Chapter 1

ThermoS26-08

1.1 Maxwell's Common Tangent Construction

Here we will review a situation for which the Helmholtz potential is important.

Consider a unary material, two phase system, for example liquid and solid iron.

We will assume the β phase is the high- density phase (a solid perhaps) and the α phase is the low-density phase (a liquid perhaps).

Both phases are in contact with a heat bath at temperature T_0.

Here the densities ρ^α and ρ^β play the roles of the numbers of moles, N^α and N^β.

We will assume, for simplicity, that parameters vary in only one spatial dimension, z.

Suppose the cross-section area of the container is A. Then

$$V^\alpha = Az_I$$

$$V^\beta = A(L - z_I)$$

$$V^\alpha + V^\beta = A \cdot L = V_0 \qquad \text{(total volume constant)}$$

Now,

$$N^\alpha = V^\alpha \rho^\alpha$$

$$N^\beta = V^\beta \rho^\beta$$

Here

$$[\rho^*] = \text{moles/unit vol}$$

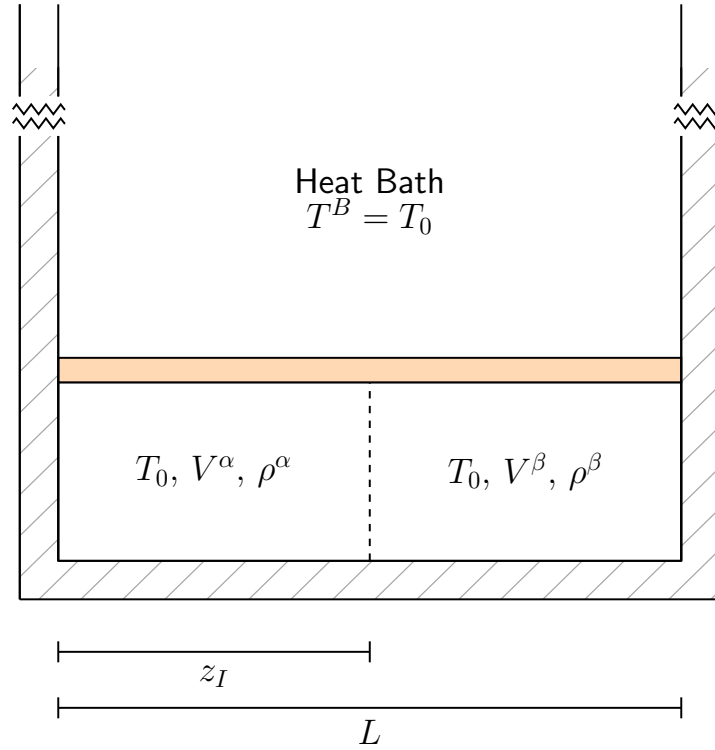$$N_0 = N^\alpha + N^\beta \qquad \text{(total mole number const)}$$

Figure 1.1: Two-phase system in contact with a heat bath, with interface at z_I.

$$= V^\alpha \rho^\alpha + V^\beta \rho^\beta$$

$$= A z_I \rho^\alpha + A(L - z_I)\rho^\beta$$

It will be convenient to introduce

$$\rho_0 = \frac{N_0}{V_0} = \frac{N_0}{L \cdot A}.$$

Hence,

$$\boxed{\rho_0 \cdot L = z_I \rho^\alpha + (L - z_I)\rho^\beta} \tag{5.1}$$

We will assume that the total free energy can be expressed as

$$F_{\alpha+\beta}(V^\alpha, V^\beta, \rho^\alpha, \rho^\beta) = V^\alpha f^\alpha(\rho^\alpha) + V^\beta f^\beta(\rho^\beta)$$

The variables f^α and f^β are called free energy densities. We can eliminate the volume variable using constraint:

$$F_{\alpha+\beta}(V^\alpha, V^\beta, \rho^\alpha, \rho^\beta) = V^\alpha f^\alpha(\rho^\alpha) + V^\beta f^\beta(\rho^\beta)$$

$$= A z_I f^\alpha(\rho^\alpha) + A(L - z_I) f^\beta(\rho^\beta)$$

Using the mass constraint (5.1), we have

$$z_I = \frac{L(\rho_0 - \rho^\beta)}{\rho^\alpha - \rho^\beta}$$

or, equivalently,

$$\boxed{z_I = \frac{L(\rho^\beta - \rho_0)}{\rho^\beta - \rho^\alpha}} \tag{5.2}$$

Similarly, we have

$$\boxed{L - z_I = \frac{L(\rho_0 - \rho^\alpha)}{\rho^\beta - \rho^\alpha}} \tag{5.3}$$

Thus,

$$F_{\alpha+\beta}(V^\alpha, V^\beta, \rho^\alpha, \rho^\beta) = L \cdot A \cdot \tilde{F}(\rho^\alpha, \rho^\beta),$$

where

$$\tilde{F}(\rho^\alpha, \rho^\beta) = \frac{\rho^\beta - \rho_0}{\rho^\beta - \rho^\alpha} f^\alpha(\rho^\alpha) + \frac{\rho_0 - \rho^\alpha}{\rho^\beta - \rho^\alpha} f^\beta(\rho^\beta).$$

Recall the setting is isothermal $T^\alpha = T^\beta = T_0$. So equilibrium is characterized by a minimum in the free energy. Thus, we seek a minimizing of $\tilde{F}$.

The setting is as follows:

We want ρ^α and ρ^β that minimize $\tilde{F}$.

$$0 = \frac{\partial \tilde{F}}{\partial \rho^\alpha}(\rho^\alpha, \rho^\beta)$$

$$0 = \frac{\partial \tilde{F}}{\partial \rho^\beta}(\rho^\alpha, \rho^\beta)$$

Now,

$$\frac{\partial \tilde{F}}{\partial \rho^\alpha} = \frac{\rho^\beta - \rho_0}{(\rho^\beta - \rho^\alpha)^2} f^\alpha(\rho^\alpha) + \frac{\rho^\beta - \rho_0}{\rho^\beta - \rho^\alpha} f^{\alpha'}(\rho^\alpha)$$

$$+ \frac{\rho_0 - \rho^\beta}{(\rho^\beta - \rho^\alpha)^2} f^\beta(\rho^\beta)$$

$$= \frac{\rho^\beta - \rho_0}{\rho^\beta - \rho^\alpha} \left\{ \frac{f^\alpha(\rho^\alpha) - f^\beta(\rho^\beta)}{\rho^\beta - \rho^\alpha} + f^{\alpha'}(\rho^\alpha) \right\}$$

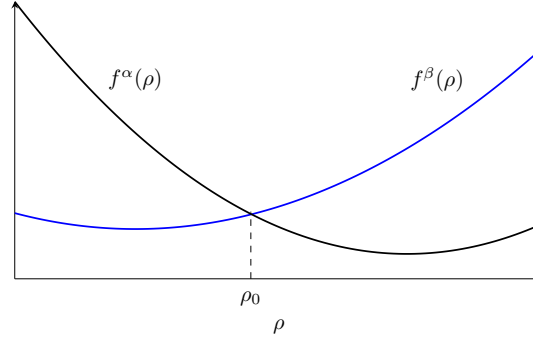Figure 1.2: Free energy densities $f^\alpha(\rho)$ and $f^\beta(\rho)$ versus ρ.

and

$$\frac{\partial \tilde{F}}{\partial \rho^\beta} = \frac{\rho_0 - \rho^\alpha}{(\rho^\beta - \rho^\alpha)^2} f^\alpha(\rho^\alpha) - \frac{\rho_0 - \rho^\alpha}{(\rho^\beta - \rho^\alpha)^2} f^\beta(\rho^\beta) + \frac{\rho_0 - \rho^\alpha}{\rho^\beta - \rho^\alpha} f^{\beta'}(\rho^\beta)$$

$$= \frac{\rho_0 - \rho^\alpha}{\rho^\beta - \rho^\alpha} \left\{ \frac{f^\alpha(\rho^\alpha) - f^\beta(\rho^\beta)}{\rho^\beta - \rho^\alpha} + f^{\beta'}(\rho^\beta) \right\}$$

Thus, the minimizers must satisfy

$$\boxed{\frac{f^\beta(\rho^\beta) - f^\alpha(\rho^\alpha)}{\rho^\beta - \rho^\alpha} = f^{\alpha'}(\rho^\alpha)} \tag{5.4}$$

and

$$\boxed{\frac{f^\beta(\rho^\beta) - f^\alpha(\rho^\alpha)}{\rho^\beta - \rho^\alpha} = f^{\beta'}(\rho^\beta)} \tag{5.5}$$

Graphically, these solutions represent the following scenario:
For everything to make sense, we require that average density

$$\rho^\alpha < \rho_0 < \rho^\beta$$

(low density phase)   (high density phase)

What happens if, say,

$$\rho^\alpha < \rho^\beta < \rho_0,$$

that is, the average is higher than the density of the high-density phase, ρ^β?

Recall,

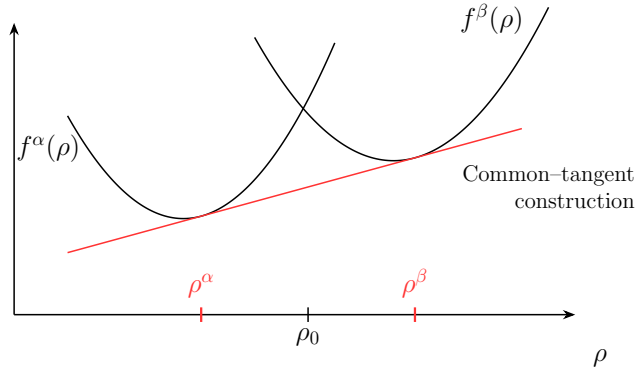$$z_I = \frac{L(\rho^\beta - \rho_0)}{\rho^\beta - \rho^\alpha}.$$

Figure 1.3: Common tangent construction for f^{α} and f^{β}.

If $\rho^{\alpha} < \rho^{\beta} < \rho_0$, it follows that

$$z_I < 0,$$

which is unphysical.

On the other hand if $\rho_0 < \rho^{\alpha} < \rho^{\beta}$ then

$$z_I > L,$$

which is unphysical.

But if

$$\rho^{\alpha} < \rho_0 < \rho^{\beta}$$

it follows that z_I is fully determined and

$$0 < z_I < L,$$

as desired.

By the way we can redefine the chemical potential such that

$$\mu^{\alpha} = \frac{\partial f^{\alpha}}{\partial \rho^{\alpha}}$$

$$\mu^{\beta} = \frac{\partial f^{\beta}}{\partial \rho^{\beta}}$$

So that equilibrium occurs when

$$\mu^{\alpha} = \mu^{\beta}.$$

1.2   Unary Isothermal Phase Diagrams (at constant volume)

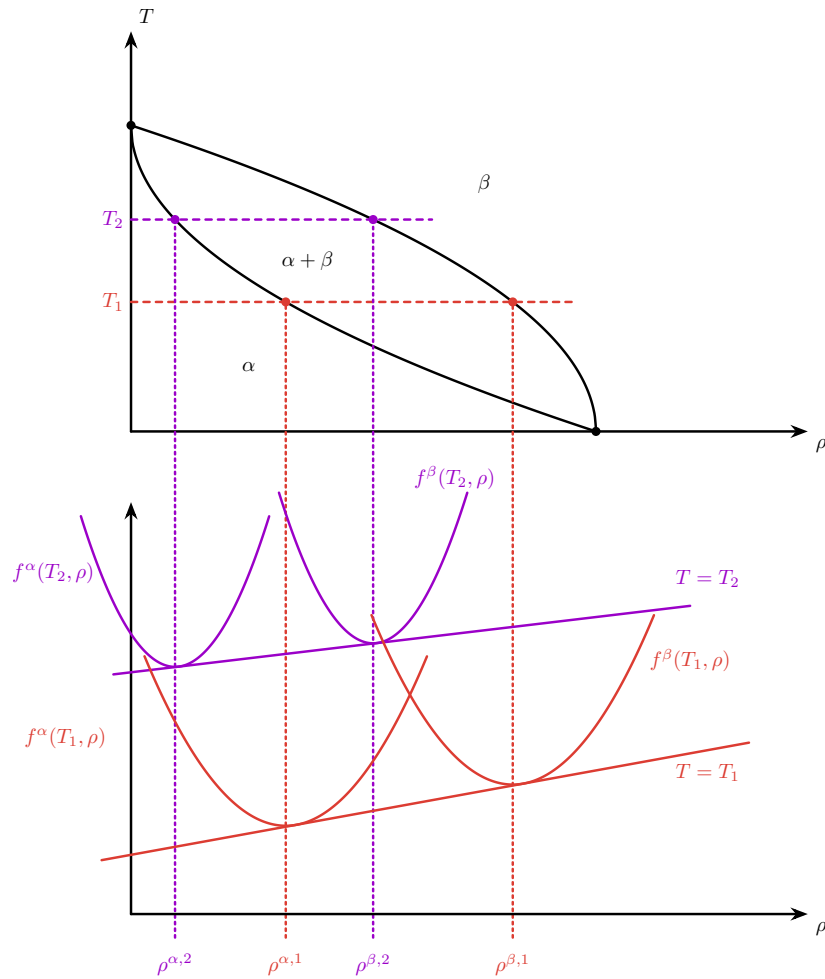let us consider the following phase diagram

Figure 1.4: Unary isothermal phase diagram and corresponding free-energy curves.