Introduction to the Materials Science of

Rechargeable Batteries

Week 2: Thermodynamics of Battery Materials

Lecture 2.2: The Electrochemical Potential

By R. Edwin Garcia
Associate Professor of Materials Engineering
Purdue University

The Electrode Potential

So the conditions for equilibrium are

$$T^\alpha = T^\beta$$ we know this one

$$\mu_1^\alpha + z_1 F \phi^\alpha = \mu_1^\beta + z_1 F \phi^\beta$$
$$\mu_2^\alpha + z_2 F \phi^\alpha = \mu_2^\beta + z_2 F \phi^\beta$$

or equivalently:

$$\eta_1^\alpha = \eta_1^\beta$$

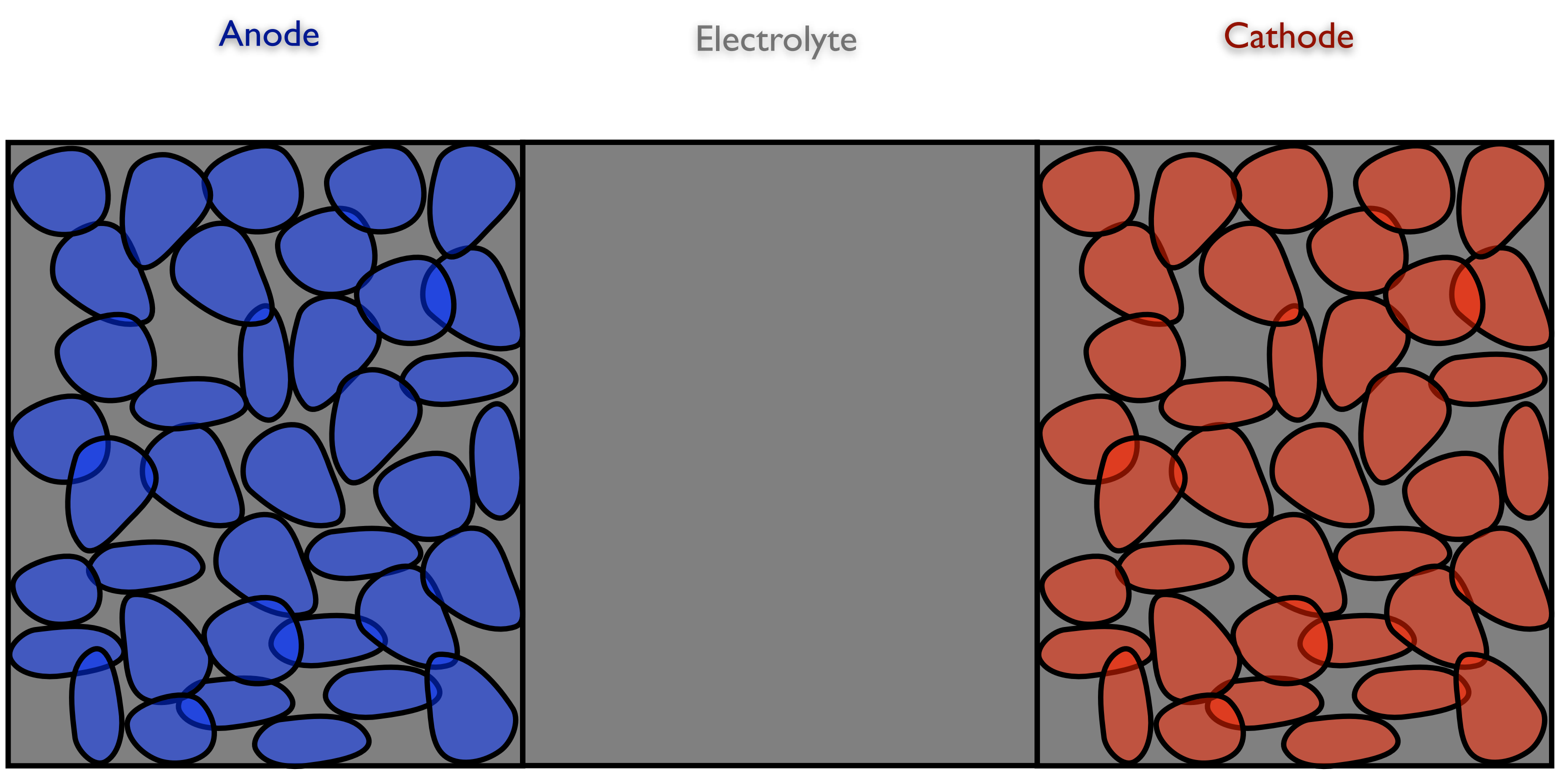
$$\eta_2^\alpha = \eta_2^\beta$$

Define this as the *electrochemical potential*

and yet, another way to look at it:

$$\Delta\phi_1^{\alpha\rightarrow\beta} = \frac{\Delta\mu_1^{\alpha\rightarrow\beta}}{z_1 F} \qquad \Delta\phi_2^{\alpha\rightarrow\beta} = \frac{\Delta\mu_2^{\alpha\rightarrow\beta}}{z_2 F}$$

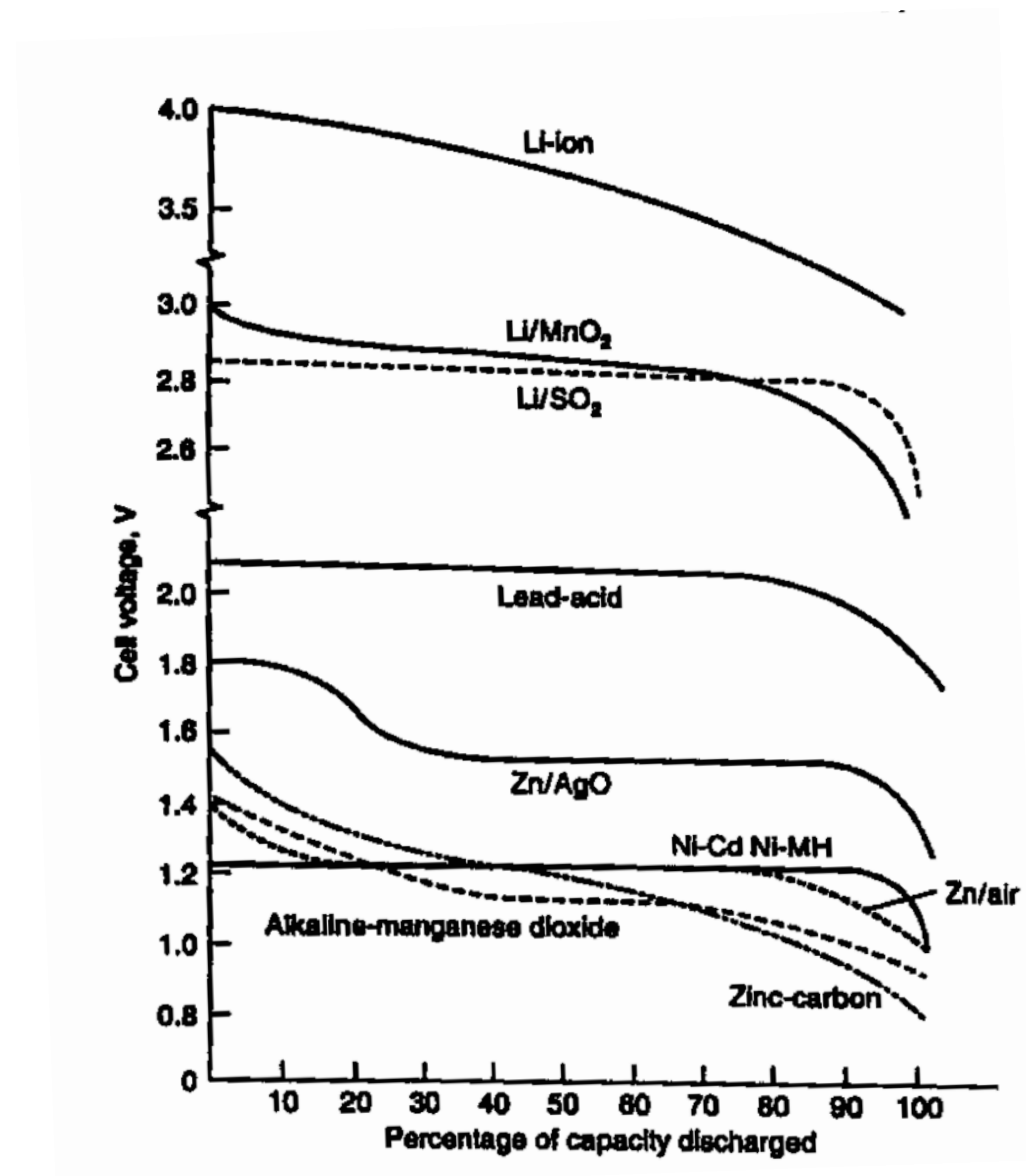
Electrochemical Driving Forces



$$\varphi_a = \frac{\mu^a_{Li}}{zF}$$

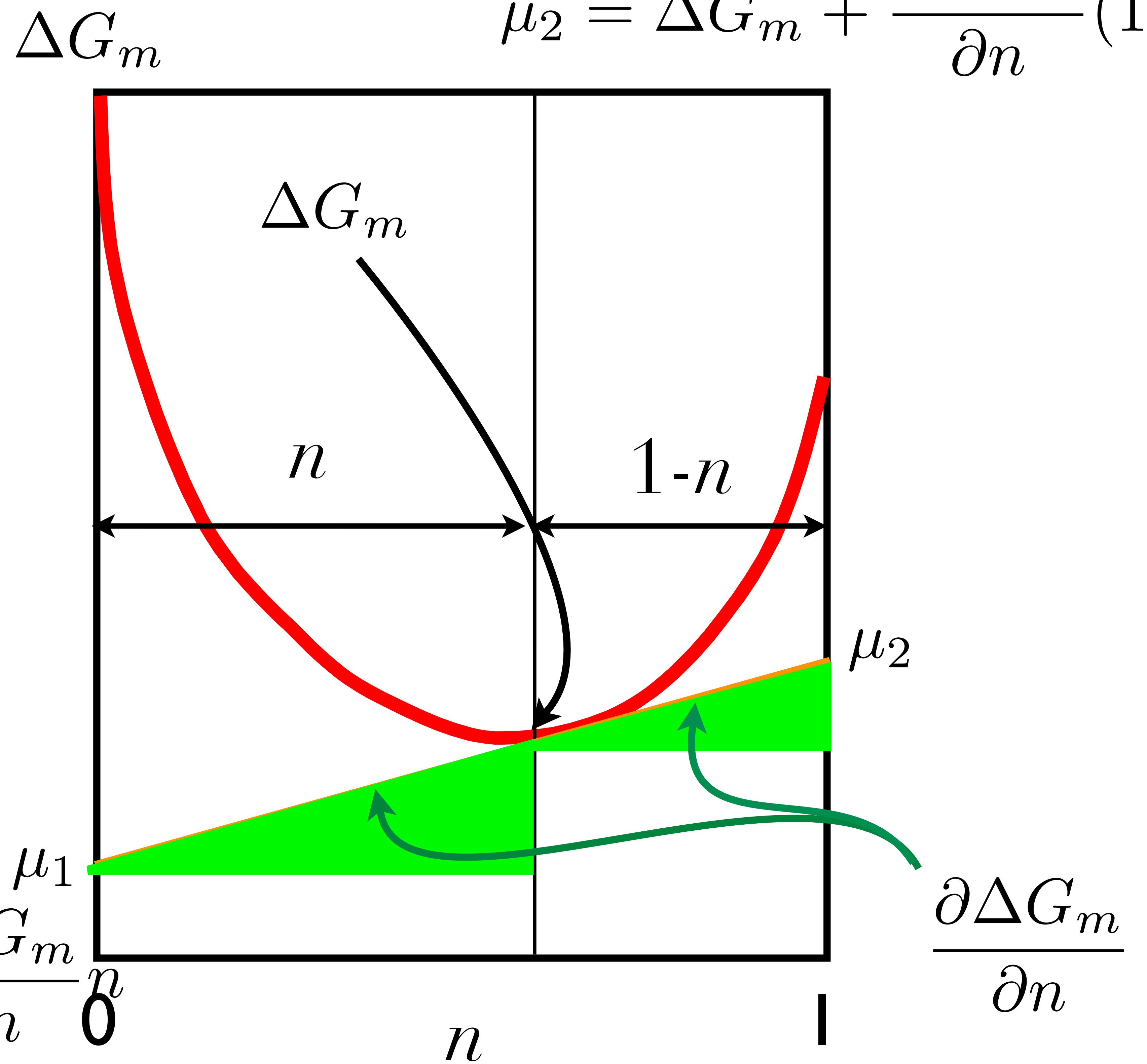
$$\varphi_c = \frac{\mu^c_{Li}}{zF}$$

$$\Delta\varphi = \frac{\mu^c_{Li}}{zF} - \frac{\mu^a_{Li}}{zF}$$



Method of Intercepts

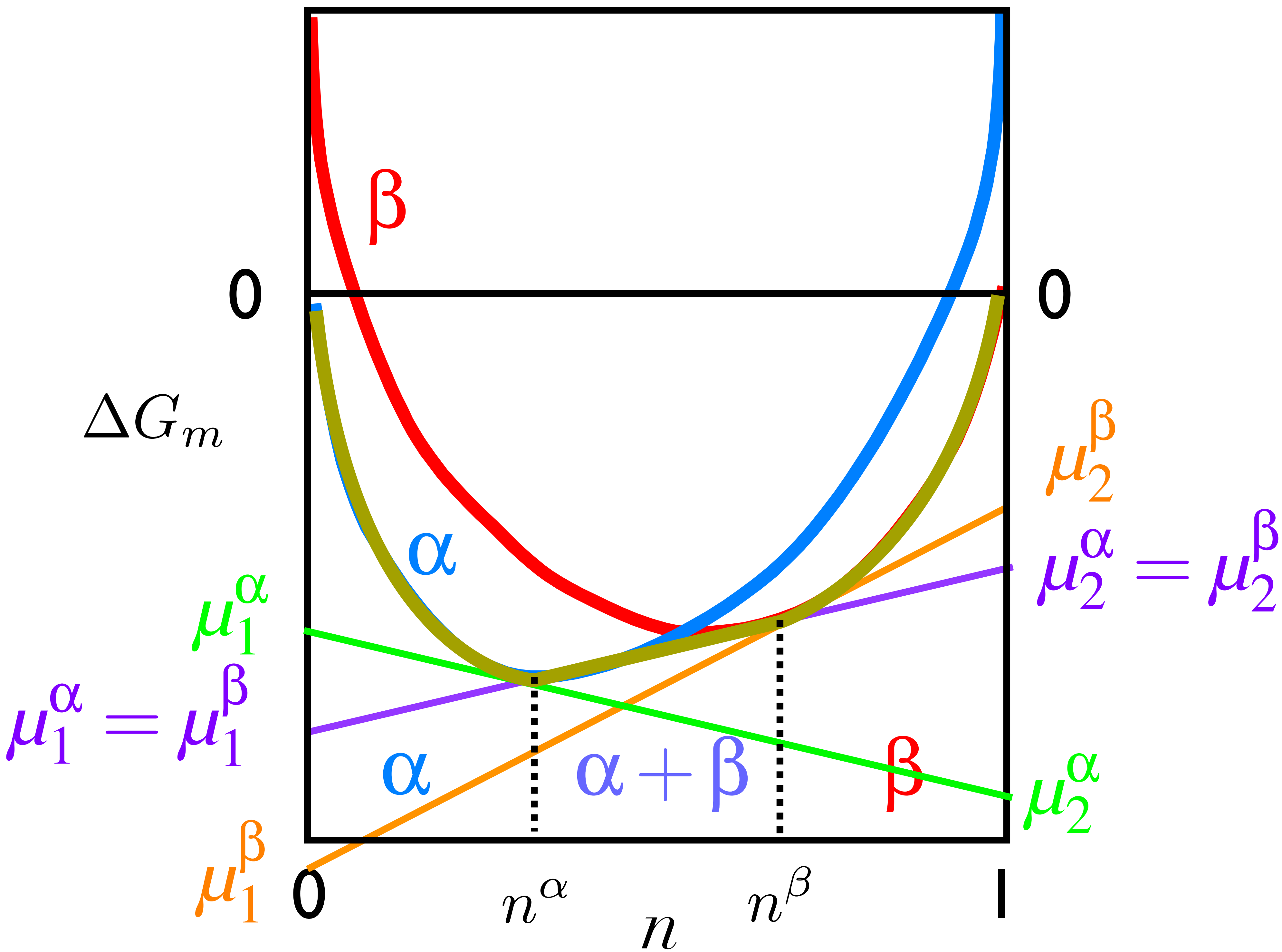
$$\mu_2 = \Delta G_m + \frac{\partial \Delta G_m}{\partial n}(1-n)$$



$$\mu_1 = \Delta G_m - \frac{\partial \Delta G_m}{\partial n} n$$

Graphical Solution

The Common Tangent Construction



The Common Tangent and Lever Rule

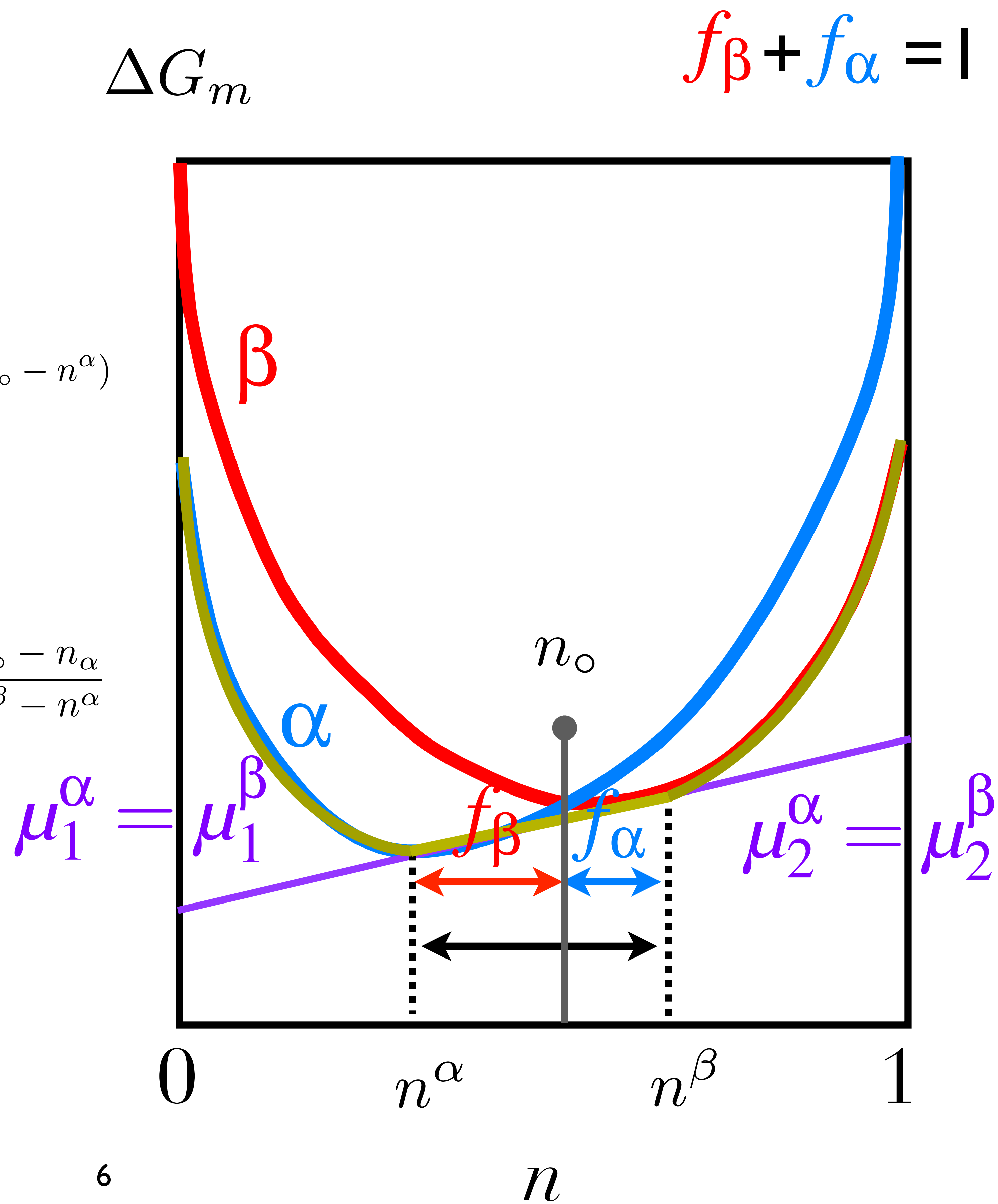
free energy in the miscibility gap:

$$\Delta G_m(n_\circ) = \Delta G_m^\alpha(n^\alpha) + \frac{\Delta G_m^\beta(n^\beta) - \Delta G_m^\alpha(n^\alpha)}{n^\beta - n^\alpha}(n_\circ - n^\alpha)$$

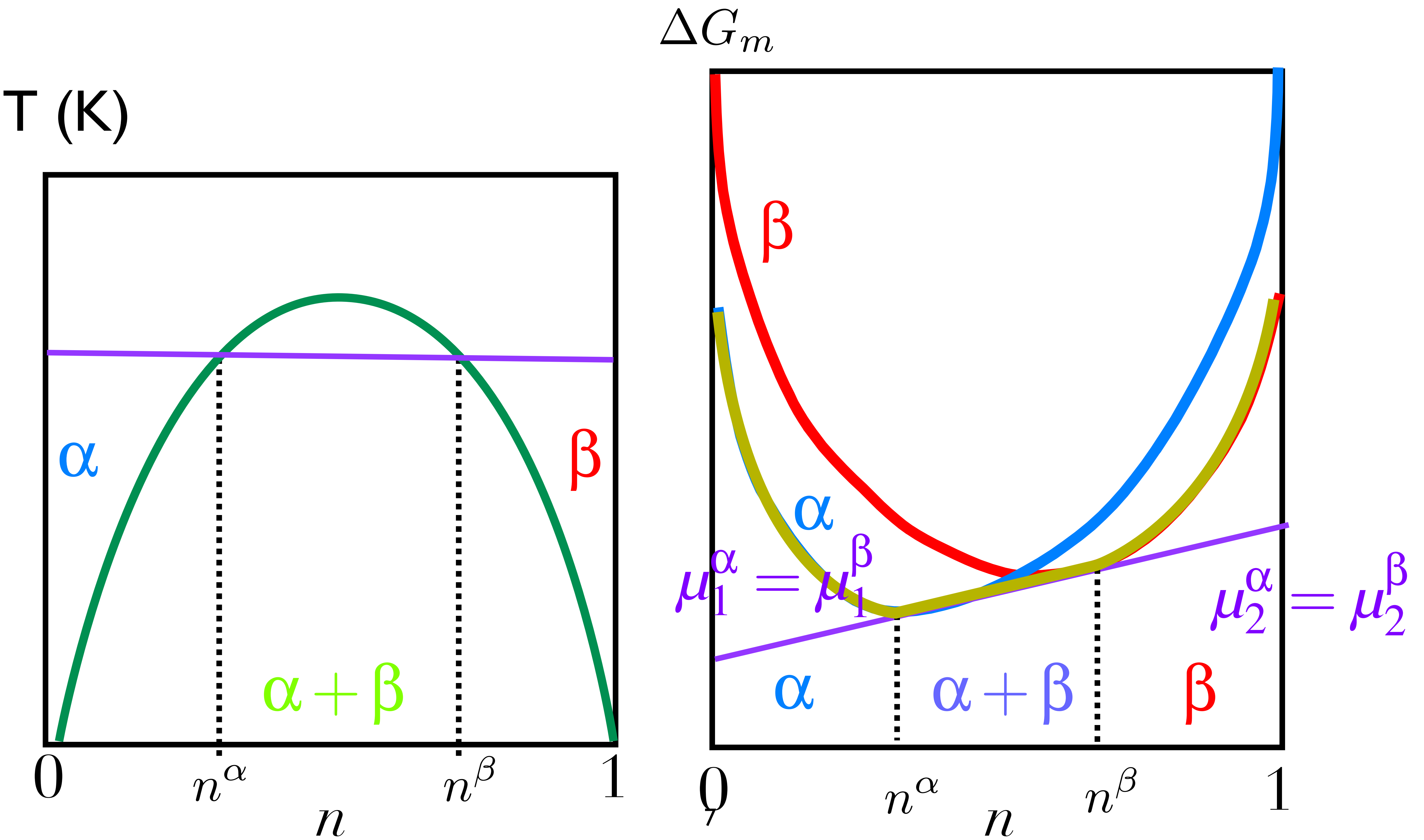
$$\Delta G_m(n_\circ) = \Delta G_m^\alpha(n^\alpha)\frac{n^\beta - n_\circ}{n^\beta - n^\alpha} + \Delta G_m^\beta(n^\beta)\frac{n_\circ - n_\alpha}{n^\beta - n^\alpha}$$

$$f_\alpha = \frac{n^\beta - n_\circ}{n^\beta - n^\alpha}$$

$$f_\beta = \frac{n_\circ - n^\alpha}{n^\beta - n^\alpha}$$



Building a Phase Diagram



Phase Diagrams and Material Potential