Chapter 2
Some Thermodynamic Aspects
of Two-Phase Systems

In this chapter we briefly recall the basic features of equilibrium thermodynamics of a two-phase system, i.e. a system consisting of two coexisting bulk phases, which will serve as ingredients for the nucleation models discussed in this book.

2.1 Bulk Equilibrium Properties

Two phases (1 and 2) can coexist of they are in thermal and mechanical equilibrium. The former implies that there is no heat flux and therefore $T_1 = T_2$, and the latter implies that there is no mass flux, which yields equal pressures $p_1 = p_2$. However, this is not sufficient. Let N be the total number of particles in the two-phase system $N = N_1 + N_2$. The number of particles in either phase can vary while N is kept fixed. If the whole system is at equilibrium, its total entropy $\mathscr{S} = \mathscr{S}_1 + \mathscr{S}_2$ is maximized, which means in particular that

$$\frac{\partial \mathscr{S}}{\partial N_1} = 0$$

Using the additivity of $\mathscr{S}$, this condition can be expressed as

$$\frac{\partial \mathscr{S}_1}{\partial N_1} = \frac{\partial \mathscr{S}_2}{\partial N_2} \tag{2.1}$$

The basic thermodynamic relationship reads:

$$dU = T d\mathscr{S} - p dV + \mu dN \tag{2.2}$$

Rewriting it in the form

$$d\mathscr{S} = \frac{dU}{T} + \frac{p}{T} dV - \frac{\mu}{T} dN$$

we find

$$\frac{\partial \mathscr{S}}{\partial N} = -\frac{\mu}{T}$$

From (2.1): $\mu_1/T_1 = \mu_2/T_2$ and since $T_1 = T_2$, the chemical potentials of the coexisting phases must be equal. Hence, two phases in equilibrium at a temperature T and pressure p must satisfy the equation

$$\mu_1(p, T) = \mu_2(p, T) \tag{2.3}$$

which implicitly determines the $p(T)$-phase equilibrium curve. Thus, T and p cannot be fixed independently, but have to provide for equality of the chemical potentials of the two phases. Differentiating this equation with respect to the temperature and bearing in mind that $p = p(T)$, we obtain:

$$\frac{\partial \mu_1}{\partial T} + \frac{\partial \mu_1}{\partial p} \frac{dp}{dT} = \frac{\partial \mu_2}{\partial T} + \frac{\partial \mu_2}{\partial p} \frac{dp}{dT} \tag{2.4}$$

From the Gibbs–Duhem equation (see e.g. [1])

$$\mathscr{S} \, dT - V \, dp + N \, d\mu = 0 \tag{2.5}$$

we find

$$d\mu = -s \, dT + v \, dp \tag{2.6}$$

where $s = \frac{\mathscr{S}}{N}$ and $v = \frac{V}{N}$ are entropy and volume per particle, implying that

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -s, \qquad \left(\frac{\partial \mu}{\partial p}\right)_T = v$$

Using (2.4), we obtain the Clapeyron equation describing the shape of the (p, T)-equilibrium curve:

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1} \tag{2.7}$$

In the case of vapor-liquid equilibrium this curve is called a *saturation line* and the pressure of the vapor in equilibrium with its liquid is called a *saturation pressure*, p_{sat}. Liquid and vapor coexist along the saturation line connecting the triple point corresponding to three-phase coexistence (solid, liquid and vapor) and the critical point. Below the critical temperature T_c one can discriminate between liquid and vapor by measuring their density. At T_c the difference between them disappears. The line of liquid-solid coexistence has no critical point and goes to infinity since the difference between the symmetric solid phase and the asymmetric liquid phase can not disappear.

Most of the first-order phase transitions are characterized by absorption or release of the *latent heat*. According to the first law of thermodynamics (expressing the principle of conservation of energy), the amount of heat supplied to the system, δQ, is equal to the change in its internal energy δU plus the amount of work performed by the system on its surroundings $p\delta V$

$$\delta Q = \delta U + p\delta V \tag{2.8}$$

In the theory of phase transitions the quantity δQ is called the latent heat L. For processes *at constant pressure* the latent heat is given by the change in the enthalpy:

$$L \equiv \delta Q = \delta(\mathscr{U} + pV) = \delta H(N, p, \mathscr{S}) = T\,(\delta\mathscr{S})_{p,N}$$

The latent heat per molecule $l = L/N$ is then

$$l = T(s_2 - s_1) \tag{2.9}$$

Using (2.9) the Clapeyron equation at $T < T_c$ can be written as

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{l}{T(v_2 - v_1)} \tag{2.10}$$

For the gas–liquid transition at temperatures far from T_c the molecular volume in the liquid phase $v_1 \equiv v^l$ is much smaller than in the vapor $v_2 \equiv v^v$. Neglecting v_1 and applying the ideal gas equation for the vapor

$$p\,v_2 = k_B T \tag{2.11}$$

we present Eq. (2.10) as

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{lp}{k_B T^2} \tag{2.12}$$

where

$$k_B = 1.38 \times 10^{-16}\mathrm{erg/K} \tag{2.13}$$

is the Boltzmann constant. Considering the specific latent heat to be constant, which is usually true for a wide range of temperatures and various substances,[1] and integrating (2.12) over the temperature, we obtain:

$$p_{\mathrm{sat}}(T) = p_\infty\,\mathrm{e}^{-\beta l}, \quad \beta = \frac{1}{k_B T} \tag{2.14}$$

where p_∞ is a constant.

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[1] For example, for water in the temperature interval between 0 and $100\,^\circ$ C, l changes by only 10 %.

2.2 Thermodynamics of the Interface

Let us discuss the *interface* between the two bulk phases in equilibrium. For concreteness we refer to the coexistence of a liquid with its saturated vapor at the temperature T. Equilibrium conditions are characterized by equality of temperature, pressure, and chemical potentials in both bulk phases. The density, however, is not constant but varies continuously along the interface between two bulk equilibrium values $\rho^{\text{v}}(T)$ and $\rho^{\text{l}}(T)$. Note, that local fluctuations of density take place even in homogeneous fluid, where, however, they are small and short-range. In the two-phase system these fluctuations are macroscopic: for vapor–liquid systems at low temperatures the bulk densities ρ^{v} and ρ^{l} can differ by 3–4 orders of magnitude.

2.2.1 Planar Interface

Consider a two-phase system contained in a volume V with a planar interface between the vapor and the liquid. Inhomogeneity is along the z direction; $z \rightarrow +\infty$ corresponds to bulk vapor, and $z \rightarrow -\infty$ to bulk liquid (see Fig. 2.1). Variations in the density give rise to an extra contribution to the thermodynamic functions: they are modified to include the work $\gamma \, dA$ which has to be imposed by external forces in order to change the interface area A by dA:

$$d\mathscr{F} = -p \, dV - \mathscr{S} \, dT + \gamma \, dA + \mu \, dN \tag{2.15}$$

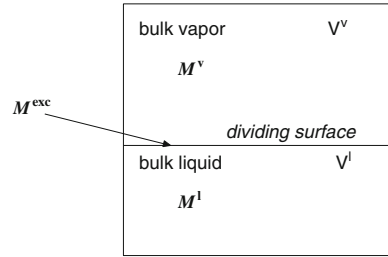$$dG = V \, dp - \mathscr{S} \, dT + \gamma \, dA + \mu \, dN \tag{2.16}$$

$$d\Omega = -p \, dV - \mathscr{S} \, dT + \gamma \, dA - N d\mu \tag{2.17}$$

(in (2.17) N is the average number of particles in the system). The coefficient γ is the surface tension; its thermodynamic definition follows from the above expressions:
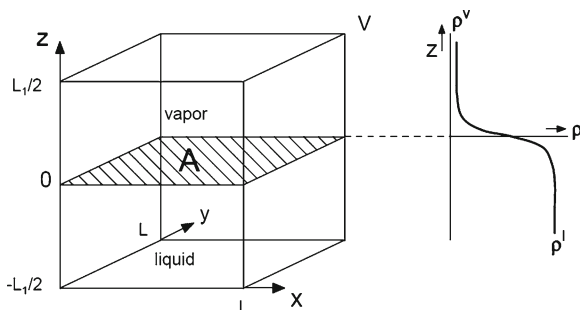
Fig. 2.1 Schematic representation of the vapor–liquid system contained in a volume $V = L^2 L_1$. Inhomogeneity is along the z axis (Reprinted with permission from Ref. [1], copyright (2001), Springer-Verlag.)

Fig. 2.2 Gibbs dividing surface

$$\gamma = \left(\frac{\partial \mathscr{F}}{\partial A}\right)_{N,V,T} \tag{2.18}$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{N,p,T} \tag{2.19}$$

$$\gamma = \left(\frac{\partial \Omega}{\partial A}\right)_{\mu,V,T} \tag{2.20}$$

Following Gibbs [2] we introduce a *dividing surface*, being a mathematical surface of zero width which establishes a boundary between the bulk phases as shown in Fig. 2.2. Although its position is arbitrary, it is convenient to locate it somewhere in the transition zone. Once the position of a dividing surface is chosen, the volumes of the two phases are fixed, and satisfy

$$V^{\mathrm{v}} + V^{\mathrm{l}} = V$$

The idea of Gibbs was that any extensive thermodynamic quantity $\mathscr{M}$ (the number of particles, energy, entropy, etc.) can be written as a sum of bulk contributions $\mathscr{M}^{\mathrm{v}}$ and $\mathscr{M}^{\mathrm{l}}$ and an excess contribution $\mathscr{M}^{\mathrm{exc}}$ that is assigned to the chosen dividing surface:

$$\mathscr{M} = \mathscr{M}^{\mathrm{v}} + \mathscr{M}^{\mathrm{l}} + \mathscr{M}^{\mathrm{exc}} \tag{2.21}$$

Equation (2.21) is in fact a definition of $\mathscr{M}^{\mathrm{exc}}$; its value depends on the location of the dividing surface, and so do the values of $\mathscr{M}^{\mathrm{v}}$ and $\mathscr{M}^{\mathrm{l}}$ (as opposed to $\mathscr{M}$, which is an actual physical property and as such can not depend on the location of the Gibbs surface). Several important examples are

$$N = N^{\mathrm{v}} + N^{\mathrm{l}} + N^{\mathrm{exc}} \tag{2.22}$$
$$\mathscr{S} = \mathscr{S}^{\mathrm{v}} + \mathscr{S}^{\mathrm{l}} + \mathscr{S}^{\mathrm{exc}}$$
$$\Omega = \Omega^{\mathrm{v}} + \Omega^{\mathrm{l}} + \Omega^{\mathrm{exc}}$$
$$\mathscr{F} = \mathscr{F}^{\mathrm{v}} + \mathscr{F}^{\mathrm{l}} + \mathscr{F}^{\mathrm{exc}}$$
$$V = V^{\mathrm{v}} + V^{\mathrm{l}}$$

By definition the dividing surface has a zero width implying that $V^{\text{exc}} = 0$. Since the location of the dividing surface is arbitrary, the excess quantities accumulated on it can be both positive or negative.

One special case that will be useful for future discussions is the *equimolar surface* defined through the requirement $N^{\text{exc}} = 0$. The surface density of this quantity

$$\Gamma = \frac{N^{\text{exc}}}{A} \tag{2.23}$$

is called *adsorption*. Thus, the equimolar surface corresponds to zero adsorption. The thermodynamic potentials, such as $\mathscr{F}$, Ω, G, are homogeneous functions of the first order with respect to their extensive variables. We can derive their expressions for the two-phase system by integrating Eqs. (2.15)–(2.17) using Euler's theorem for homogeneous functions (see e.g. [1], Sect. 1.4). In particular, integration of (2.17) results in

$$\Omega = -p\,V + \gamma\,A \tag{2.24}$$

whereas in each of the bulk phases $\Omega^{\text{v}} = -p\,V^{\text{v}}$, $\Omega^{\text{l}} = -p\,V^{\text{l}}$, where we used the equality of pressures in the coexisting phases. Thus,

$$\Omega^{\text{exc}} = \gamma\,A \tag{2.25}$$

irrespective of the choice of the dividing surface. Independence of Ω^{exc} on the location of a dividing surface gives rise to the most convenient thermodynamic route for determination of the surface tension. Equation (2.25) is used in density functional theories of fluids (discussed in Chap. 5) to determine γ from the form of the intermolecular potential.

By definition

$$\Omega^{\text{exc}} = \Omega - \Omega^{\text{v}} - \Omega^{\text{l}} \tag{2.26}$$

For each of the bulk phases

$$d\Omega^{\text{v}} = -p\,dV^{\text{v}} - \mathscr{S}^{\text{v}}\,dT - N^{\text{v}}d\mu \tag{2.27}$$
$$d\Omega^{\text{l}} = -p\,dV^{\text{l}} - \mathscr{S}^{\text{l}}\,dT - N^{\text{l}}d\mu \tag{2.28}$$

Differentiating (2.26) using (2.17) and (2.27)–(2.28) yields

$$d\Omega^{\text{exc}} = -\mathscr{S}^{\text{exc}}\,dT + \gamma\,dA - N^{\text{exc}}\,d\mu$$

On the other hand, from (2.25)

$$d\Omega^{\text{exc}} = \gamma\,dA + A\,d\gamma$$

Comparison of these two equalities leads to the *Gibbs adsorption equation*

$$A\,\mathrm{d}\gamma + \mathscr{S}^{\mathrm{exc}}\,\mathrm{d}T + N^{\mathrm{exc}}\,\mathrm{d}\mu = 0 \tag{2.29}$$

describing the change of the surface tension resulting from the changes in T and μ. An important consequence of (2.29) is the expression for adsorption:

$$\Gamma = -\left(\frac{\partial\gamma}{\partial\mu}\right)_T \tag{2.30}$$

where the surface tension refers to a particular dividing surface.

2.2.2 Curved Interface

Gibbs' notion of a dividing surface is a useful concept for thermodynamic description of an interface. At the same time, as we saw in Sect. 2.2.1, the planar surface tension is not affected by a particular location of a dividing surface since the surface area A remains constant at any position of the latter. The situation drastically changes when we discuss a *curved* interface. Here *the position of the dividing surface determines* not only the volumes of the two bulk phases but also *the interfacial area*. An arbitrary curved surface is characterized by two radii of curvature. Consider a liquid droplet inside a fixed total volume V of the two-phase system containing in total N molecules at the temperature T. The "radius" of the droplet is smeared out on the microscopic level since it can be defined to within the width of the interfacial zone, which is of the order of the correlation length. Let us choose a spherical dividing surface with a radius R. The sizes of the two phases and the surface area are fully determined by a set of four variables for which it is convenient to use R, A, V^{l} and V^{v} [3], where V^{l} and V^{v} are the bulk liquid and vapor volumes and A is the surface area:

$$V^{\mathrm{l}} = \frac{4\pi}{3}R^3, \quad V^{\mathrm{v}} = V - \frac{4\pi}{3}R^3, \quad A = 4\pi R^2$$

A sketch of a spherical interface is shown in Fig. 2.3. The change of the Helmholtz free energy $\mathscr{F}$ of the two-phase system "droplet + vapor" when its variables change at isothermal conditions is given by [3]:

$$(\mathrm{d}\mathscr{F})_T = -p^{\mathrm{l}}(\mathrm{d}V^{\mathrm{l}})_T - p^{\mathrm{v}}(\mathrm{d}V^{\mathrm{v}})_T + \mu(\mathrm{d}N)_T + \gamma(\mathrm{d}A)_T + A\left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right](\mathrm{d}R)_T \tag{2.31}$$

Here by a differential in square brackets we denote a *virtual change* of a thermodynamic parameter, corresponding to a change in R. The pressure p^{l} inside the liquid phase refers to the bulk liquid held at the same chemical potential as the surrounding vapor with the pressure p^{v}: $\mu^{\mathrm{v}}(p^{\mathrm{v}}) = \mu^{\mathrm{l}}(p^{\mathrm{l}})$. The surface tension $\gamma(R)$ refers to the
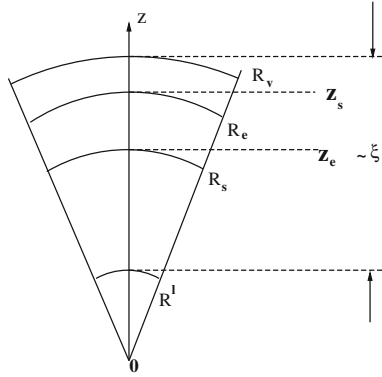
Fig. 2.3 Sketch of a spherical interface. The z axis is perpendicular to the interface pointing away from the center of curvature. R_e and $R_s \equiv R_t$ denote, respectively, the location of the equimolar surface and the surface of tension (see the text). The width of the transition zone between bulk vapor and bulk liquid is of the order of the correlation length ξ (Reprinted with permission from Ref. [1], copyright (2001), Springer-Verlag.)

dividing surface of the radius R; the term in the square brackets gives the change of γ with respect to a mathematical displacement of the dividing surface. It is important to stress that the physical quantities $\mathscr{F}$, p^v, p^l, μ, N, V, do not depend on the location of a dividing surface. So they remain unchanged when only R is changed and from (2.31)

$$0 = [\mathrm{d}\mathscr{F}] = -\Delta p\, 4\pi R^2\, [\mathrm{d}R] + 8\pi R\, \gamma\, [\mathrm{d}R] + 4\pi R^2 \left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right][\mathrm{d}R]$$

where $\Delta p = p^l - p^v$. Dividing by $4\pi R^2\,[\mathrm{d}R]$ we obtain the *generalized Laplace equation*:

$$\Delta p = \frac{2\gamma[R]}{R} + \left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right] \tag{2.32}$$

It is clear that since Δp, as a physical property of the system, is independent of R, the surface tension *must* depend on the choice of dividing surface. A particular choice $R = R_t$, such that

$$\left[\frac{\mathrm{d}\gamma}{\mathrm{d}R}\right]_{R=R_t} = 0, \tag{2.33}$$

corresponds to the so-called surface of tension; it converts (2.32) into the standard *Laplace equation*

$$\Delta p = \frac{2\gamma_t}{R_t} \tag{2.34}$$

where $\gamma_t = \gamma[R_t]$. One can relate the surface tension taken at an arbitrary dividing surface R of a radius R to γ_t. To this end let us write (2.32) in the form

$$\Delta p \, R^2 = \left[\frac{d}{dR} \right] R^2 \gamma[R]$$

and integrate it from R_t to R. Using (2.34) for Δp we obtain the Ono-Kondo equation [4]

$$\gamma[R] = \gamma_t \, f_{OK}\left(\frac{R}{R_t}\right), \quad \text{with} \quad f_{OK} = \frac{1}{3}\frac{1}{x^2} + \frac{2}{3}x \tag{2.35}$$

Elementary analysis shows that f_{OK} has a minimum at $x = 1$ corresponding to $R = R_t$. Thus, γ_t is the minimum surface tension among all possible choices of the dividing surface:

$$\gamma[R] = \gamma_t \left[1 + O\left(\frac{R - R_t}{R_t}\right)^2 \right] \tag{2.36}$$

When R differs from R_t by a small value, $\gamma[R]$ remains constant to within terms of order $1/R_t^2$.

Among various dividing surfaces we distinguished two special cases—the equimolar surface R_e and the surface of tension R_t—which are related to the certain physical properties of the system. Let us introduce a quantity describing the separation between them

$$\delta = R_e - R_t$$

The limiting value of δ at the planar limit

$$\delta_T = \lim_{R_t \to \infty} \delta = z_e - z_t \tag{2.37}$$

is called the *Tolman length*. Its sign can be both positive and negative depending on the relative location of the two dividing surfaces. By definition δ_T does not depend on either radius R_t, or R_e (whereas δ does) but can depend on the temperature. Both dividing surfaces lie in the interfacial zone implying that δ_T is of the order of the correlation length. Let Γ_t be the adsorption at the surface of tension. From the Gibbs adsorption equation

$$\Gamma_t = -\left(\frac{\partial \gamma_t}{\partial \mu}\right)_T$$

Using the thermodynamic relationship (2.6) in both phases we rewrite this result as

$$d\gamma_t = -\Gamma_t \, d\mu = -\Gamma_t \frac{dp^v}{\rho^v} = -\Gamma_t \frac{dp^l}{\rho^l}$$

From the second and the third equations of this chain

$$dp^l = dp^v \frac{\rho^l}{\rho^v}$$

resulting in

$$d(\Delta p) = \Delta\rho \, d\mu$$

Substituting Δp from the Laplace equation (2.34) we obtain

$$d\gamma_t = -\frac{\Gamma_t}{\Delta\rho} \, d\left(\frac{2\gamma_t}{R_t}\right) \tag{2.38}$$

For a curved surface Tolman [5] showed (see also [3]) that

$$\frac{\Gamma_t}{\Delta\rho} = \delta_T \left(1 + \frac{\delta_T}{R_t} + \frac{1}{3}\frac{\delta_T^2}{R_t^2}\right) \tag{2.39}$$

but the terms in (δ_T/R_t) and $(\delta_T/R_t)^2$ can be omitted to the order of accuracy we need. This means that in all derivations below we need to keep only the linear terms in δ_T. With this in mind Eqs. (2.38) and (2.39) give

$$d\gamma_t = -\delta_T \, d\left(\frac{2\gamma_t}{R_t}\right)$$

which after simple algebra yields

$$d\ln\gamma_t = \frac{2\delta_T}{R_t(R_t + 2\delta_T)} \, dR_t = \left[\frac{1}{R_t} - \frac{1}{R_t + 2\delta_T}\right] dR_t$$

Integrating from the planar limit ($R_t \to \infty$) to R_t we obtain:

$$\frac{\gamma_t}{\gamma_\infty} = \frac{R_t}{R_t + 2\delta_T} \tag{2.40}$$

where γ_∞ is the planar surface tension discussed in Sect. 2.2.1. Keeping the linear term in δ_T we finally obtain the *Tolman equation*

$$\gamma_t = \gamma_\infty \left(1 - \frac{2\delta_T}{R_t} + \dots\right) \tag{2.41}$$

It is important to emphasize that the second order term in the δ_T can not be obtained from (2.40) since this equation is derived to within the linear accuracy in the Tolman length.

 Equation (2.41) represents the expansion of the surface tension of a curved interface (droplet) in powers of the curvature. Its looses its validity when the radius of the droplet becomes of the order of molecular sizes. The concept of a curvature dependent surface tension frequently emerges in nucleation studies. It is therefore important to estimate the minimal size of the droplet for which the Tolman equation holds. For simple fluids (characterized by the Lennard-Jones and Yukawa intermolecular potentials) near their triple points the density functional calculations [6] reveal that the Tolman equation is valid for droplets containing more than 10^6 molecules.

References

1. V.I. Kalikmanov, in *Statistical Physics of Fluids. Basic Concepts and Applications* (Springer, Berlin, 2001)
2. J.W. Gibbs, in *The Scientific Papers* (Ox Bow, Woodbridge, 1993)
3. J.S. Rowlinson, B. Widom, *Molecular Theory of Capillarity* (Clarendon Press, Oxford, 1982)
4. S. Ono, S. Kondo, in *Encyclopedia of Physics*, vol. 10, ed. by S. Flugge (Springer, Berlin, 1960), p. 134
5. R.C. Tolman, J. Chem. Phys. **17**(118), 333 (1949)
6. K. Koga, X.C. Zeng, A.K. Schekin, J. Chem. Phys. **109**, 4063 (1998)