

Math Thermo
class # 08
02/12/2026

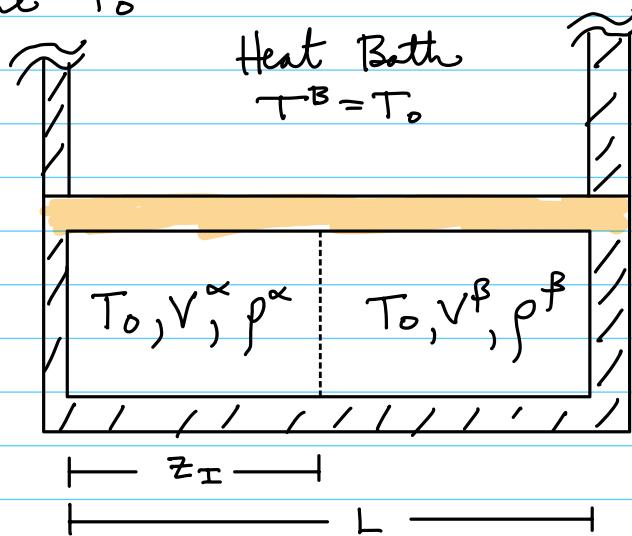
Maxwell's Common Tangent Construction

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

$$V^\alpha = A z_I$$

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

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

Now,

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

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

Here

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

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

It will be convenient to introduce

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

Hence,

(8.1)

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

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:

$$\begin{aligned} F_{\alpha+\beta}(V^\alpha, V^\beta, \rho^\alpha, \rho^\beta) &= V^\alpha f^\alpha(\rho^\alpha) + V^\beta f^\beta(\rho^\beta) \\ &= A z_I f^\alpha(\rho^\alpha) + A(L-z_I) f^\beta(\rho^\beta) \end{aligned}$$

Using the mass constraint (8.1), we have

$$z_I = \frac{L(p_0 - \rho_\beta)}{\rho_\alpha - \rho_\beta}$$

or

(8.2)

$$z_I = \frac{L(\rho^\beta - p_0)}{\rho^\beta - \rho^\alpha}$$

Similarly, we have

(8.3)

$$L - z_I = \frac{L(p_0 - \rho^\alpha)}{\rho^\beta - \rho^\alpha}$$

Thus,

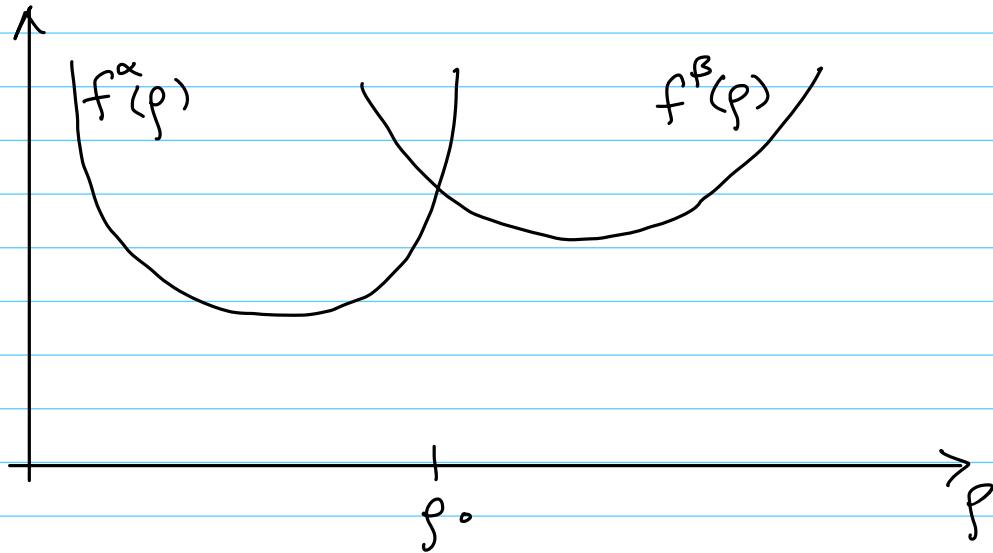
$$F_{\alpha+\beta}(V^\alpha, V^\beta, \rho^\alpha, \rho^\beta) = L \cdot A \cdot \tilde{F}(\rho^\alpha, \rho^\beta),$$

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,

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

$$+ \frac{p_0 - p^{\beta}}{(p^{\beta} - p^{\alpha})^2} f^{\beta}(p^{\beta})$$

$$= \frac{p^{\beta} - p_0}{p^{\beta} - p^{\alpha}} \left\{ \frac{f^{\alpha}(p^{\alpha}) - f^{\beta}(p^{\beta})}{p^{\beta} - p^{\alpha}} + f^{\alpha'}(p^{\alpha}) \right\}$$

and

$$\frac{\partial \tilde{F}}{\partial p^{\beta}} = \frac{p_0 - p^{\alpha}}{(p^{\beta} - p^{\alpha})^2} f^{\alpha}(p^{\alpha})$$

$$- \frac{p_0 - p^{\alpha}}{(p^{\beta} - p^{\alpha})^2} f^{\beta}(p^{\beta}) + \frac{p_0 - p^{\alpha}}{p^{\beta} - p^{\alpha}} f^{\beta'}(p^{\beta})$$

$$= \frac{p_0 - p^{\alpha}}{p^{\beta} - p^{\alpha}} \left\{ \frac{f^{\alpha}(p^{\alpha}) - f^{\beta}(p^{\beta})}{p^{\beta} - p^{\alpha}} + f^{\beta'}(p^{\beta}) \right\}$$

Thus, the minimizer must satisfy

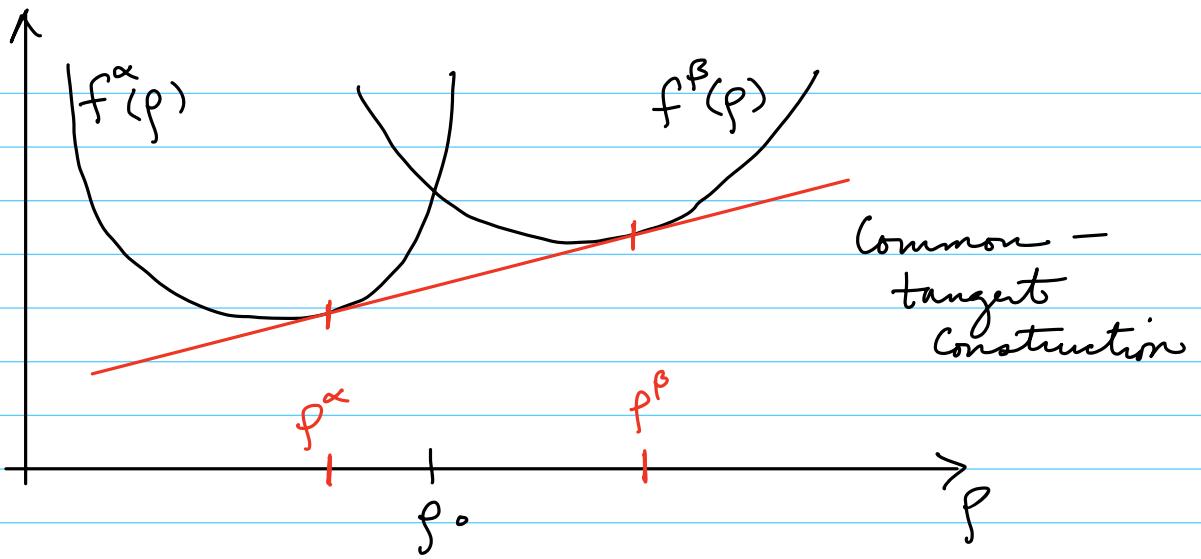
(8.4)

$$\frac{f^{\beta}(p^{\beta}) - f^{\alpha}(p^{\alpha})}{p^{\beta} - p^{\alpha}} = f^{\alpha'}(p^{\alpha})$$

(8.5) and

$$\frac{f^{\beta}(p^{\beta}) - f^{\alpha}(p^{\alpha})}{p^{\beta} - p^{\alpha}} = f^{\beta'}(p^{\beta})$$

Graphically, these solutions represent the following scenario:



For everything to make sense, we require that

$$\begin{array}{c}
 \text{average density} \\
 \downarrow \\
 f^\alpha < p_0 < f^\beta \\
 \uparrow \qquad \qquad \qquad \uparrow \\
 \text{high density phase} \\
 \text{low density phase}
 \end{array}$$

What happens if, say,

$$f^\alpha < f^\beta < p_0$$

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

Recall,

$$z_I = \frac{L(p^\beta - p_0)}{p^\beta - p^\alpha}.$$

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

