

Maths Thermo
class # 08
02/12/2026

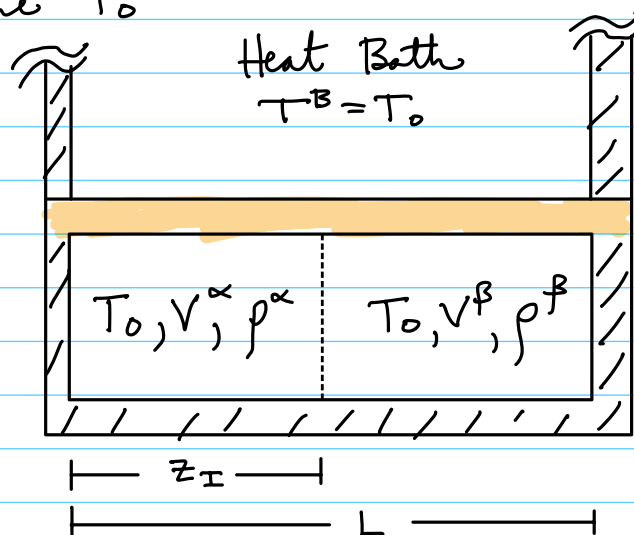
Maxwell's Common Tangent Construction

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

$$V^\alpha = A z_\pm$$

$$V^\beta = A (L - z_\pm)$$

$$V^\alpha + V^\beta = A \cdot L =: V_0 \quad \left(\begin{array}{l} \text{total volume} \\ \text{constant} \end{array} \right)$$

Now,

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

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

Here

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

$$N_0 = N^\alpha + N^\beta \quad \left(\begin{array}{l} \text{total mole} \\ \text{number const} \end{array} \right)$$

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

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

It will be convenient to introduce

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

Hence,

(8.1)

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

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

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

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

$$\begin{aligned} F_{\alpha+\beta}(V^\alpha, V^\beta, p^\alpha, p^\beta) &= V^\alpha f^\alpha(p^\alpha) + V^\beta f^\beta(p^\beta) \\ &= A z_{\text{I}} f^\alpha(p^\alpha) + A(L - z_{\text{I}}) f^\beta(p^\beta) \end{aligned}$$

Using the mass constraint (8.1), we have

$$z_{\text{I}} = \frac{L(p_0 - p^\beta)}{p^\alpha - p^\beta}$$

or

(8.2)

$$z_{\text{I}} = \frac{L(p^\beta - p_0)}{p^\beta - p^\alpha}$$

Similarly, we have

(8.3)

$$L - z_{\text{I}} = \frac{L(p_0 - p^\alpha)}{p^\beta - p^\alpha}$$

Thus,

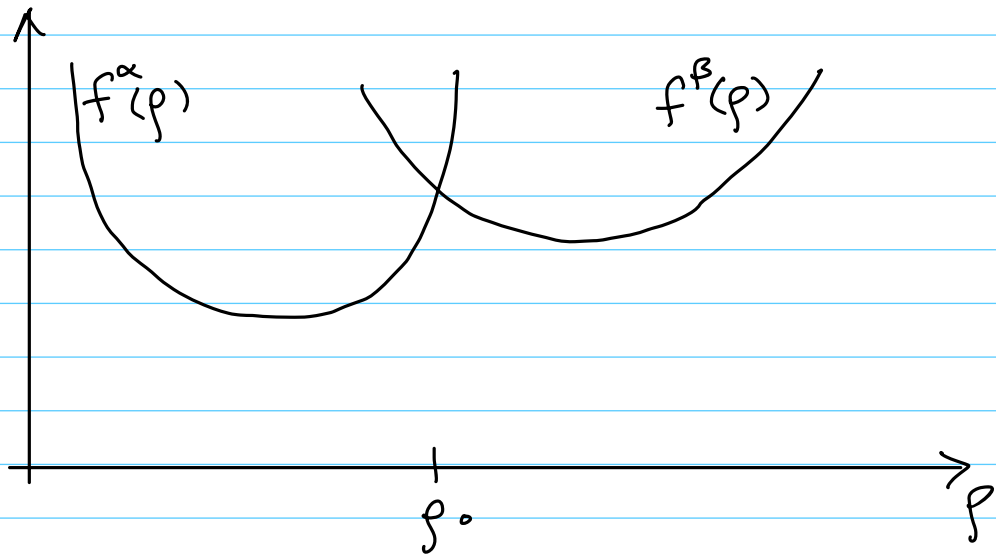
$$F_{\alpha+\beta}(V^\alpha, V^\beta, p^\alpha, p^\beta) = L \cdot A \cdot \tilde{F}(p^\alpha, p^\beta),$$

where

$$\tilde{F}(p^\alpha, p^\beta) = \frac{p^\beta - p_0}{p^\beta - p^\alpha} f^\alpha(p^\alpha) + \frac{p_0 - p^\alpha}{p^\beta - p^\alpha} f^\beta(p^\beta).$$

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 p^α and p^β that minimize \tilde{F} .

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

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

Now,

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

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

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

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)

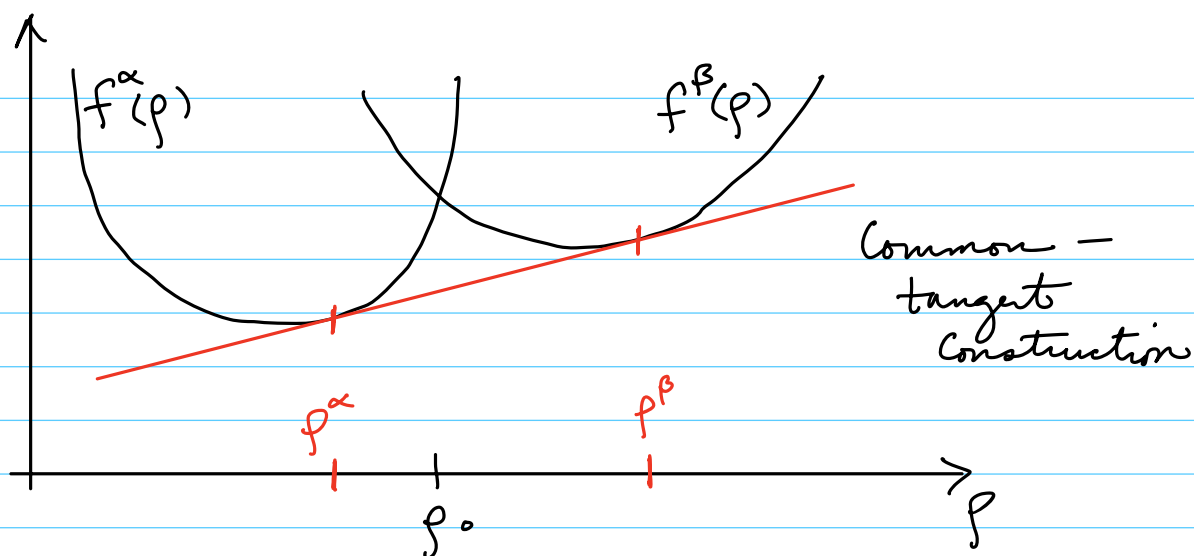
$$\frac{f^\beta(p^\beta) - f^\alpha(p^\alpha)}{p^\beta - p^\alpha} = f^{\alpha'}(p^\alpha)$$

(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

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

What happens if, say,

$$p^\alpha < p^\beta < p_0,$$

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

Recall,

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

If $p^\alpha < p^\beta < p_0$, it follows that

$$z_I < 0,$$

which is unphysical.

On the other hand if $p_0 < p^\alpha < p^\beta$, then

$$z_I > L,$$

which is unphysical.

But, if

$$p^\alpha < p_0 < p^\beta,$$

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

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

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

So that equilibrium occurs when

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

Unary, Isothermal Phase Diagrams (at constant volume)

let us consider the following phase diagram

