules near the boundary at R_0.

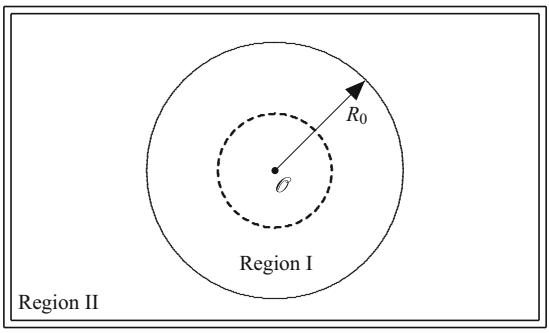

Fig. 6.3 An isolated system containing a metastable vapor phase and a spherical liquid droplet (*dashed line*). The sphere of radius R_0 (*solid line*) separates the isolated system into regions I and II.

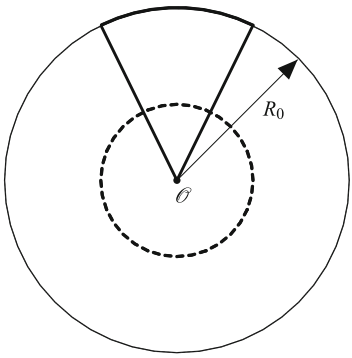

Fig. 6.4 The system defined as the conic region (*thick solid lines*).

To define N_i^I, we adopt the convention that a molecule of species i belongs to region I if its center of mass is inside I.[29] How about U^I? Due to our choice of R_0, the region of inhomogeneity is contained in region I, and region II is homogeneous. Thus, the internal energy density is uniform throughout region II and its internal energy is this energy density multiplied by the volume of region II. Because the macroscopic body is isolated, its internal energy is a well-defined quantity. We obtain U^I as the difference between these energies. The same argument applies to S^I.

Now that region I is shown to have well-defined U^I, S^I, and N_i^I, can we choose it as our system? Not quite. Recall that thermodynamic quantities are classified into either extensive or intensive quantities. This classification plays an essential role in thermodynamics and gives rise to such important identities as the Euler and the Gibbs–Duhem relations. When extending thermodynamics to include effects of interfaces, it is highly desirable that we maintain this classification. To say that U^I is extensive, we must show that the internal energy of a system that is λ times region I is λU^I. But, what is that system when $\lambda = \sqrt{2}$, for example?

Instead of region I, we define our system as a conic region with its apex at $\mathcal{O}$ and a portion of the boundary at R_0 as its base as shown in Fig. 6.4. We use ω to denote the solid angle subtended by the base at $\mathcal{O}$.

The **solid angle** subtended by an object at a point is the area occupied by the object when it is projected onto a unit sphere centered around the point by means of rays of light emanating from or converging onto that point. So, the solid angle of a sphere at its center is 4π, while that of the hemisphere is 2π. The solid angle subtended at the center of a cube by one of its six faces is $4\pi/6 = 2\pi/3$.[30]

Because of the spherical symmetry of region I, the internal energy, entropy, and the number of moles of species i in the system are given by

$$U = \frac{\omega}{4\pi} U^I \,, \quad S = \frac{\omega}{4\pi} S^I \,, \quad \text{and} \quad N_i = \frac{\omega}{4\pi} N_i^I \,, \tag{6.2}$$

respectively. Since U^I, S^I, and N_i^I are all well-defined, so are U, S, and N_i for any ω between 0 and 4π.

6.3 Condition of Equilibrium

To formulate the condition of equilibrium, we will have to consider variations in the state of the system. Here again, a careful analysis is required to account for the interaction across the system boundaries. This is the subject of Sect. 6.3.1. The key conclusion is that, to the first order of variations, we may regard the variations to be affecting the state of the system only, while leaving the surroundings unaffected. This is despite the fact that these two parts are in direct contact with each other. If you wish to omit Sect. 6.3.1, keep this conclusion in mind and head to Sect. 6.3.2.

6.3.1 †Variations in the State of the System

Because the system is inhomogeneous, densities of the internal energy, entropy, and the number of molecules vary across the system, and collectively determine the state of the matter. In what follows, we adopt a generic notation $\xi(\boldsymbol{r})$ for these densities. At the initial state, ξ depends only on the radial distance $r := \|\boldsymbol{r}\|$ from $\mathscr{O}$ and reaches a constant as R_0 is approached from $\mathscr{O}$.

Let us now consider a variation in the state of the system, and denote by $\xi(\boldsymbol{r}) + \delta\xi(\boldsymbol{r})$ the value of ξ in the varied state. Unless the variation is accompanied by a similar change in the surroundings, $\xi(\boldsymbol{r}) + \delta\xi(\boldsymbol{r})$ will not be spherically symmetric over the entire 4π nor is it uniform across R_0. The resulting infinitesimal discrepancy in the state of the matter between the two parts may cause $\delta\xi$ to exhibit a complex $\boldsymbol{r}$ dependence across the system boundaries, which is very difficult to account for. For these more general variations, called **discontinuous variation** for brevity,[31] how do we evaluate the values of δU and δS?

The simplest approach is to ignore the complex behavior of $\delta\xi(\boldsymbol{r})$ across the boundaries. When figuring out U and S of the system in its varied state, we *pretend* that the surroundings have experienced a similar variation to ensure the spherical symmetry of region I over the entire 4π and the uniformity across R_0.[32] This is indicated by the dashed line in Fig. 6.5. *For the same varied state* we are considering, the internal energy and entropy of the surroundings are computed by assuming that the state of the matter in the surroundings continues beyond the boundaries and that the spherical symmetry of region I and the uniformity across R_0 still hold. The same convention can be adopted when considering simultaneous variations involving both the system and the surroundings.

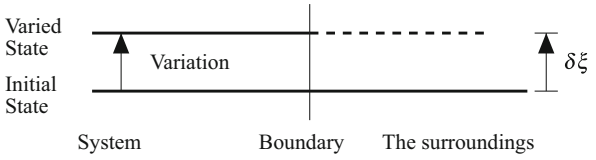

Fig. 6.5 Discontinuous variation of the system.

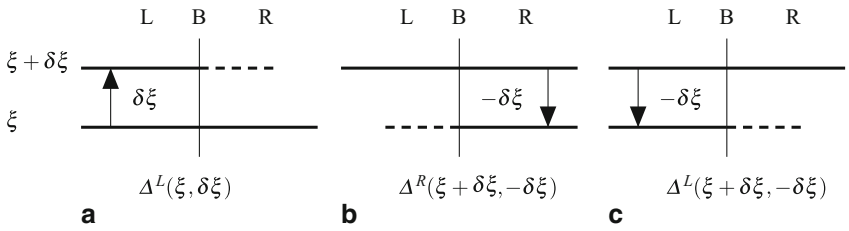

Fig. 6.6 Three distinct discontinuous variations either in the system (L) or in the surroundings (R). In each diagram, the *long horizontal solid lines* indicates the initial state, while the *shorter horizontal line* continued across the boundary (B) in *dashed line* indicates the varied state.

This is how we proceed. As far as the internal energy and entropy of the *entire* isolate system is concerned, the error thus committed is in the higher order terms of the variations, and does not affect our discussion of the condition of equilibrium.

To see this, let us consider the three distinct variations illustrated in Fig. 6.6. In Fig. 6.6a, we consider an infinitesimal variation $\delta\xi$ in the state of the system starting from the initial state specified by ξ. Our method of computing the variation of the internal energy (or the entropy) in the system (L) and the surroundings (R) leads to an error in our estimate of the variation of the internal energy of the composite system, which we denote by $\Delta^L(\xi,\delta\xi)$, where the superscript L indicates that the variation is taken in L. Similarly for the superscript R in the case of variations in R.

But, in the vicinity of the boundary (B), the varied state in Fig. 6.6a is identical to that in Fig. 6.6b. Thus,

$$\Delta^L(\xi,\delta\xi) = \Delta^R(\xi+\delta\xi,-\delta\xi)\,. \tag{6.3}$$

Now, Fig. 6.6b, c share the identical initial state in which the state of the matter is locally symmetric around B. If we focus only on the immediate vicinity of B, their varied states are the mirror images of each other. This implies that

$$\Delta^R(\xi+\delta\xi,-\delta\xi) = \Delta^L(\xi+\delta\xi,-\delta\xi)\,. \tag{6.4}$$

Thus, we have an equality

$$\Delta^L(\xi,\delta\xi) = \Delta^L(\xi+\delta\xi,-\delta\xi)\,. \tag{6.5}$$

Expanding the expression on the left in the Maclaurin series (see Appendix B.1) with respect to the second argument, we have

$$\Delta^L(\xi,\delta\xi) = \Delta^L(\xi,0) + \Delta_2^L(\xi,0)\delta\xi + \text{h.o.} = \Delta_2^L(\xi,0)\delta\xi + \text{h.o.}\,, \tag{6.6}$$

where Δ_2^L is the partial derivative of Δ^L with respect to its second argument. We also used the fact that $\Delta^L(\xi,0)\equiv 0$ for any ξ. That is, no error is introduced if no

variation is taken. Likewise, we have

$$\Delta^L(\xi+\delta\xi,-\delta\xi)=-\Delta_2^L(\xi+\delta\xi,0)\delta\xi+\text{h.o.}=-\Delta_2^L(\xi,0)\delta\xi+\text{h.o.}\,, \tag{6.7}$$

where the last step follows from the Taylor expansion with respect to the first argument. Using (6.6) and (6.7) in (6.5), we see that $\Delta_2(\xi,0)$ can only be zero. Thus,

$$\Delta^L(\xi,\delta\xi)=\text{h.o.} \tag{6.8}$$

For alternative demonstrations of the same idea, see Refs. [4, 11].

We note that the symmetry around B of the initial state of the matter entered as a key ingredient of our analysis. However, because the system boundaries are curved, one side of B is not entirely equivalent to the other if we focus on a larger portion of the boundary. This is why we have taken a "local" view when looking for the symmetry. Because our system is made of atoms, one may argue that $\xi(\boldsymbol{r})$ loses its meaning in an extremely local view. This is not so. In thermodynamics, we are interested in thermally averaged quantities, and $\xi(\boldsymbol{r})$ is well defined at every point in space.

If there should remain any doubt about our analysis, it is with variations taken near the apex $\mathscr{O}$ of the cone. (See Fig. 6.4.) For a sufficiently small ω, a discontinuous variation taken in the system affects only those molecules of the surroundings near $\mathscr{O}$. A similar discontinuous variation taken in the surroundings may affect all the molecules of the system near $\mathscr{O}$. In that case, it seems unreasonable to expect (6.4) to hold.

We can easily circumvent the difficulty indicated here for a nucleus with a homogeneous core. We simply exclude the apex and its vicinity by means of another spherical boundary passing through the homogeneous core. For the situation indicated by Fig. 6.2b, however, this is not possible. Even in such cases, one can insist on the *formal* significance of the theory we develop on the basis of (6.8) provided that various physical quantities behave in a physically sensible manner, for example, a quantity that must be real and positive remains so.

Far more satisfactory will be methods based on the principle of statistical mechanics that apply regardless of the presence or absence of the homogeneous core. Classical density functional theory discussed in Chap. 7 is one such theory. Molecular simulation is another satisfactory approach. The important point is that thermodynamics of interfaces provides a useful framework when trying to interpret the predictions of these statistical mechanical approaches. In fact, no inconsistency has ever been discovered to implicate (6.8).

6.3.2 Fixed System Boundaries

As we have just demonstrated, we may suppose that the state of the system can be varied without affecting the surroundings to the first order of the variation. Thus, if we limit our considerations up to this order, the system can be treated as if it is iso-

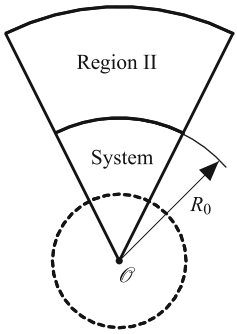

Fig. 6.7 The composite system consisting of the system and a portion of region II.

lated. This being case, the condition of its equilibrium is that S takes the maximum possible value for given $U, N_1, \ldots, N_c$, and the fixed system boundaries specified by R_0 and ω. It is important to note that specification of the system volume alone is not sufficient for an inhomogeneous system. We can adjust R_0 and ω without changing the system volume. But this will certainly affect the amount of the interfacial region included in our system.

The condition of equilibrium can be expressed in different ways. For example, we may demand that U be minimum for given S, $N_1, \ldots, N_c$, R_0, and ω. But, the most convenient formulation is that of Sect. 2.9.3, according to which the necessary condition of equilibrium is that

$$\delta U = A_0 \delta S + \sum_{i=1}^{c} A_i \delta N_i \,, \quad R_0, \omega \text{ const.} \tag{6.9}$$

holds for any *reversible* variations with fixed system boundaries.[33] Here, A_0 and $A_1, \ldots, A_c$ are constants yet to be determined. We recall from Sect. 2.9.3 that a variation δX_i of some additional variable X_i is said to be reversible if it can take both positive and negative values.

To determine the values of A_0 and A_i, which are the temperature and chemical potentials of species i of the system, we consider a composite system consisting of our original system and a portion of region II as shown in Fig. 6.7. The composite system itself may be regarded as isolated in the same way the original system was. Because the boundary between the original system and region II is purely a construct of our imagination, it exerts no physical effect. In other words, it is a diathermal and rigid wall permeable to all species. Thus, provided that S and $N_1, \ldots, N_c$ of the system are all capable of reversible variations, the condition of equilibrium of the composite system demands that A_0 be equal to the temperature T of the surroundings and A_i to the chemical potential μ_i of species i of the surroundings. Accordingly, (6.9) now reads

$$\delta U = T \delta S + \sum_{i=1}^{c} \mu_i \delta N_i \,, \quad R_0, \omega \text{ const.} \tag{6.10}$$

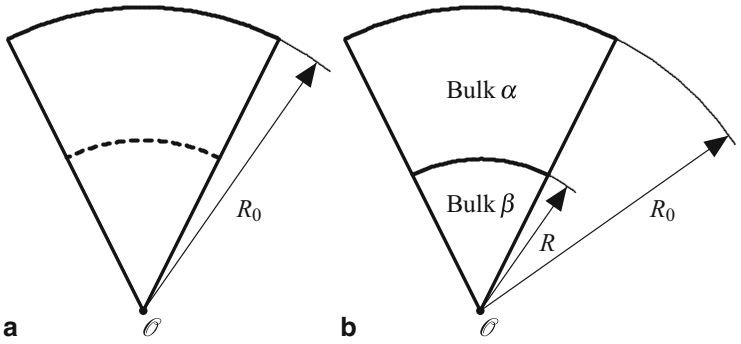

Fig. 6.8 Construction of a reference system. **a** Actual system. **b** Reference system with a dividing surface at R.

6.3.3 Reference System

Before considering the generalization of (6.10) for the case of movable system boundaries in Sect. 6.3.4, it is convenient to introduce the **reference system**, also known as the **hypothetical system**, as illustrated in Fig. 6.8. First, we draw a spherical surface, called the **dividing surface**, of radius R ($< R_0$) according to some arbitrary rule to be decided on later. Then, we fill the space between R and R_0 of the system by bulk phase α. By "bulk phase," we mean that it behaves as if it is a portion of macroscopic and homogeneous phase α. The space between $\mathcal{O}$ and R is filled with bulk phase β *that has the same temperature and chemical potentials* as α phase. This does *not* imply that phase β is identical to phase α. In other words,

$$\mu_i^{\alpha}(T,P^{\alpha},x_1^{\alpha},\ldots,x_{c-1}^{\alpha}) = \mu_i^{\beta}(T,P^{\beta},x_1^{\beta},\ldots,x_{c-1}^{\beta})\,, \quad i=1,\ldots,c \tag{6.11}$$

where x_i is the mole fraction of species i, has a nontrivial solution with $P^{\alpha} \neq P^{\beta}$.

For these bulk phases, we have

$$\delta U^{\alpha} = T\delta S^{\alpha} + \sum_{i=1}^{c} \mu_i \delta N_i^{\alpha} \quad \text{and} \quad \delta U^{\beta} = T\delta S^{\beta} + \sum_{i=1}^{c} \mu_i \delta N_i^{\beta} \tag{6.12}$$

for variations that do not affect the system boundaries. Subtracting (6.12) from (6.10), we find

$$\delta U^{s} = T\delta S^{s} + \sum_{i=1}^{c} \mu_i \delta N_i^{s}\,, \quad R_0, \omega \text{ const.} \tag{6.13}$$

In this equation, the quantities defined by

$$U^{s} := U - (U^{\alpha} + U^{\beta})\,, \quad S^{s} := S - (S^{\alpha} + S^{\beta})\,, \quad \text{and} \quad N_i^{s} := N_i - (N_i^{\alpha} + N_i^{\beta})\,. \tag{6.14}$$

are known as the **surface excess quantities**.

By construction, the reference system has no interface. Thus, any difference between the actual and the reference systems can be attributed to the presence of the interface. We emphasize that the reference system is purely a theoretical construct that cannot be created in practice. The role it plays is entirely analogous to that of various ideal systems, such as ideal gas mixture and ideal mixtures, introduced in order to characterize the behavior of real mixtures.

6.3.4 Movable System Boundaries

Equation (6.10) can be generalized easily for the case of movable system boundaries. Because the system boundary at R_0 is passing through a homogeneous region, its motion introduces a simple work term that may be written as

$$-\omega {R_0}^2 P^\alpha \delta R_0 \,, \tag{6.15}$$

where $\omega {R_0}^2 \delta R_0$ is the volume swept out by the boundary as it moves to the new position $R_0 + \delta R_0$. In contrast, a change in ω involves stretching or compressing of the inhomogeneous region and the associated work term seems difficult to compute. We do know, however, that it should be proportional to $\delta\omega$. That is, since U is a function of $S, N_1, \ldots, N_c, R_0$, and ω, the work term in question is $(\partial U/\partial\omega)_{S,N,R_0}\delta\omega$, which we shall denote simply as $\sigma\delta\omega$. Thus,

$$\delta U = T\delta S + \sum_{i=1}^{c} \mu_i \delta N_i - \omega {R_0}^2 P^\alpha \delta R_0 + \sigma\delta\omega \,. \tag{6.16}$$

But, how do we evaluate the value of σ? For our thermodynamic formulation to be of any use, this quantity must be related to something we can measure at least in principle. For this purpose, it proves useful to consider the generalization of (6.13).

We note that δU^s is determined completely if δU, δU^α, and δU^β are given. The latter two quantities refer to the bulk homogeneous phases and are given, respectively, by

$$\delta U^\alpha = T\delta S^\alpha - P^\alpha \delta V^\alpha + \sum_{i=1}^{c} \mu_i \delta N_i^\alpha \tag{6.17}$$

and

$$\delta U^\beta = T\delta S^\beta - P^\beta \delta V^\beta + \sum_{i=1}^{c} \mu_i \delta N_i^\beta \tag{6.18}$$

for movable system boundaries.

A part of δV^α comes from a change in R_0 and makes the identical contribution to δU and δU^α, thus dropping out from δU^s. The remaining part of δV^α, δV^β, and $\delta\omega$ are completely determined once δR and δA are given, where A is the area of the dividing surface, because of the geometric relations

$$A = \omega R^2 \,, \quad V^\alpha = \frac{\omega}{3}\left({R_0}^3 - R^3\right) \,, \quad \text{and} \quad V^\beta = \frac{\omega}{3}R^3 \,. \tag{6.19}$$

The validity of these equations is most readily seen by applying them for the entire spherical region, for which $\omega = 4\pi$. It follows that

$$\delta U^s = T\delta S^s + \sum_{i=1}^{c} \mu_i \delta N_i^s + \gamma \delta A + C\delta R \,. \tag{6.20}$$

Because this result holds for any variation and S^s, $N_1^s, \ldots, N_c^s$, A, and R are path-independent state functions, we conclude that

$$U^s = U^s(S^s, N_1^s, \ldots, N_c^s, A, R) \,. \tag{6.21}$$

From these two equations, we see that

$$C = \left(\frac{\partial U^s}{\partial R}\right)_{S^s, N^s, A} = C(S^s, N_1^s, \ldots, N_c^s, A, R) \,. \tag{6.22}$$

Combining (6.17), (6.18), and (6.20), we obtain

$$\delta U = T\delta S + \sum_{i=1}^{c} \mu_i \delta N_i - P^\alpha \delta V^\alpha - P^\beta \delta V^\beta + \gamma \delta A + C\delta R \,. \tag{6.23}$$

Exercise 6.1. Express σ in terms of γ, P^α, P^β, R and R_0. ///

6.3.5 Laplace Equation

As we saw in Sect. 6.3.2, the equilibrium of the system demands that its temperature and chemical potentials be equal to those in the surrounding phase α. In this section, we derive an additional condition of equilibrium.

For variations taken while holding $S, N_1, \ldots, N_c, R_0$ and ω constant, we have

$$\begin{aligned} &\delta S = 0 \,, \quad \delta N_1 = \cdots = \delta N_c = 0 \,, \\ &\delta V^\alpha = -\omega R^2 \delta R \,, \quad \delta V^\beta = \omega R^2 \delta R \,, \quad \text{and} \quad \delta A = 2\omega R \delta R \,. \end{aligned} \tag{6.24}$$

Substituting these relations into (6.23), we find

$$(\delta U)_{S,N,R_0,\omega} = (P^\alpha - P^\beta)\omega R^2 \delta R + 2\gamma\omega R \delta R + C\delta R = \left(P^\alpha - P^\beta + \frac{2\gamma}{R} + c_a\right) A \delta R \,, \tag{6.25}$$

where $c_a := C/A$.

Provided that $R > 0$, δR can be either positive or negative. Recalling (2.97), we conclude that

$$P^\beta - P^\alpha = \frac{2\gamma}{R} + c_a \,. \tag{6.26}$$

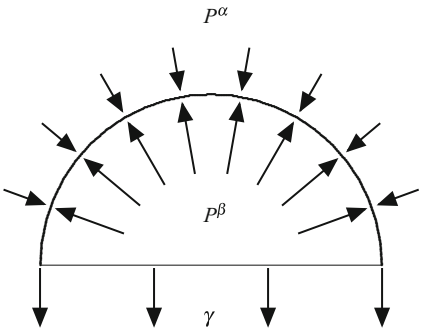

Fig. 6.9 The surrounding fluid pushes the hemisphere of radius R downward with the pressure $\pi R^2 P^\alpha$, and so does the tension γ with the force $2\pi R\gamma$. (From (6.20), we see that γ has the dimension of energy per unit area or force per unit length.) The fluid in the sphere pushes the hemisphere upward with the force $\pi R^2 P^\beta$. The balance of these forces leads to (6.28).

So far, we have left unspecified how we choose the radius R of the dividing surface for a given state of the system. Accordingly, (6.26) holds for any choice for the dividing surface. One common choice is to determine R by

$$C = 0\,. \tag{6.27}$$

For any given state of the system in equilibrium, the quantities S^s, $N_1^s, \ldots, N_c^s$, and A in (6.22) all depend only on R. Thus, (6.27) indeed is an equation for R. For a sufficiently large droplet (or bubble) shown in Fig. 6.2a, the thickness of the interfacial region is considerably smaller than its radius of curvature. In this case, the solution of (6.27) exists and the dividing surface so determined is located within the inhomogeneous transition region. An explicit demonstration is found in Ref. [4].

For the choice of the dividing surface just indicated, (6.26) reduces to

$$P^\beta - P^\alpha = \frac{2\gamma}{R}\,. \tag{6.28}$$

This is known as the **Laplace equation**, and is identical to the condition of mechanical equilibrium of a membrane of zero thickness having the tension γ but no rigidity while separating a spherical region at P^β from the surroundings at P^α. This is illustrated in Fig. 6.9. For this reason, the dividing surface defined by (6.27) and γ associated with this dividing surface are called the **surface of tension** and the **surface tension**, respectively. We choose the surface of tension as the dividing surface with the expectation that γ may be measurable by some mechanical measurement technique.

In the $R \to \infty$ limit, a spherical interface becomes a flat interface separating two macroscopic phases in equilibrium. At the same time, (6.28) reduces to $P^\alpha = P^\beta$, which is just the second equation in (6.1). In other words, the presence of an interface does not affect the condition of phase coexistence across a flat interface.

6.4 Euler Relation

Applying (6.20) to an infinitesimal process that takes the system from a state of equilibrium to another,[34] we obtain

$$\mathrm{d}U^s = T\mathrm{d}S^s + \sum_{i=1}^{c} \mu_i \mathrm{d}N_i^s + \gamma \mathrm{d}A + C\mathrm{d}R \,. \tag{6.29}$$

We now integrate (6.29) from $\omega = 0$ to some nonzero ω ($\leq 4\pi$) without changing the intensive state of the system. During such a process, T and $\mu_1, \ldots, \mu_c$ are constant. If we do not vary the condition to determine the radius of the dividing surface, γ and R are also constant. (Because U^s and A are both extensive variables, $\gamma = (\partial U^s/\partial A)_{S^s,N^s,R}$ should be intensive.) Thus,

$$U^s = TS^s + \sum_{i=1}^{c} \mu_i N_i^s + \gamma A \,, \tag{6.30}$$

which is the Euler relation for the inhomogeneous system.

According to (6.30), γA is *the reversible work required to convert the reference system into the actual system by creating an interface*. (See Fig. 6.10.) To see this, let $[U]$ denote the increase in the internal energy of the system upon the reversible creation of the interface. Because the surroundings can be made arbitrarily large, T and $\mu_1, \ldots, \mu_c$ remain constant during the process. Thus, if we regard the system and its surroundings as forming an isolated system, the increase in the internal energy of the surroundings is given by

$$-T[S] - \sum_{i=1}^{c} \mu_i [N_i] \,, \tag{6.31}$$

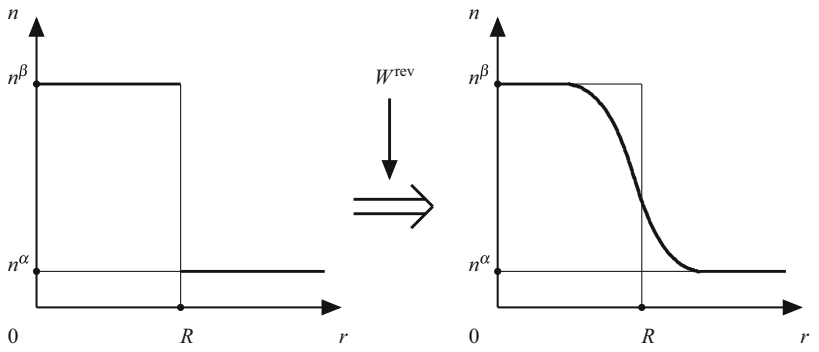

Fig. 6.10 Introduction of an interface into the reference system by means of a reversible work source. The number density of molecules is denoted by n with a *superscript* indicating its values in the bulk reference phases.

where $[S]$ and $[N_i]$ are defined similarly to $[U]$. This expression follows from the fundamental property relation (2.37) applied to the surroundings and the fact that the number of molecules of each species is constant in the isolated system (in the absence of chemical reactions). Its entropy also remains constant for a reversible process.

In the isolated system, any increase in its internal energy must be due to the reversible work source. Recalling that

$$[U] = U - (U^{\alpha} + U^{\beta}) = U^{s} , \quad \text{etc.} , \tag{6.32}$$

we obtain the desired reversible work as

$$[U] - T[S] - \sum_{i=1}^{c} \mu_i [N_i] = U^{s} - TS^{s} - \sum_{i=1}^{c} \mu_i N_i^{s} = \gamma A . \tag{6.33}$$

We note that γ must be positive in order for the interface to be stable. Otherwise, the system can lower its free energy simply by increasing A.[35]

6.5 Gibbs–Adsorption Equation

Upon differentiation of (6.30), we obtain

$$\mathrm{d}U^{s} = T\mathrm{d}S^{s} + \sum_{i=1}^{c} \mu_i \mathrm{d}N_i^{s} + \gamma \mathrm{d}A + S^{s}\mathrm{d}T + \sum_{i=1}^{c} N_i^{s}\mathrm{d}\mu_i + A\mathrm{d}\gamma . \tag{6.34}$$

Substituting (6.29) into this expression, we find

$$\mathrm{d}\gamma = -s^{s}\mathrm{d}T - \sum_{i=1}^{c} \Gamma_i \mathrm{d}\mu_i + c_a \mathrm{d}R , \tag{6.35}$$

where

$$s^{s} := \frac{S^{s}}{A} \quad \text{and} \quad \Gamma_i := \frac{N_i^{s}}{A} \tag{6.36}$$

are called the **superficial densities** of the entropy and the number of molecules of species i. We observe from (6.35) that

$$\gamma = \gamma(T, \mu_1, \ldots, \mu_c, R) \tag{6.37}$$

and that

$$s^{s} = -\left(\frac{\partial \gamma}{\partial T}\right)_{\mu,R} , \quad \Gamma_i = -\left(\frac{\partial \gamma}{\partial \mu_i}\right)_{T,\mu_{j\neq i},R} , \quad \text{and} \quad c_a = \left(\frac{\partial \gamma}{\partial R}\right)_{T,\mu} . \tag{6.38}$$

If we fix the condition for locating the dividing surface, R will change in response to changes in T and $\mu_1, \ldots, \mu_c$. For example, the radius of the surface of tension,

assumed to be finite, is determined by

$$c_a(T,\mu_1,\ldots,\mu_c,R)=0\,. \tag{6.39}$$

The radius R we find by solving this equation, in general, is a function of T and $\mu_1,\ldots,\mu_c$.[36] Thus, the partial derivatives in (6.38) are all taken *while modifying the condition for locating the dividing surface.* For a reformulation of thermodynamics of interfaces emphasizing this perspective, see Ref. [6].

For the surface of tension, the last equation in (6.38) gives

$$c_a=\left(\frac{\partial\gamma}{\partial R}\right)_{T,\mu}=0\,, \tag{6.40}$$

which has the following interpretation. For a given intensive state of the system, γ changes depending on our choice for the dividing surface. But, this dependence is such that γ takes an extremum value for the surface of tension. Using (6.39) in (6.35), we see that

$$\mathrm{d}\gamma=-s^s\mathrm{d}T-\sum_{i=1}^{c}\Gamma_i\mathrm{d}\mu_i\,, \tag{6.41}$$

for this dividing surface. This result is known as the **Gibbs adsorption equation**. Instead of (6.38), we now have

$$s^s=-\left(\frac{\partial\gamma}{\partial T}\right)_{\mu}\qquad\text{and}\quad\Gamma_i=-\left(\frac{\partial\gamma}{\partial\mu_i}\right)_{T,\mu_{j\neq i}}\,. \tag{6.42}$$

In these equations, R is absent from the list of variables that are held fixed. Instead, R is a function of T and $\mu_1,\ldots,\mu_c$, and is allowed to change in response to infinitesimal changes of these variables so as to satisfy (6.40).

6.6 Flat Interface

In contrast to the case of a spherical interface, the value of γ of a flat interface does not depend on the choice of the dividing surface.

To see this,we note that the reversible work required to create a unit area of the interface from a reference system should remain finite even in the $R\to\infty$ limit for any choice of the dividing surface. In this limit, therefore, (6.26) reduces to

$$\left(\frac{\partial\gamma}{\partial R}\right)_{T,\mu}=c_a=P^\beta-P^\alpha-\frac{2\gamma}{R}\to 0\quad\text{as}\quad R\to\infty\,, \tag{6.43}$$

where we recall that P^α and P^β are independent of the choice of the dividing surface and that $P^\alpha=P^\beta$ in the same limit we are considering.

We can reach the same conclusion through a more explicit computation. Let $\gamma_{\infty,1}$ denote the value of γ of a flat interface for the dividing surface at z_1 in Fig. 6.11.

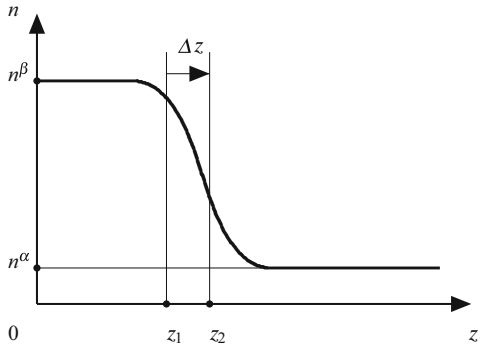

Fig. 6.11 The number density profile $n(z)$ of molecules across a flat interface. Two possible choices are shown for the dividing surface.

Using (6.30),

$$\gamma_{\infty,1}A = U - (U^\alpha + U^\beta) - T[S - (S^\alpha + S^\beta)] - \sum_{i=1}^{c} \mu_i [N_i - (N_i^\alpha + N_i^\beta)] \,. \tag{6.44}$$

When we move the dividing surface to $z_2 := z_1 + \Delta z$ as shown in Fig. 6.11, U^α and U^β in (6.44) must be replaced by

$$U^\alpha - u^\alpha A \Delta z \quad \text{and} \quad U^\beta + u^\beta A \Delta z \,, \tag{6.45}$$

respectively, where u^α is the internal energy density of the bulk α phase. Similarly for u^β. Denoting the entropy density by s and the number density of molecules of species i by n_i, we have

$$\begin{aligned} \gamma_{\infty,2}A &= \gamma_{\infty,1}A + \left[\left(u^\alpha - Ts^\alpha - \sum_{i=1}^{c} \mu_i n_i^\alpha \right) - \left(u^\beta - Ts^\beta - \sum_{i=1}^{c} \mu_i n_i^\beta \right) \right] A\Delta z \\ &= \gamma_{\infty,1}A + (P^\beta - P^\alpha) A \Delta z = \gamma_{\infty,1}A \,, \end{aligned} \tag{6.46}$$

where we used $P^\beta = P^\alpha$ for the flat interface.

6.7 W^{rev} as a Measure of Stability

As an application of thermodynamics of interfaces, let us compute the reversible work W^{rev} required to create a spherical fragment of a new phase β within a metastable phase α. Because our formalism applies only to systems in equilibrium, we shall limit our consideration to a **critical nucleus**, which is in equilibrium with a given metastable phase.

As we shall see, $W^{\text{rev}} > 0$, implying that the equilibrium is unstable. The system containing a critical nucleus can lower its free energy not only by shrinking the nucleus but also by growing it further until a macroscopic portion of a new phase forms. In this sense, formation of a critical nucleus, called **nucleation**, marks the first successful stage of new phase formation, thus the word "critical."

Nucleation is ubiquitous in nature and plays an important role in atmospheric science, biological processes, and chemical and pharmaceutical manufacturing. See Refs. [16, 19] for recent reviews.

According to (2.180), nucleation and the subsequent transition to a new phase become more probable with decreasing W^{rev}. In this sense, W^{rev} serves as a measure of stability of the metastable phase. More quantitatively, the **nucleation rate**, defined as the rate of critical nucleus formation per unit volume of the metastable phase, is proportional to $e^{-\beta W^{\text{rev}}}$. This follows from (2.180) and additional considerations regarding the kinetics of the process. The details can be found in Ref. [15], for example.

We emphasize that the results of this section apply *only to* a critical nucleus, that is, to a single value of R determined by a specific rule for locating the dividing surface for a given intensive state of the metastable phase. A generalization of our results to noncritical nuclei is possible. An interested reader should consult Refs. [1, 2, 3, 8, 13].

6.7.1 Exact Expression

Suppose that a supersaturated multicomponent macroscopic phase α is contained in an adiabatic, rigid, and impermeable wall. We take imaginary boundary B in this isolated system and refer to the region inside B as system I. The remaining part of the isolated system will be referred to as system II.

We suppose that a nucleus forms in system I. If B is taken to enclose a sufficiently large region compared to the physical extent of the nucleus, B can be made to pass through a homogeneous region both before and after the formation of the nucleus.[37]

Let $[U]$ denote the increment of the internal energy of system I upon nucleation. The corresponding quantity in system II is given by

$$-T[S] - \sum_i \mu_i [N_i] \tag{6.47}$$

with $[S]$ and $[N_i]$ defined similarly to $[U]$. Because the system as a whole is isolated, the net increase in its internal energy must be due to the reversible work source. That is,

$$W^{\text{rev}} = [U] - T[S] - \sum_i \mu_i [N_i] \,. \tag{6.48}$$

Initially, system I is filled with uniform bulk phase α. Thus, the number of molecules of species i in system I is

$$n_i^\alpha (V^\alpha + V^\beta) \,, \tag{6.49}$$

where $V^\alpha + V^\beta$ is the volume of system I expressed in terms of those of the bulk reference phases. The number of molecules in the final state may be expressed as

$$n_i^\alpha V^\alpha + n_i^\beta V^\beta + \Gamma_i A \,. \tag{6.50}$$

Thus,

$$[N_i] = n_i^\alpha V^\alpha + n_i^\beta V^\beta + \Gamma_i A - n_i^\alpha (V^\alpha + V^\beta) = (n_i^\beta - n_i^\alpha) V^\beta + \Gamma_i A \,. \tag{6.51}$$

Using (6.51) and other similar expressions in (6.48), we find

$$\begin{aligned} W^{\text{rev}} &= (u^\beta - u^\alpha) V^\beta + u^s A - T[(s^\beta - s^\alpha) V^\beta + s^s A] - \sum_{i=1}^{c} \mu_i [(n_i^\beta - n_i^\alpha) V^\beta + \Gamma_i A] \\ &= -V^\beta (P^\beta - P^\alpha) + \gamma A \,, \end{aligned} \tag{6.52}$$

where we used (2.148) and (6.30).

The term γA is referred to as the surface term and is positive since γ is positive, while $-V^\beta (P^\beta - P^\alpha)$ is called the bulk term and is negative because $P^\beta > P^\alpha$ as seen from (6.28). The balance of these two terms leads to a nonnegative value of W^{rev}. In fact, using (6.28) and noting that the nucleus by our assumption is spherical, we can rewrite (6.52) as

$$W^{\text{rev}} = \frac{1}{3}\gamma A = \frac{1}{2}(P^\beta - P^\alpha) V^\beta = \frac{16\pi\gamma^3}{3(P^\beta - P^\alpha)^2} \,, \tag{6.53}$$

in which each expression is manifestly nonnegative. Thus, nucleation is an unfavorable event. This is the origin of the metastability of phase α.

Exercise 6.2. Because (6.30) holds for an arbitrary dividing surface, so does (6.52). But, W^{rev} has a physical significance, and its value cannot depend on the convention we adopt for the dividing surface. Based on this observation, derive (6.26). (In contrast, (6.53) is a result of combining (6.52) and (6.28), and holds only for the surface of tension.) ///

Because every point in the macroscopic metastable phase is equivalent to any other, a critical nucleus can form anywhere in the system. As pointed out by Lothe and Pound as early as in 1962 [10], it is very unreasonable to expect that these "translational (and rotational) degrees of freedom" are properly reflected in the bulk thermodynamic quantities, such as the pressure and the chemical potentials. The same concern can be raised against γ. This observation casts a shadow of doubts on the validity of (6.52), which appears otherwise exact. For a detailed discussion on this point, see Ref. [7] and references therein.

According to the formalism we developed, we compute W^{rev} as follows:

a. For a given intensive state of a metastable phase, as specified by T, P^α, and $x_1^\alpha,\ldots,x_{c-1}^\alpha$, solve

$$\mu_i^\alpha(T,P^\alpha,x_1^\alpha,\ldots,x_{c-1}{}^\alpha)=\mu_i^\beta(T,P^\beta,x_1^\beta,\ldots,x_{c-1}{}^\beta)\,,\quad i=1,\ldots,c\,. \tag{6.54}$$

for P^β and $x_1^\beta,\ldots,x_{c-1}^\beta$.
b. Solve (6.28) for R, the radius of the surface of tension.
c. Compute $W^{\rm rev}$ by (6.52) or (6.53).

Step a requires only the equations of state of the bulk phases. According to (6.41),

$$\gamma=\gamma(T,\mu_1,\ldots,\mu_c)\,. \tag{6.55}$$

To execute step b, therefore, the explicit form of this function must be known. This is often, if not always, a very difficult requirement to meet, and we are forced to introduce an approximation for γ. In the next subsection, we present one such approximation scheme.

6.7.2 ‡*Classical Theory Approximations*

In a very popular approximation scheme known as **classical theory approximation**, we simply replace γ by experimentally measurable γ_∞, the value of the surface tension for a flat interface at saturation, and obtain

$$W^{\rm rev}\approx -V^\beta(P^\beta-P^\alpha)+\gamma_\infty A=\frac{16\pi{\gamma_\infty}^3}{3(P^\beta-P^\alpha)^2}\,. \tag{6.56}$$

If the nucleating phase is incompressible between P^α and P^β, the bulk term $-V^\beta(P^\beta-P^\alpha)$ can be expressed in terms of the chemical potentials. To see this, let us apply the Gibbs–Duhem relation (2.155) to a constant temperature process:

$$V^\beta\mathrm{d}P^\beta=\sum_{i=1}^{c}N_i^\beta\,\mathrm{d}\mu_i^\beta\,,\quad T\ \text{const.} \tag{6.57}$$

Here, $N_i^\beta=n_i^\beta V^\beta$ is the number of molecules of species i in V^β taken inside a macroscopic reference phase β. Integrating (6.57) from P^α to P^β without changing T or $N_1^\beta,\ldots,N_c^\beta$, we find

$$V^\beta(P^\beta-P^\alpha)=\sum_{i=1}^{c}N_i^\beta\Delta\mu_i\,, \tag{6.58}$$

where

$$\begin{aligned}\Delta\mu_i&:=\mu_i^\beta(T,P^\beta,x_1^\beta,\ldots,x_{c-1}^\beta)-\mu_i^\beta(T,P^\alpha,x_1^\beta,\ldots,x_{c-1}^\beta)\\&=\mu_i^\alpha(T,P^\alpha,x_1^\alpha,\ldots,x_{c-1}^\alpha)-\mu_i^\beta(T,P^\alpha,x_1^\beta,\ldots,x_{c-1}^\beta)\,.\end{aligned} \tag{6.59}$$

In the last equality, we used (6.54). Introducing (6.58) into (6.56), we arrive at

$$W^{\mathrm{rev}} \approx -\sum_{i=1}^{c} N_i^{\beta} \Delta\mu_i + \gamma_\infty A = \frac{16\pi {\gamma_\infty}^3}{3(\sum_{i=1}^{c} n_i^{\beta} \Delta\mu_i)^2} \,. \tag{6.60}$$

If $P^{\beta} \gg P^{\alpha}$, then,

$$P^{\beta} - P^{\alpha} = (P^{\beta} - P_{\mathrm{sat}}) - (P^{\alpha} - P_{\mathrm{sat}}) \approx P^{\beta} - P_{\mathrm{sat}} \,, \tag{6.61}$$

where P_{sat} is the pressure at saturation. Under this approximation, (6.59) gives

$$\begin{aligned} \Delta\mu_i &\approx \mu_i^{\beta}(T, P^{\beta}, x_1^{\beta}, \ldots, x_{c-1}^{\beta}) - \mu_i^{\beta}(T, P_{\mathrm{sat}}, x_1^{\beta}, \ldots, x_{c-1}^{\beta}) \\ &= \mu_i^{\alpha}(T, P^{\alpha}, x_1^{\alpha}, \ldots, x_{c-1}^{\alpha}) - \mu_i^{\alpha}(T, P_{\mathrm{sat}}, x_{1,\mathrm{sat}}^{\alpha}, \ldots, x_{c-1,\mathrm{sat}}^{\alpha}) \,, \end{aligned} \tag{6.62}$$

where we used

$$\mu_i^{\beta}(T, P_{\mathrm{sat}}, x_1^{\beta}, \ldots, x_{c-1}^{\beta}) = \mu_i^{\alpha}(T, P_{\mathrm{sat}}, x_{1,\mathrm{sat}}^{\alpha}, \ldots, x_{c-1,\mathrm{sat}}^{\alpha}) \,, \quad i = 1, \ldots, c \,. \tag{6.63}$$

at the two-phase coexistence. To apply (6.62) for a given intensive state of the metastable phase α, we first find the intensive state of bulk β phase by solving (6.54). Then, we solve (6.63) to find P_{sat} and $x_{1,\mathrm{sat}}, \ldots, x_{c,\mathrm{sat}}$.

If bulk phase α may be regarded as an ideal gas mixture, (2.201) applies:

$$\Delta\mu_i = k_B T \ln \frac{x_i^{\alpha} P^{\alpha}}{x_{i,\mathrm{sat}}^{\alpha} P_{\mathrm{sat}}} \,, \quad i = 1, \ldots, c \,. \tag{6.64}$$

We replaced the gas constant R in (2.201) by k_B since μ_i in this chapter has the dimension of energy per molecule. For a single component system, (6.64) reduces to

$$\Delta\mu = k_B T \ln \frac{P^{\alpha}}{P_{\mathrm{sat}}} \,, \tag{6.65}$$

in which $P^{\alpha}/P_{\mathrm{sat}}$ is commonly called the **supersaturation ratio**. By means of (6.65), (6.60) becomes

$$W^{\mathrm{rev}} \approx -N^{\beta} k_B T \ln \frac{P^{\alpha}}{P_{\mathrm{sat}}} + \gamma_\infty A \,. \tag{6.66}$$

6.7.3 †Thermodynamic Degrees of Freedom

In step a of Sect. 6.7.1, we took it for granted that (6.54) has a nontrivial solution ($P^{\beta} \neq P^{\alpha}$) for given $T, x_1^{\alpha}, \ldots, x_{c-1}^{\alpha}$, and for any P^{α}, which we choose between P_{sat} and the pressure at the onset of instability. According to the Gibbs phase rule we saw in Sect. 2.12, however, the thermodynamic degrees of freedom should be just c for a c component system in two-phase coexistence. So, all degrees of freedom appear to be used up by T and $x_1^{\alpha}, \ldots, x_{c-1}^{\alpha}$. How is it then that we can specify P^{α} also?

We must remember that the Gibbs phase rule was derived on the basis of the conditions of equilibrium and the Gibbs–Duhem relations for macroscopic homogeneous phases. Our attempt to provide an explicit account of the interfacial region brought about some modifications to this basic construct. Let us find out how this modification impacts the Gibbs phase rule.

Consider a metastable phase α containing a critical nucleus. As we have seen, thermodynamic behavior of this inhomogeneous system can be described in terms of a composite system consisting of the bulk reference phases and the sharp interface located at the surface of tension with the fundamental equation of the interface given by either (6.20) or (6.21).[38]

At equilibrium, T and $\mu_1, \ldots, \mu_c$ are uniform throughout the system. If the equilibrium is to be maintained after some perturbation, they must remain so. Thus, $\mathrm{d}T$ and $\mathrm{d}\mu_1, \ldots, \mathrm{d}\mu_c$ are subject to the Gibbs–Duhem relations for the bulk phases

$$\begin{aligned} S^\alpha \mathrm{d}T - V^\alpha \mathrm{d}P^\alpha + \sum_{i=1}^{c} N_i^\alpha \mathrm{d}\mu_i = 0 \,, \\ S^\beta \mathrm{d}T - V^\beta \mathrm{d}P^\beta + \sum_{i=1}^{c} N_i^\beta \mathrm{d}\mu_i = 0 \,, \end{aligned} \tag{6.67}$$

and also to the Gibbs adsorption equation (6.41). In addition, the Laplace equation (6.28), providing the condition of mechanical equilibrium, must hold both before and after the perturbation, thus leading to

$$\mathrm{d}P^\beta - \mathrm{d}P^\alpha = \frac{2}{R}\mathrm{d}\gamma - \frac{2\gamma}{R^2}\mathrm{d}R \,. \tag{6.68}$$

In total, therefore, we have four equations among $c+5$ infinitesimal quantities $\mathrm{d}T$, $\mathrm{d}\mu_1, \ldots, \mathrm{d}\mu_c$, $\mathrm{d}P^\alpha$, $\mathrm{d}P^\beta$, $\mathrm{d}\gamma$ and $\mathrm{d}R$. Accordingly, the thermodynamic degrees of freedom is $c+1$ as opposed to just c as might be expected on the basis of the usual Gibbs phase rule.

For given values of $\mathrm{d}T$ and $\mathrm{d}\mu_1, \ldots, \mathrm{d}\mu_c$, for example, the values of $\mathrm{d}P^\alpha$, $\mathrm{d}P^\beta$, and $\mathrm{d}\gamma$ are determined uniquely by (6.41) and (6.67). The equilibrium is maintained by adjusting R according to (6.68). This additional degrees of freedom is absent if we limit ourselves to phase coexistence across a flat interface.

6.7.4 Small Nucleus

With increasing degree of supersaturation, the metastable phase eventually becomes unstable. At the onset of instability, we expect that $W^{\rm rev} = 0$. (Recall that $W^{\rm rev}$ is the measure of stability of the supersaturated phase.) Equation (6.53) implies that γ and R must *also* vanish at the onset. This is because $P^\beta - P^\alpha \neq 0$ for P^β determined by (6.54). Otherwise, we would simply have the phase coexistence across a flat interface. In addition, since μ_i^α and μ_i^β are finite, $P^\beta - P^\alpha$ should remain finite at the onset as well.

We expect that γ, R, and W^{rev} vary continuously with the degree of supersaturation. Thus, when the degree of supersaturation is increased, a critical nucleus is expected to become smaller and gradually lose its homogeneous core.

In classical theory approximation, the supersaturation dependence of γ is ignored. Thus, its predictions are likely to worsen with increasing degree of supersaturation. How about the exact expression (6.53)? As we remarked in Sect. 6.1, the formalism we developed remains applicable even in such cases. Nevertheless, its practical utility is severely limited due to our inability to experimentally determine the fundamental equation (6.55) in this regime.

For example, in very small nuclei, such as a liquid water droplet consisting only of a few tens of molecules or less, P^{β} may no longer be equal to the mechanical pressure at the center of the nucleus, and the identification of γ with the mechanical tension becomes questionable at best. Simultaneously, the thickness of the interfacial region becomes comparable with R itself because the majority of molecules are in the interfacial region. This will frustrate any attempt to locate the surface of tension precisely.

Recall that the nucleation rate is proportional to $e^{-\beta W^{\mathrm{rev}}}$ and thus vanishes exponentially fast with increasing W^{rev}. The implication is that nucleation is likely to occur under the condition where classical theory approximation is inadequate *but* the input needed for the exact theory is inaccessible. This is a fundamental challenge in thermodynamics of interfaces that can only be addressed by statistical mechanics. Before we turn to this subject in Chap. 7, we shall discuss an approach that lies between pure thermodynamics we have seen so far and full-fledged statistical mechanics in the following two optional sections. Two equations, (6.92) and (6.98), derived in Sect. 6.9 find their applications in Sect. 7.6.

6.8 †Gibbs–Tolman–Koenig Equation

The form of the function (6.55) cannot be determined either within the framework of thermodynamics itself or by experiments. Starting with the Gibbs adsorption equation, however, we can derive an exact differential equation for this function. The differential equation, known as the **Gibbs–Tolman–Koenig** (GTK) **equation**, was first derived by Tolman for single component systems [18] and was almost immediately generalized to multicomponent systems by Koenig [5]. In this section, we derive the GTK equation for single component systems.

Before we get started, we note that the GTK equation cannot be solved without a detailed knowledge regarding the molecular-level structure of the interfacial region. Nevertheless, the equation forms a basis for improving the classical approximation through the **Tolman correction**, which we discuss toward the end of this section.

Writing down (6.41) and (6.67) for a single component system ($c = 1$) and recalling (6.68), we see that the values of $\mathrm{d}P^{\alpha}$, $\mathrm{d}P^{\beta}$, $\mathrm{d}\gamma$, and $\mathrm{d}\mu$ are completely determined once the values of $\mathrm{d}T$ and $\mathrm{d}R$ are given. Thus, we can use T and the curvature $q := 1/R$ of the surface of tension as the independent variables instead of T and μ.

In fact, the dependence of γ on the degree of supersaturation is usually formulated as its curvature dependence.

For a constant T process, (6.41) reduces to

$$\mathrm{d}\gamma = -\Gamma \mathrm{d}\mu \,, \quad T \text{ const.} \tag{6.69}$$

Dividing both sides by $\mathrm{d}q$,

$$\left(\frac{\partial \gamma}{\partial q}\right)_T = -\Gamma \left(\frac{\partial \mu}{\partial q}\right)_T \,. \tag{6.70}$$

To rewrite the right-hand side, we recall the Gibbs–Duhem relation for bulk phase α:

$$\mathrm{d}P^\alpha = n^\alpha \mathrm{d}\mu \,, \quad T \text{ const.} \tag{6.71}$$

and obtain

$$\left(\frac{\partial P^\alpha}{\partial q}\right)_T = n^\alpha \left(\frac{\partial \mu}{\partial q}\right)_T \,. \tag{6.72}$$

Similarly,

$$\left(\frac{\partial P^\beta}{\partial q}\right)_T = n^\beta \left(\frac{\partial \mu}{\partial q}\right)_T \,. \tag{6.73}$$

From (6.68), we also have

$$\mathrm{d}P^\beta - \mathrm{d}P^\alpha = 2\gamma \mathrm{d}q + 2q\mathrm{d}\gamma \,, \tag{6.74}$$

which holds for any process including the constant T process. Thus,

$$\left(\frac{\partial P^\beta}{\partial q}\right)_T - \left(\frac{\partial P^\alpha}{\partial q}\right)_T = 2\gamma + 2q\left(\frac{\partial \gamma}{\partial q}\right)_T \,. \tag{6.75}$$

Using (6.72) and (6.73) in (6.75),

$$\left(\frac{\partial \mu}{\partial q}\right)_T = \frac{2}{n^\beta - n^\alpha}\left[\gamma + q\left(\frac{\partial \gamma}{\partial q}\right)_T\right] \,. \tag{6.76}$$

Substituting this expression into (6.70) and solving the resulting equation for $(\partial\gamma/\partial q)_T$, we find

$$\left(\frac{\partial \ln \gamma}{\partial q}\right)_T = -\frac{2\Gamma}{n^\beta - n^\alpha + 2\Gamma q} \,. \tag{6.77}$$

This is the desired differential equation. But, one commonly eliminates Γ by introducing an **auxiliary surface**. *For the case of single component systems*, this is the **equimolar dividing surface** defined by

$$\Gamma_e(T, \mu, R_e) = 0 \,, \tag{6.78}$$

where the subscript e refers to the quantities pertaining to this dividing surface. The indicated dependence of Γ_e on T, μ, and R_e follows from (6.37) and (6.38).

Corresponding to the two choices for the dividing surface, we now have two reference systems. Using the surface of tension, we can express the number N of molecules in the system as

$$N = \frac{1}{3}\omega R^3 n^\beta + \frac{1}{3}\omega({R_0}^3 - R^3)n^\alpha + \omega R^2 \Gamma \,. \tag{6.79}$$

The same quantity may be expressed for the equimolar dividing surface as

$$N = \frac{1}{3}\omega {R_e}^3 n^\beta + \frac{1}{3}\omega({R_0}^3 - {R_e}^3)n^\alpha \,. \tag{6.80}$$

Subtracting (6.80) from (6.79) and solving the resulting equation for Γ, we obtain

$$\Gamma = (n^\beta - n^\alpha)\delta\left(1 + \delta q + \frac{1}{3}\delta^2 q^2\right) \,, \tag{6.81}$$

where

$$\delta := R_e - R \,. \tag{6.82}$$

This distance between the surface of tension and the auxiliary surface is known as the **Tolman length**. By means of (6.81), (6.77) finally becomes

$$\left(\frac{\partial \ln \gamma}{\partial q}\right)_T = -\frac{2\delta\left(1 + \delta q + \frac{1}{3}\delta^2 q^2\right)}{1 + 2\delta q\left(1 + \delta q + \frac{1}{3}\delta^2 q^2\right)} \,, \tag{6.83}$$

which is the GTK equation. Interestingly, the GTK equation retains this basic form when generalized to multicomponent systems. But the proper choice for the auxiliary surface will have to be modified.

The GTK equation can be solved only if we know δ as a function of q. As we shall see in Sect. 6.9, this requires that the (position dependent) free energy density be known across the interface. This is where we must resort to statistical mechanics. Within the framework of pure thermodynamics, the GTK equation simply replaces the difficulty of measuring γ by that of measuring δ.

Nevertheless, recasting of the original problem in the language of GTK equation may suggest a different set of approximations that are inconceivable in its absence. The famous Tolman correction is one such example. At saturation, $q = 0$ and the GTK equation yields

$$\left(\frac{\partial \gamma}{\partial q}\right)_T\Bigg|_{q=0} = -\frac{2\gamma\delta\left(1 + \delta q + \frac{1}{3}\delta^2 q^2\right)}{1 + 2\delta q\left(1 + \delta q + \frac{1}{3}\delta^2 q^2\right)}\Bigg|_{q=0} = -2\gamma_\infty \delta_\infty \,, \tag{6.84}$$

where δ_∞ is the Tolman length in the flat interface. In accordance with (6.82) for a spherical nucleus, δ_∞ is positive if the surface of tension penetrates deeper toward the nucleating phase (β) than does the equimolar dividing surface. Integrat-

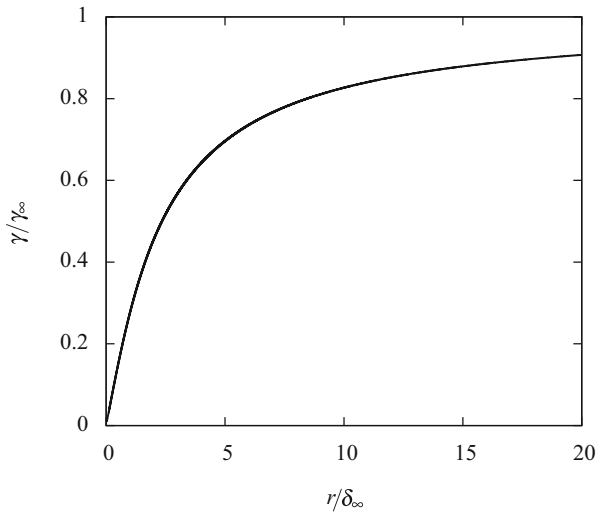

Fig. 6.12 A numerical solution of the GTK equation under the assumption that $\delta = \delta_\infty > 0$. *GTK* Gibbs-Tolman-Koenig.

ing (6.84), we have

$$\gamma \approx \gamma_\infty - 2\gamma_\infty \delta_\infty q \approx \frac{\gamma_\infty}{1+2\delta_\infty q} \tag{6.85}$$

to the first order of q. This result is known as the **Tolman correction**.

If we assume that $\delta \equiv \delta_\infty \neq 0$, (6.83) can be written as

$$\left(\frac{\partial \ln \gamma^*}{\partial x}\right)_T = -\frac{2\left(1+x+\frac{1}{3}x^2\right)}{1+2x\left(1+x+\frac{1}{3}x^2\right)}, \tag{6.86}$$

where $\gamma^* := \gamma/\gamma_\infty$ and $x := \delta_\infty q$. For a positive value of δ_∞, x varies from 0 (flat interface) to $+\infty$ (onset of instability). Equation (6.86) can be integrated either numerically or analytically [17] over the entire range of x with the result shown in Fig. 6.12. For a negative value of δ_∞, x varies from 0 to $-\infty$. But, the denominator on the right-hand side of (6.86) becomes zero at $x \approx -1.794$, leading to an unphysical behavior of γ^*. Thus, the assumption of constant δ is untenable if $\delta_\infty < 0$. According to (6.82), however, if $\delta_\infty > 0$ for droplet formation, then $\delta_\infty < 0$ for bubble formation, and vice versa.

As we have remarked already, γ_∞ is often accessible experimentally. In contrast, the prediction of δ_∞ must rely on a statistical mechanical approach. All we can say here is that δ_∞ *for the case of single component systems* is not expected to exceed a typical thickness of the interfacial region, say several atomic diameters. This is because both the surface of tension and the equimolar dividing surface are expected to reside within the interfacial region. For multicomponent systems, the same may not hold because the equimolar dividing surface is not in general the appropriate choice for the auxiliary surface. See Refs. [9, 14], for example.

6.9 †Interfacial Properties

As we shall see in Chap. 7, the grand potential of an inhomogeneous system may be written as the integral of the grand potential density $\chi(\boldsymbol{r})$ over its volume V:

$$\Omega = \int_V \chi(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \,. \tag{6.87}$$

In this section, we shall develop expressions for γ_∞ and δ_∞ assuming that the function $\chi(\boldsymbol{r})$ is known. The method for finding $\chi(\boldsymbol{r})$ will be developed in Chap. 7.

Let us first recall (6.48), which is an exact expression for the reversible work of formation of a spherical critical nucleus inside imaginary boundary B. In Sect. 6.7.1, we obtained (6.48) as the increment upon the nucleus formation of the internal energy of the isolated system that contains B. But, the same expression can also be regarded as the increment of the grand potential inside B. Thus, using a spherical coordinate system whose origin coincides with the center of the nucleus, we have

$$W^{\mathrm{rev}} = 4\pi \int_0^\infty [\chi(r) + P^\alpha] r^2 \mathrm{d}r \,, \tag{6.88}$$

where we recognize $-P^\alpha$ as the grand potential density of the homogeneous α phase. The upper limit ∞ of the integral simply indicates that the integration extends sufficiently deep into the α phase, where the integrand vanishes. This is an acceptable convention provided that the integrand approaches zero sufficiently fast to ensure the convergence of the integral. In what follows, we shall assume this to be the case for all integrals involving $\pm\infty$ in their limits. (If this is not allowed, the effect of container walls must be accounted for explicitly.)

We can separate the integral at the dividing surface at R and rewrite (6.88) as

$$W^{\mathrm{rev}} = 4\pi \int_0^R [\chi(r) + P^\beta] r^2 \mathrm{d}r + 4\pi \int_R^\infty [\chi(r) + P^\alpha] r^2 \mathrm{d}r - \frac{4\pi}{3} R^3 (P^\beta - P^\alpha) \,, \tag{6.89}$$

which may be compared with (6.52) to yield

$$\gamma = \frac{1}{R^2} \left\{ \int_0^R [\chi(r) + P^\beta] r^2 \mathrm{d}r + \int_R^\infty [\chi(r) + P^\alpha] r^2 \mathrm{d}r \right\} \,. \tag{6.90}$$

Exercise 6.3. As we saw in Exercise 6.2, (6.52) holds for an arbitrary dividing surface. The same applies for (6.89) and (6.90). Based on this observation, derive (6.26) from (6.90). ///

The expression for γ_∞ should emerge from (6.90) as its $R \to \infty$ limit is taken without changing the convention for the dividing surface. To evaluate this limit, let us rewrite (6.90) using a new variable $\xi := r - R$:

$$\gamma = \int_{-R}^0 [\chi(\xi + R) + P^\beta] \left(1 + \frac{\xi}{R}\right)^2 \mathrm{d}\xi + \int_0^\infty [\chi(\xi + R) + P^\alpha] \left(1 + \frac{\xi}{R}\right)^2 \mathrm{d}\xi \,. \tag{6.91}$$

For a sufficiently large R, the nucleus has a homogeneous core, implying that $\chi + P^\beta$ vanishes rapidly once $|\xi|$ exceeds a few times the width of the interfacial thickness. The same applies to $\chi + P^\alpha$. In the $R \to \infty$ limit, therefore, $1 + \xi/R$ may safely be replaced by unity without worrying about its large $|\xi|$ behavior. Since $P^\beta \to P^\alpha$ in this limit, (6.91) becomes the integral of $\chi(\xi) + P^\alpha$ over the interval of ξ that fully contains the interfacial region. Thus, writing $\chi(\xi)$ for $\chi(\xi + R)$ so that $\chi(0)$ gives the grand potential density at $r = R$, we have

$$\gamma_\infty = \int_{-\infty}^{\infty} [\chi(\xi) + P^\alpha] \, \mathrm{d}\xi \,, \tag{6.92}$$

which is manifestly independent of the choice of the dividing surface. (See Sect. 6.6.) At the two-phase coexistence, the two bulk reference phases have the same grand potential density $-P^\alpha$. According to (6.92), γ_∞ is the superficial density of the grand potential. This is in agreement with the physical interpretation given to γ in Sect. 6.4.

Using (6.91) in the third equation of (6.38), in which the partial derivative is taken while holding the intensive state of the system constant, we find

$$\begin{aligned} c_a = &-\frac{2}{R^2} \int_{-R}^{0} [\chi(\xi + R) + P^\beta] \xi \left(1 + \frac{\xi}{R}\right) \mathrm{d}\xi + \int_{-R}^{\infty} \frac{\mathrm{d}\chi(\xi + R)}{\mathrm{d}R} \left(1 + \frac{\xi}{R}\right)^2 \mathrm{d}\xi \,. \\ &-\frac{2}{R^2} \int_{0}^{\infty} [\chi(\xi + R) + P^\alpha] \xi \left(1 + \frac{\xi}{R}\right) \mathrm{d}\xi \end{aligned} \tag{6.93}$$

The lower limit $-R$ of the first integral in (6.91) does not contribute to c_a because the integrand is zero at $\xi = -R$. (For a sufficiently large R, we may first replace the lower limit by some constant ξ_c $(-R < \xi_c \ll 0)$ without affecting the value of the integral because the integrand will be zero if $\xi \le \xi_c$. Then, we can take the derivative to obtain (6.93).)

The second integral of (6.93) is zero. To see this, we first rewrite it as

$$\lim_{\Delta R \to 0} \frac{1}{\Delta R} \int_0^\infty [\chi(r + \Delta R) - \chi(r)] \left(\frac{r}{R}\right)^2 \mathrm{d}r \,, \tag{6.94}$$

where we used the definition of the derivative:

$$\frac{\mathrm{d}\chi(\xi + R)}{\mathrm{d}R} = \lim_{\Delta R \to 0} \frac{\chi(\xi + R + \Delta R) - \chi(\xi + R)}{\Delta R} \tag{6.95}$$

and reverted to the original variable $r = \xi + R$. But, the quantity $\chi(r + \Delta R) - \chi(r)$ represents the change in $\chi(r)$ that is observed at r when the function $\chi(r)$ is shifted by ΔR in the direction of decreasing r. This same change may also be regarded as being brought about by an infinitesimal variation in the state of the system. But, because the system is in equilibrium initially, the grand potential of the system remains unaffected to the first order of such variations. (See Sect. 7.2.1 for details.) It follows that the integral in (6.94) is at most second order of ΔR. This proves the assertion.

Because of the assumption we made earlier, the remaining integrals in (6.93) converge and c_a vanishes in the $R \to \infty$ limit as demanded by (6.43). To find the location of the surface of tension, we recall that $C = 4\pi R^2 c_a$ and use (6.27), which now reads

$$\int_{-R}^{0} [\chi(\xi + R) + P^{\beta}] \xi \left(1 + \frac{\xi}{R}\right) \mathrm{d}\xi + \int_{0}^{\infty} [\chi(\xi + R) + P^{\alpha}] \xi \left(1 + \frac{\xi}{R}\right) \mathrm{d}\xi = 0 \,. \tag{6.96}$$

Provided that $\chi(r)$ is known, this equation can be solved (numerically in most cases) for R, which is then the radius of the surface of tension. The $R \to \infty$ limit of this equation can be evaluated by repeating the same argument we have given to (6.91). In this way, we obtain

$$\int_{-\infty}^{\infty} [\chi(\xi) + P^{\alpha}] \, \xi \mathrm{d}\xi = 0 \tag{6.97}$$

for a flat interface. We replace the relation $\xi = r - R$ by $\xi = z - z_s$, where the z-axis is perpendicular to the interface and z_s is the location of the surface of tension. Using (6.92), we arrive at

$$z_s = \frac{1}{\gamma_{\infty}} \int_{-\infty}^{\infty} [\chi(z) + P^{\alpha}] \, z \mathrm{d}z \,. \tag{6.98}$$

Once again, we note that the integrand is zero as we move sufficiently away from the interfacial region.

The location z_e of the equimolar dividing surface is determined by

$$\int_{-\infty}^{z_e} [n(z) - n^{\beta}] \mathrm{d}z + \int_{z_e}^{\infty} [n(z) - n^{\alpha}] \mathrm{d}z = 0 \,, \tag{6.99}$$

where $n(z)$ is the density profile, that is, the z-dependent number density of molecules across the system. Then, the Tolman length for the flat interface is given by $\delta_{\infty} = z_e - z_s$.

Finally, it should be noted that the above elaboration is entirely unnecessary for spherical critical nuclei. Once $\chi(r)$ is known, we can simply compute W^{rev} using (6.88). Then, (6.28) and (6.53) serve as the set of simultaneous equations for γ and R. However, such an approach cannot be applied directly to flat interfaces.

6.10 Frequently Used Symbols

$[\theta]$, increment of an extensive quantity θ during a process under consideration.
θ^s , surface excess quantity of an extensive variable θ.

c , the number of species.
c_a , C/A.
k_B , Boltzmann constant, 1.3806×10^{-23} J/K.
n_i , the number density of species i.

q , curvature $1/R$ of the surface of tension.
s^s , S^s/A.
u^s , U^s/A.
x_i , mole fraction of species i.

A , area of a dividing surface.
C , $(\partial U^s/\partial R)_{S^s,N^s,A}$.
N_i , the number of molecules of species i. We drop the subscript i for a pure system.
P , pressure.
R , radius of the dividing surface.
R_0 , radius of the spherical region containing an inhomogeneous region.
R_e , radius of the equimolar dividing surface.
S , entropy.
T , absolute temperature.
U , internal energy.
V , volume.
W^{rev} , reversible work of critical nucleus formation.

α , label for the bulk metastable phase.
β , label for the bulk nucleating phase.
δ , Tolman length.
δ_∞ , Tolman length of a flat interface.
γ , $(\partial U^s/\partial A)_{S^s,N^s,R}$ for a generic dividing surface and surface tension if the dividing surface is the surface of tension.
γ_∞ , surface tension of a flat interface.
μ_i , chemical potential of species i. We drop the subscript i for a pure system.
χ , grand potential per unit volume.
ω , solid angle.

Γ_i , N_i^s/A.
Ω , grand potential.

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