

S3.A. Surface Tension

In this section, we shall derive the corrections, due to surface tension, to the conditions of mechanical equilibrium between two coexisting phases.

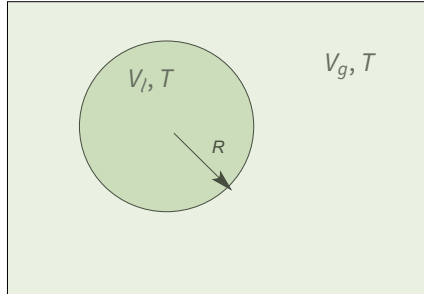


Fig.3.27.

Consider a single liquid droplet of radius R floating in equilibrium with its vapor and ignore gravity [see Fig.3.27]. The entire system is at temperature T and volume

$$V_{\text{tot}} = V_g + V_l$$

where V_g is the volume of the vapor and

$$V_l = \frac{4}{3} \pi R^3 \quad V_g, T$$

is the volume of the droplet. The area of the droplet is $A = 4 \pi R^2$ and its surface tension σ . As explained in §2.C.6, unbalanced molecular forces at a liquid surface tend to contract the surface. Thus, increasing the surface area requires work $-\bar{d}W = \sigma dA$ done to the liquid and hence increases its internal energy by $dU = \sigma dA$ [see (2.22) of §2.D.2].

If we ignore the changes in the number of molecules at the liquid surface, the grand potential of the system is [see (2.122) of §2.F.5]

$$\begin{aligned} \Omega(T, V_g, V_l, \mu_g', \mu_l', A) &\equiv U - TS - \mu_g' N_g - \mu_l' N_l \\ &= -P_g V_g - P_l V_l + \sigma A \\ &= -P_g \left(V_{\text{tot}} - \frac{4}{3} \pi R^3 \right) - \frac{4}{3} \pi R^3 P_l + 4 \pi R^2 \sigma \\ &= \Omega(T, V_{\text{tot}}, \mu_g', \mu_l', R) \end{aligned} \quad (3.94)$$

Since molecules can pass freely between the droplet and its vapor, the condition for chemical equilibrium is

$$\mu_g(P_g, T) = \mu_l(P_l, T, \sigma) \quad (3.93)$$

Condition for mechanical equilibrium can be obtained from the requirement that, in a thermodynamic equilibrium, all thermodynamic potentials must be at some local extrema with respect to their natural variables. Hence,

$$\begin{aligned} \left(\frac{\partial \Omega}{\partial R} \right)_{T, V_{\text{tot}}, \mu_g, \mu_l} &= 4 \pi R^2 (P_g - P_l) + 8 \pi R \sigma \quad [(3.94) \text{ used. }] \\ &= 0 \end{aligned} \quad (3.95)$$

$$\rightarrow P_l - P_g = \frac{2\sigma}{R} \quad (3.96)$$

(3.96) is simply the special case $R_1 = R_2 = R$ of the Laplace's formula,

$$\Delta P = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (3.96a)$$

where R_1 and R_2 are the principal radii of curvature of the surface.

For a derivation of (3.96a), see §60 of "Fluid Mechanics" by L.D.Landau & E.M.Lifshitz.

Ex.3.5.

Use purely mechanical arguments to derive (3.96).

Answer

Consider a wire in the shape of a circular arc of radius R and subtended angle ψ . If forces of magnitude T are applied at both ends along the outward tangential directions, the net force is then along the inward radial direction with magnitude

$$\begin{aligned} F &= 2T \sin \frac{\psi}{2} \\ &\approx T\psi \quad \text{for } \psi \rightarrow 0 \\ &= T \frac{L}{R} \end{aligned}$$

where L is the arc length and T is called the *tension* of the wire. This leads to the definition

$$d\mathbf{F}_T = -\hat{\mathbf{r}} T \frac{dL}{R}$$

for any infinitesimal line element dL of radius of curvature R .

Generalization to a surface gives [see Landau & Lifshitz]

$$d\mathbf{F}_\sigma = -\sigma \hat{\mathbf{n}} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) dL_1 dL_2$$

where dL_1 & dL_2 are principal line elements of the surface element $d\mathbf{A} = \hat{\mathbf{n}} dL_1 dL_2$, with radii of curvature R_1 & R_2 , respectively. Note that while T is a force, σ is a force per unit length.

The net force due to the pressure difference is

$$d\mathbf{F}_p = \Delta P \hat{\mathbf{n}} dL_1 dL_2$$

where $\Delta P = P_{\text{in}} - P_{\text{out}}$ and $\hat{\mathbf{n}}$ points from the "inside" to the "outside" of the surface.

Mechanical equilibrium is given by

$$d\mathbf{F}_\sigma + d\mathbf{F}_p = 0$$

which gives (3.96a).

===== Ex.3.5 ends

(3.96) allows us to express the equilibrium vapor pressure P_g as a function of the droplet size R .

Since the surface tension σ usually depends only on the temperature T [see §2.C.6],

$$d\sigma = 0 \quad \text{if} \quad T = \text{constant}$$

The Gibbs-Duhem equation then simplifies to

$$d\mu_j' = \frac{V_j}{N_j} dP_j = \frac{n_j}{N_j} v_j dP_j = \frac{1}{N_A} v_j dP_j \quad j = l, g$$

where N_A is the Avogadro's number.

At equilibrium,

$$\mu_l' = \mu_g' \quad \rightarrow \quad v_l dP_l = v_g dP_g \quad [dT = 0] \quad (3.97)$$

On the other hand, (3.96) gives

$$dP_l - dP_g = d\left(\frac{2\sigma}{R}\right) \quad (3.97a)$$

so that with the help of (3.97), we have

$$\begin{aligned} \left(\frac{v_g}{v_l} - 1\right) dP_g &= d\left(\frac{2\sigma}{R}\right) \\ &\approx \frac{v_g}{v_l} dP_g \quad [\text{Since } v_g \gg v_l \text{ away from the critical point.}] \end{aligned} \quad (3.98)$$

Approximating the vapor as an ideal gas, we have

$$v_g \approx \frac{\mathcal{R}T}{P_g}$$

so that (3.98) becomes

$$\frac{\mathcal{R}T}{v_l} \frac{dP_g}{P_g} \approx d\left(\frac{2\sigma}{R}\right) \quad (3.99)$$

Approximating the droplet as an ideal liquid, we have

$$v_l \approx \text{constant}$$

and (3.99) can be integrated to give

$$P_g(R) \approx P_g(\infty) \exp\left(\frac{2\sigma v_l}{\mathcal{R}TR}\right) \quad (3.100)$$

Owing to the exponential dependence, P_g is very sensitive to any change in the value of R . Conversely, at a given equilibrium value of P_g , little deviation from the equilibrium value R_0 is allowed so that all droplets are about the same size.