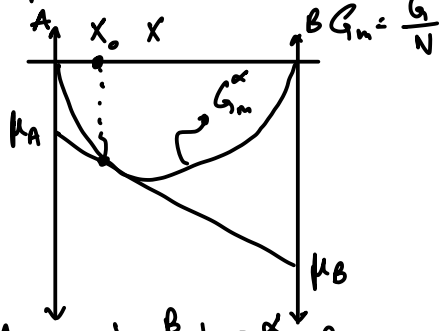
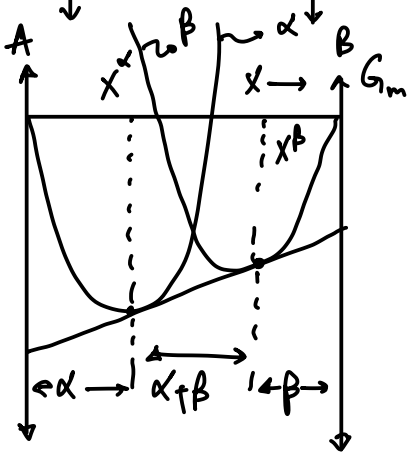
RECAP

① Graphical Constructions

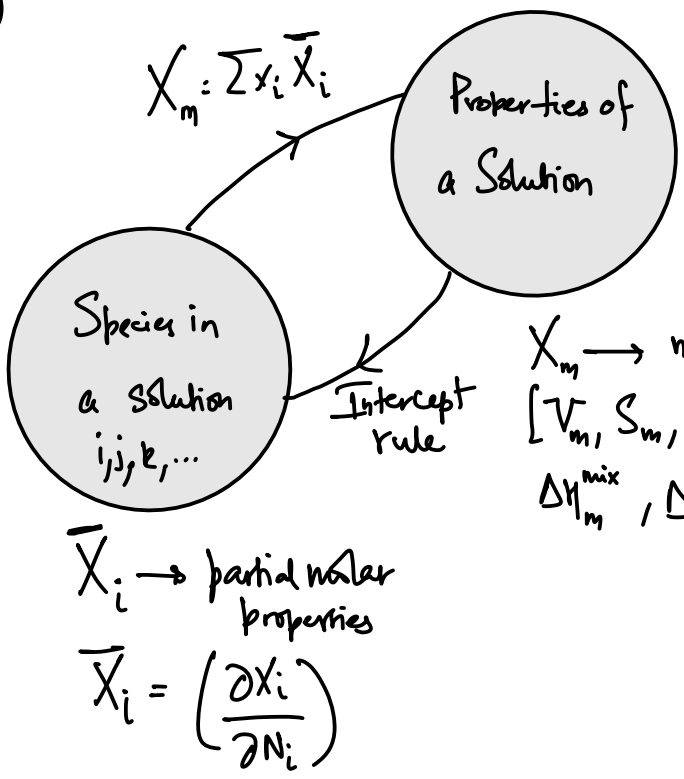


②



Chord Rule + Lever Rule + Common Tangent Construction.

③



PLAN FOR THE DAY:

① Ideal & regular solutions
② Phase Diagrams / free energies.
③ Basics of stat. mechanics.

★ REFERENCE STATE:

- energy has no absolute zero ⟶ only relative changes are important
- Entropy: 3rd Law allows us to set the Zero and scale of entropy.

All derived characteristic potentials such as H, G, f, ...

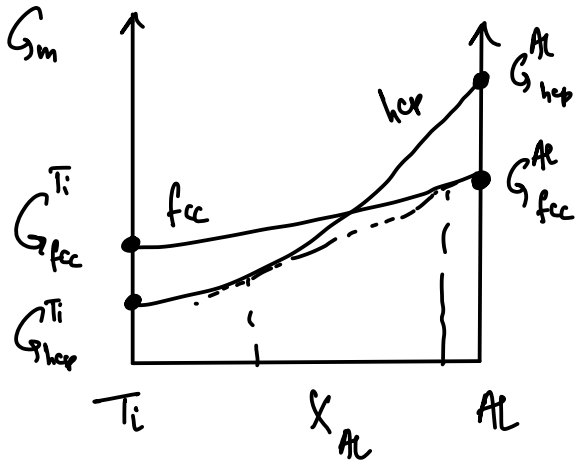
⟹ no absolute scale.

⟹ We can arbitrarily choose a reference state.

example: Ti-Al alloy

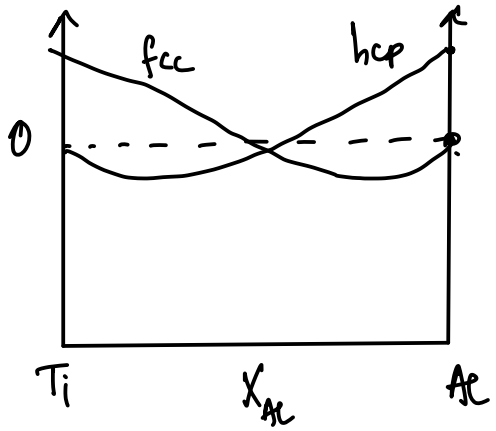
Ti at low T is stable in hcp → hexagonal close-packed

Al is stable in fcc → face-centered cubic



← arbitrary reference state

$\tilde{G}_m$



reference state of

Ti in hcp & Al in fcc

Changing reference states does not change relative stabilities at all.

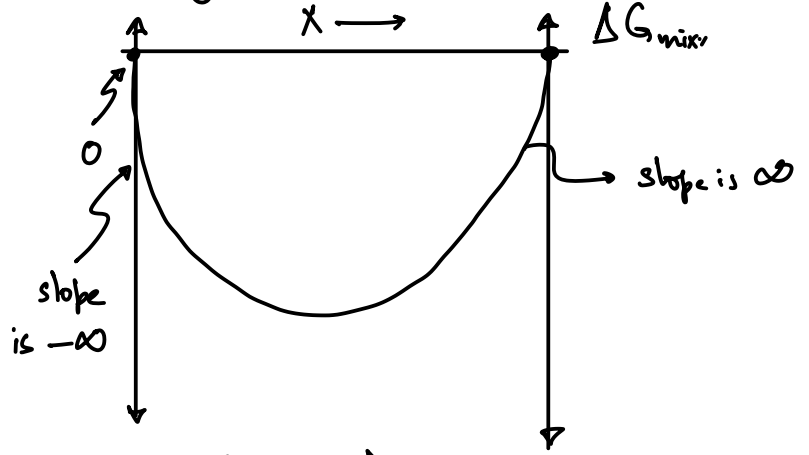
★ IDEAL SOLUTION:

$$\Delta G_{mix} = G_m - \sum_i x_i G_i^0$$ → free energy of the pure state $= \mu_i^0$

$$\boxed{\Delta G_{mix} = RT \sum_i x_i \log x_i}$$ → definition.

for a binary mixture/alloy:

$$\Delta G_{mix} = RT\left[x \log x + (1-x)\log(1-x)\right]$$



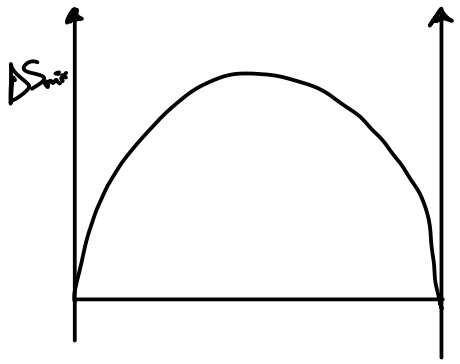
Notice:

$$\frac{\partial \Delta G_{mix}}{\partial x} = \left[\log \frac{x}{1-x}\right] RT$$

$$\mu_B(x_B = 0) = -\infty$$

$$\mu_B(x_B = 1) = +\infty$$

$$\Delta S_{mix} = -\left(\frac{\partial \Delta G_{mix}}{\partial T}\right) = -R \sum_i x_i \log x_i$$



$$\boxed{\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = 0}$$ → mixing does not release or absorb heat

→ Notice: $\Delta S = \frac{Q}{T} = \frac{\Delta H}{T} = 0$???

II Law: $\Delta S \geq Q/T \Rightarrow$ Mixing is irreversible. ← an ideal solution.

★ REGULAR SOLUTION:

ΔS^{mix} = ideal solution entropy

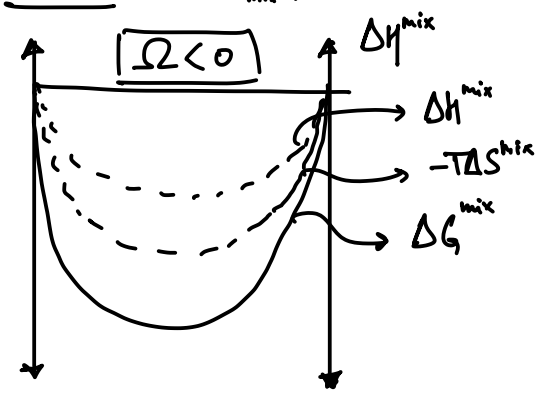
$= R_T [X_A \log X_A + X_B \log X_B]$

$\Delta H^{mix} = \Omega X_A X_B$

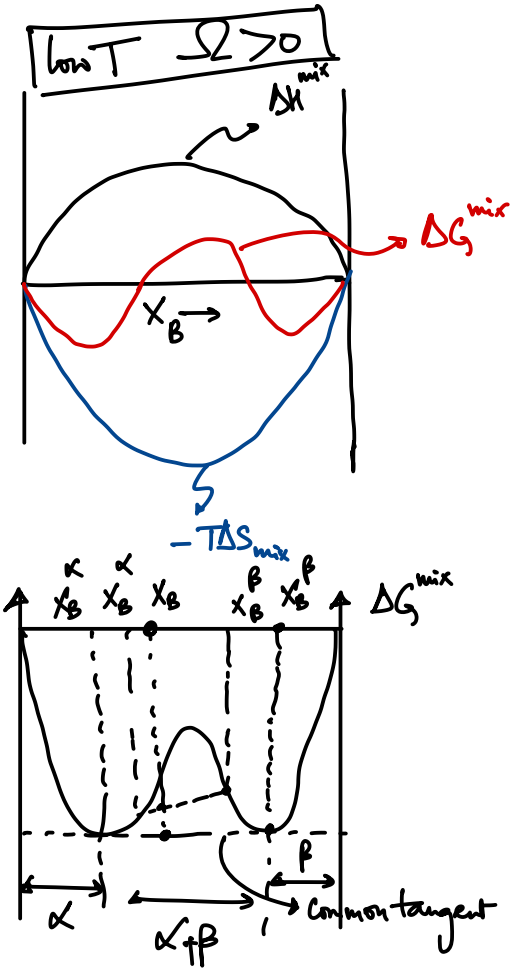
$\Delta G^{mix} = \Delta H^{mix} - T\Delta S^{mix}$

$\Omega < 0$: $\Delta H_{mix} < 0$

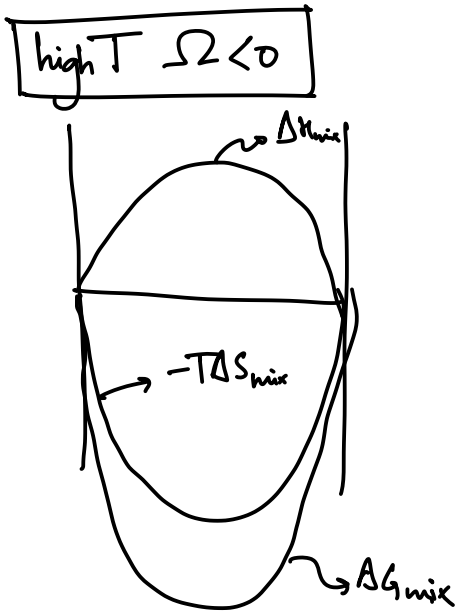
$\Omega > 0$: $\Delta H_{mix} > 0$



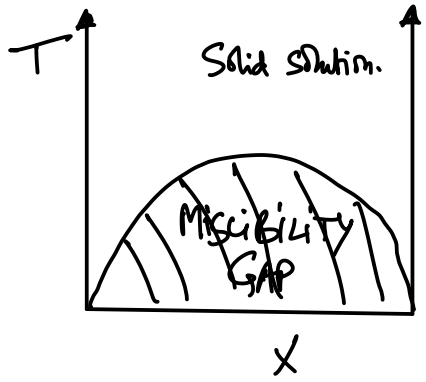
perfect mixing @ all temperatures.



ΔG^{mix} has regions of non-convexity.

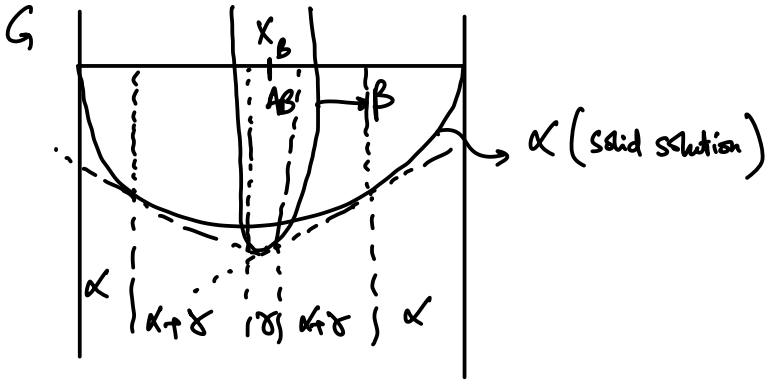


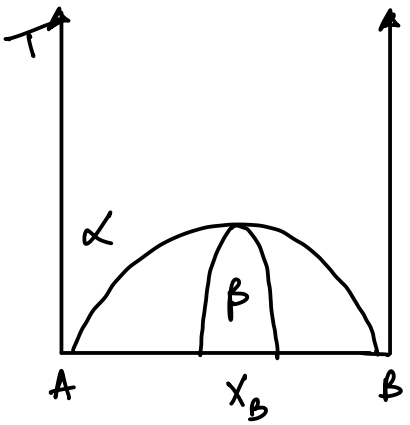
phase diagram: $\Omega > 0$



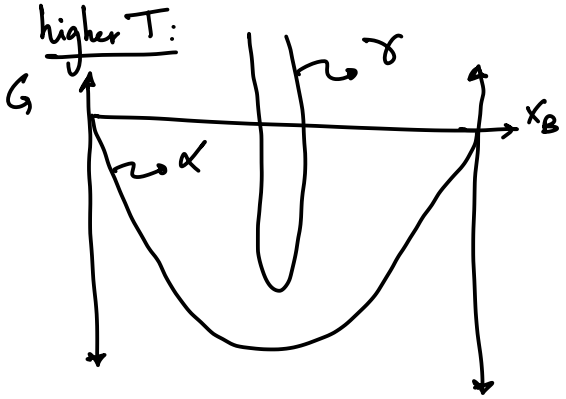
* SYSTEMS WITH COMPOUND FORMATION:

A & B atoms like to form bonds (eg) NaCl @ NiAl

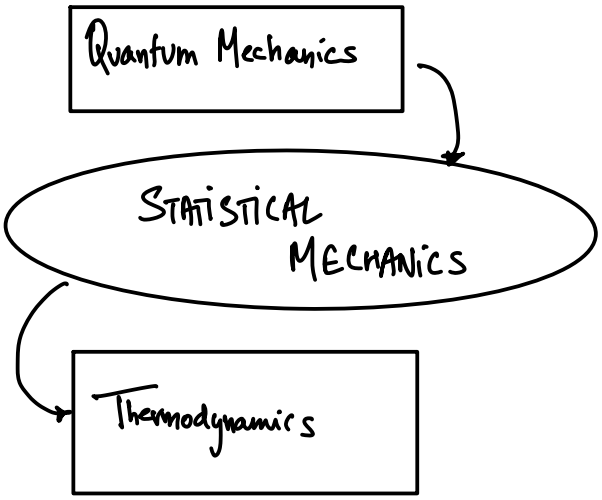




higher T:



STATISTICAL MECHANICS:



for (eg)

thermodynamics tells us → thermal expansion.

$$C_p - C_V = T V \beta^2 / \underline{K}$$ → compressibility

relates these quantities but does not tell us how to calculate any of them.

① Coarse-graining

* macroscopic thermodynamics ⟶ few variables. ⟵ Stat mech will tell us how to "Simplify"
* atomistic scale ⟶ many variables ~ 10^{23}

②

STATIC v/s DYNAMIC:

Thermo ⟶ eqm state is static

Microscopic / Atomic level ⟶ a system is fluctuating

How do we relate eqm thermodynamic quantities to fluctuating microscopic quantities?

③ What is entropy, internal energy etc. ... ?

BASIC IDEAS BEHIND STAT MECH:

— Mechanical variables $[H, X_i, \cdots]$ are time averages.

$$H = \langle E \rangle = \lim_{t \to \infty} \frac{1}{t} \int_0^t E(\tau)\, d\tau$$

— What is needed?

① How do I do the averaging?

In principle for time averages:

- dynamics (equations of motion)
- how atoms interact
- ∞ time!!

very HARD $\Longrightarrow$ POSTULATE (I) OF STAT MECH

time average = weighted average over all possible states

$$U = \langle E \rangle = \lim_{t\to\infty} \frac{1}{t}\int_0^t E(z)\,dz = \int E(\vec{r},\vec{p})\, P(\vec{r},\vec{p})\, d\vec{r}\, d\vec{p}$$

Consider N particles:

each particle has a position $\vec{r}_i = (r_{ix}, r_{iy}, r_{iz})$

momentum $\vec{p}_i = (p_{ix}, p_{iy}, p_{iz})$

The entire system can then be characterized by 2 vector of dimension 3N

$$\vec{r} = (r_{1x}, r_{1y}, \cdots, r_{Nz})$$

$$\vec{p} = (p_{1x}, p_{1y}, \cdots, p_{Nz})$$

$P(\vec{r},\vec{p})$ = probability density

P is "large" in regions of $\vec{p},\vec{r}$ that are likely and small in regions that are unlikely.

$P(\vec{r},\vec{p})\, d\vec{r}\, d\vec{p}$ $\longrightarrow$ measure of time that the system spends in a state between $[(\vec{r},\vec{p}) : (\vec{r}+d\vec{r}, \vec{p}+d\vec{p})]$

$$\langle E \rangle = \int E(\vec{r},\vec{p})\, P(\vec{r},\vec{p})\, d\vec{r}\, d\vec{p} \longrightarrow \text{"ENSEMBLE" average.}$$

"ENSEMBLE" $\longrightarrow$ all possible microscopic states of the system

② Probability that a system occupies a give state

③ Which states to average over?

$\longrightarrow$ Eigen states of a system $\leftarrow$ formally from QM.

④ Relate to thermo quantities