

Chapter 1

ThermoS26-06

Math Thermo
Class #06
02/05/2026

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

$$V^\alpha = Az_l$$

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

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

Now,

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

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

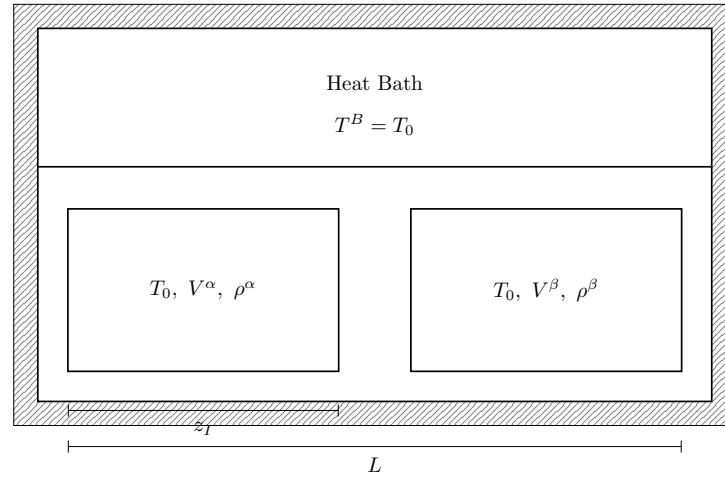


Figure 1.1: Two-phase system in contact with a heat bath, with interface at z_I .

Here

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

$$\begin{aligned} N_0 &= N^\alpha + N^\beta \quad (\text{total mole number const}) \\ &= V^\alpha \rho^\alpha + V^\beta \rho^\beta \\ &= A z_I \rho^\alpha + A(L - z_I) \rho^\beta \end{aligned}$$

It will be convenient to introduce

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

Hence,

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

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:

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

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

Using the mass constraint (5.1), we have

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

or, equivalently,

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

Similarly, we have

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

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:

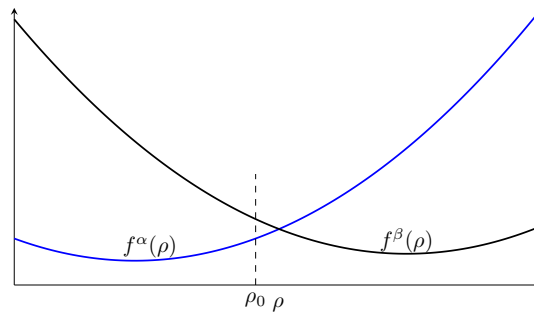


Figure 1.2: Free energy densities $f^\alpha(\rho)$ and $f^\beta(\rho)$ versus ρ .

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,

$$\begin{aligned} \frac{\partial \tilde{F}}{\partial \rho^\alpha} &= \frac{\rho^\beta - \rho_0}{(\rho^\beta - \rho^\alpha)^2} f^\alpha(\rho^\alpha) + \frac{\rho^\beta - \rho_0}{\rho^\beta - \rho^\alpha} f^{\alpha'}(\rho^\alpha) \\ &\quad + \frac{\rho_0 - \rho^\beta}{(\rho^\beta - \rho^\alpha)^2} f^\beta(\rho^\beta) \\ &= \frac{\rho^\beta - \rho_0}{\rho^\beta - \rho^\alpha} \left\{ \frac{f^\alpha(\rho^\alpha) - f^\beta(\rho^\beta)}{\rho^\beta - \rho^\alpha} + f^{\alpha'}(\rho^\alpha) \right\} \end{aligned}$$

and

$$\begin{aligned} \frac{\partial \tilde{F}}{\partial \rho^\beta} &= \frac{\rho_0 - \rho^\alpha}{(\rho^\beta - \rho^\alpha)^2} f^\alpha(\rho^\alpha) - \frac{\rho_0 - \rho^\alpha}{(\rho^\beta - \rho^\alpha)^2} f^\beta(\rho^\beta) + \frac{\rho_0 - \rho^\alpha}{\rho^\beta - \rho^\alpha} f^{\beta'}(\rho^\beta) \\ &= \frac{\rho_0 - \rho^\alpha}{\rho^\beta - \rho^\alpha} \left\{ \frac{f^\alpha(\rho^\alpha) - f^\beta(\rho^\beta)}{\rho^\beta - \rho^\alpha} + f^{\beta'}(\rho^\beta) \right\} \end{aligned}$$

Thus, the minimizers must satisfy

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

and

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

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,

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

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

$$z_I < 0,$$

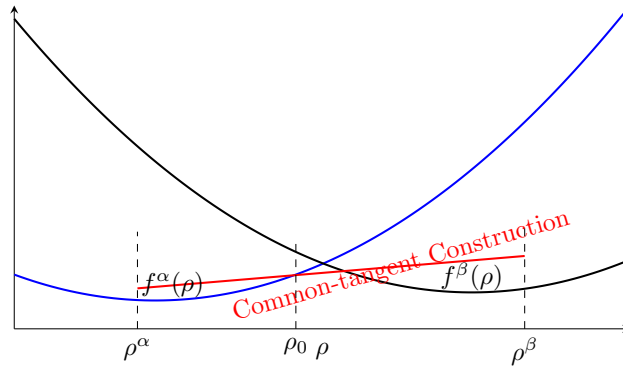


Figure 1.3: Common tangent construction for f^α and f^β .

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

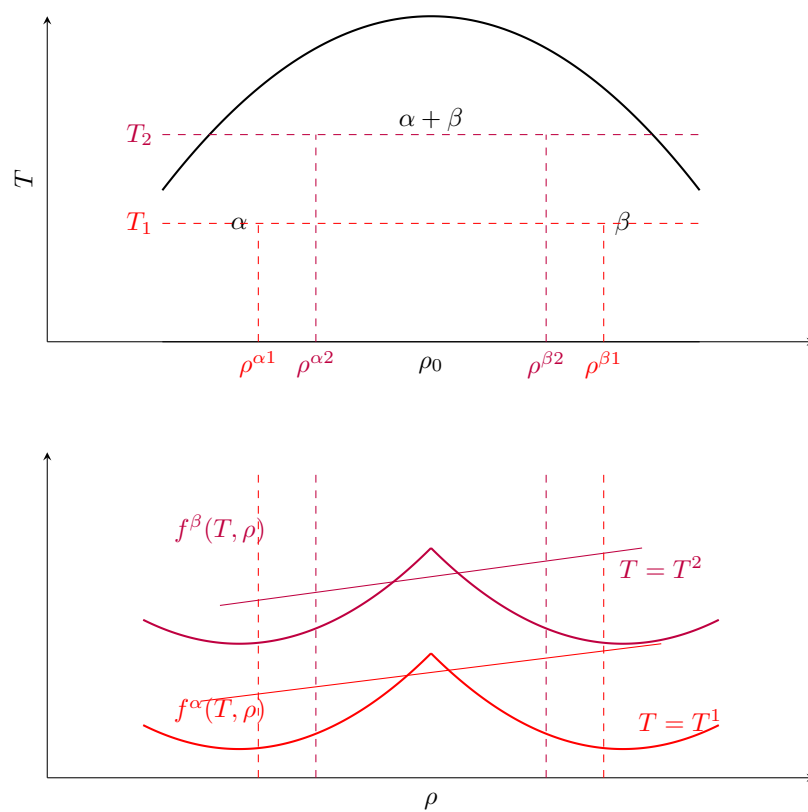


Figure 1.4: Unary isothermal phase diagram and corresponding free-energy curves.