Math Thermo
class # 06
02/05/2026

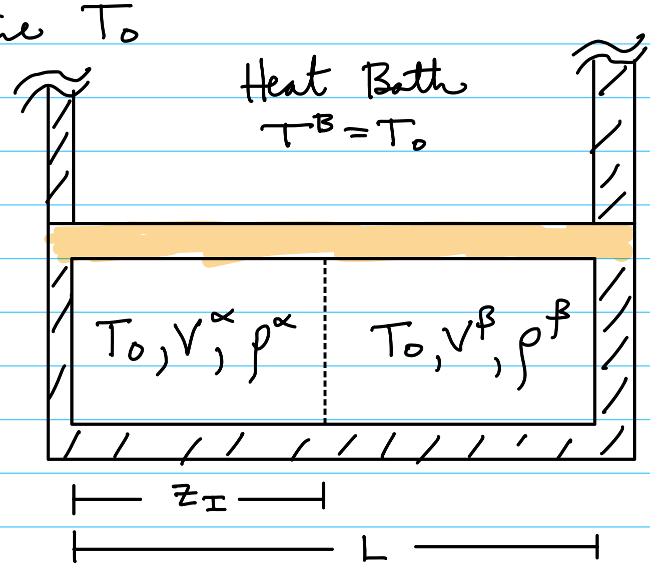
Maxwell's Common Tangent Construction

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

Consider a unary, isothermal, 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

$$V^\alpha = A\, z_I$$

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

$$V^\alpha + V^\beta = A \cdot L =: V_0$$ (total volume constant)

Now,

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

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

Here

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

$$N_0 = N^\alpha + N^\beta$$ (total mole number const)

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

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

It will be convenient to introduce

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

Hence,

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

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 variables using constraints:

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

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

Using the mass constraint (5.1), we have

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

or

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

Similarly, we have

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

Thus,

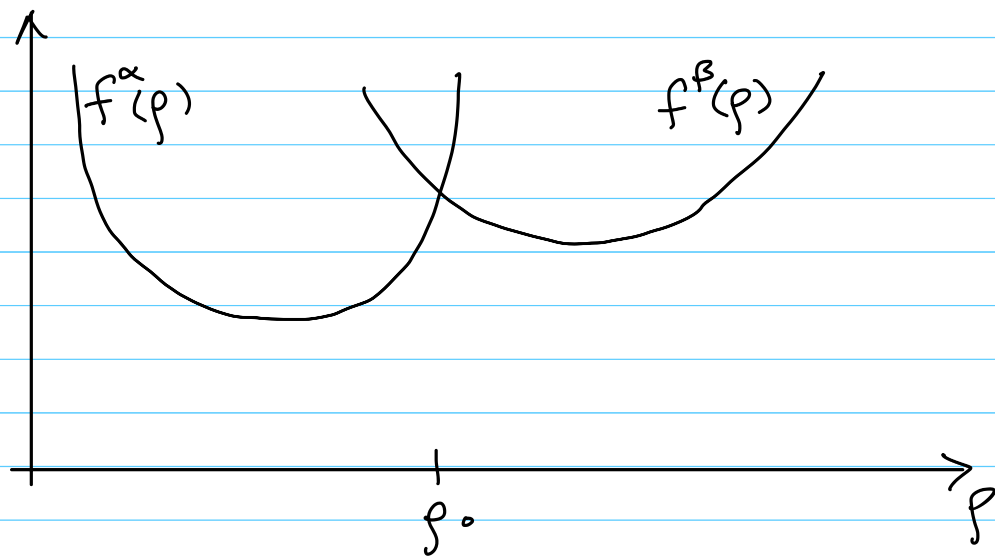
$$F_{\alpha+\beta}(V^\alpha, V^\beta, \rho^\alpha, \rho^\beta) = L \cdot A \cdot \tilde{F}(\rho^\alpha, \rho^\beta),$$

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 minimizer 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,

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

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

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

and

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

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

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

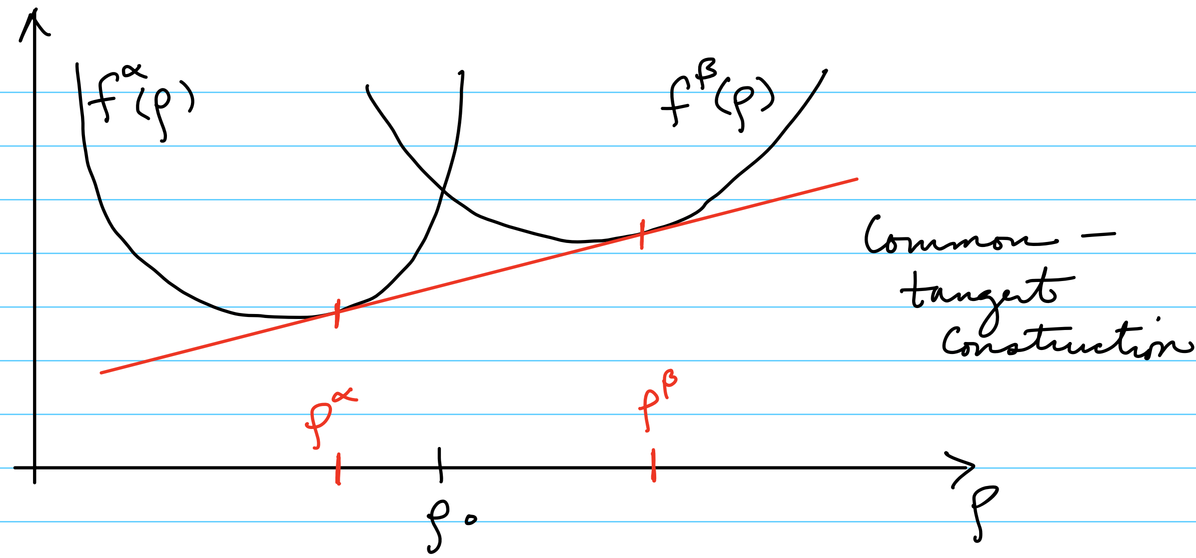
Thus, the minimizer must satisfy

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

and

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

Graphically, these solutions represent the following scenario:



For everything to make sense, we require that

$$\underset{\text{low density phase}}{\rho^\alpha} < \overset{\text{average density}}{\rho_0} < \underset{\text{high density phase}}{\rho^\beta}$$

What happens if, say,

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

that is, the average is bigger than the density of the high-density phase, β?

Recall,

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

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

$$z_I < 0,$$

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

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

Unary, Isothermal Phase Diagrams
(at constant volume)

Let us consider the following phase diagram