Phases of matter

Last time: mixtures

N_A molecules of type A

N_B molecules of type B

Example: mix $n_{water} + n_{EtOH}$

non ideal mixing, Volume shrinks

Connect some ideas to phase transitions

Phases of matter: solid, liquid, gas
[same bulk properties everywhere]
Density, compressibility, heat capacity

most stable: which phase should your system be in

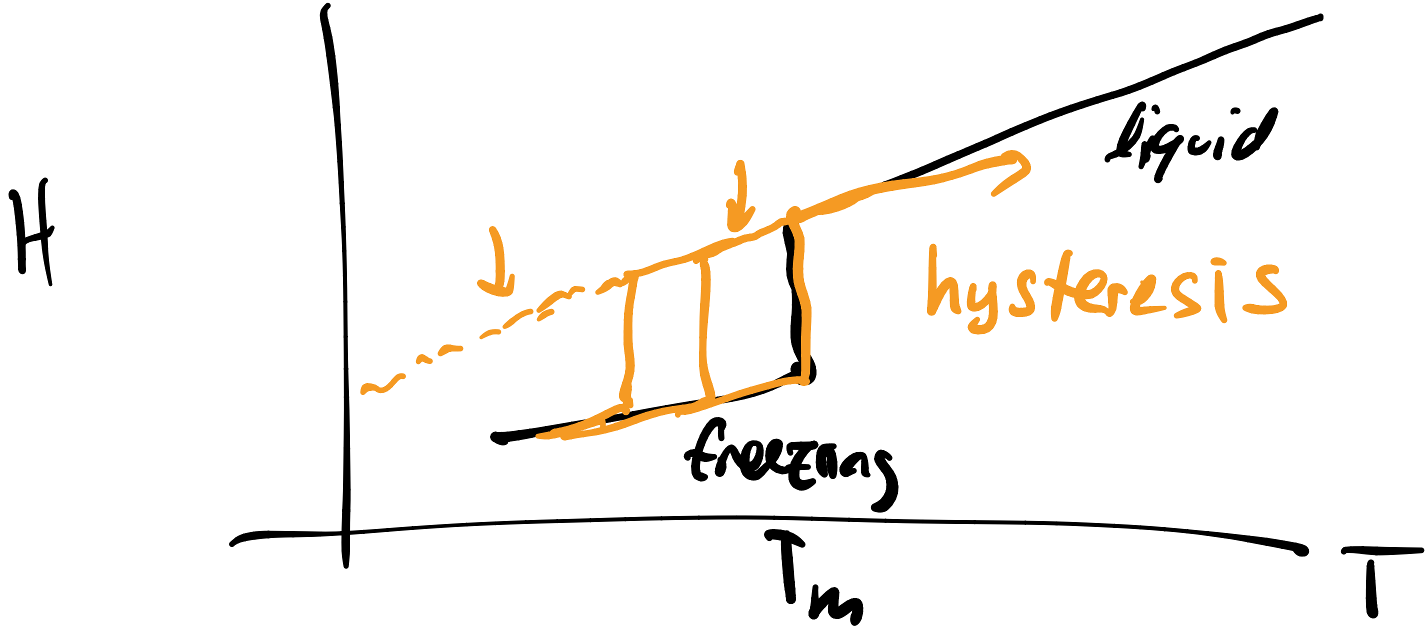
Kinetics can play a role in real world

- Carbon: diamond, graphite, C60

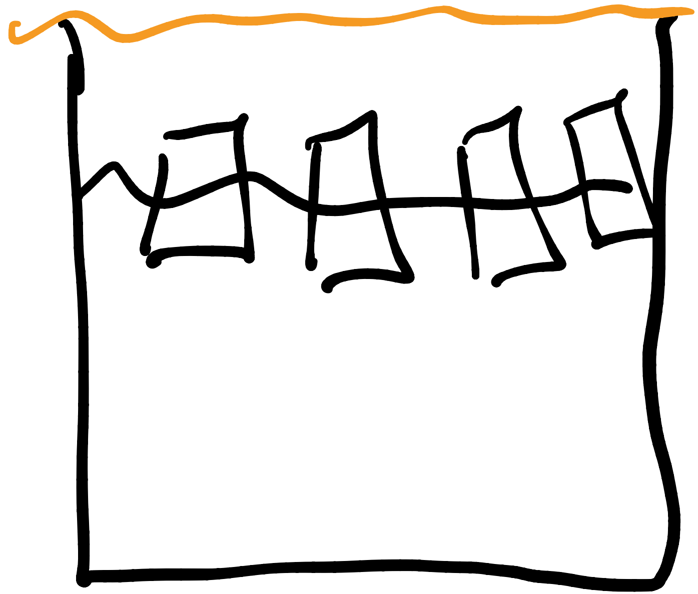
Non equilibrium "phase"

glassy materials → extremely high viscosity

disordered


H
liquid
hysteresis
freezing
Tm
T

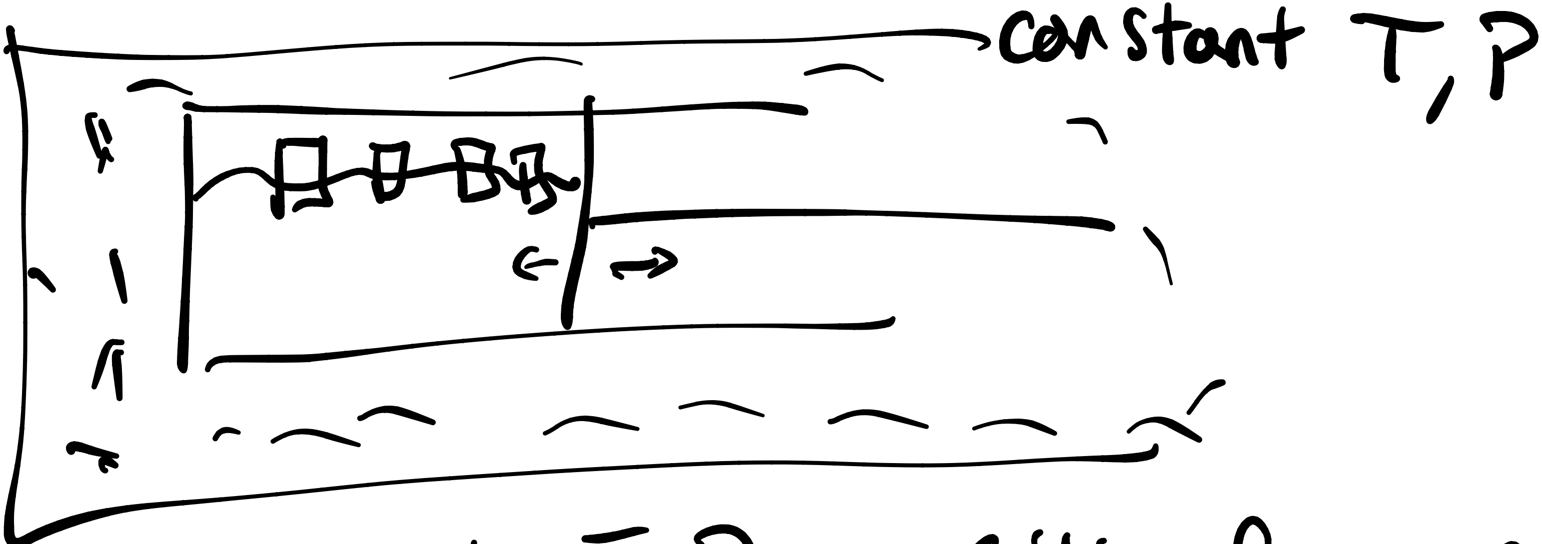
Why is this like a mixture?



fixed # molecules of water

n ice are in solid

n water are in liq



@ constant T, P → Gibbs free energy
is a thermodynamic potential

G↓

$$G = H - TS$$

$$G(P, T, N_A, N_B)$$

$$dG = \underbrace{\left(\frac{\partial G}{\partial P}\right)_{T,N_A,N_B}}_{=V} dP + \overbrace{\left(\frac{\partial G}{\partial T}\right)_{P,N_A,N_B}}^{=-S} dT + \overbrace{\left(\frac{\partial G}{\partial N_A}\right)_{P,T,N_B}}^{\equiv \mu_A} dN_A + \underbrace{\left(\partial G/\partial N_B\right)_{P,T,N_A}}_{=\mu_B} dN_B + \ldots$$

Chemical potential –

how much does G change if N changes

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{n \text{ speices}} \mu_i\,dn_i$$

μ as $\dfrac{\partial G}{\partial N}$ or $\dfrac{\partial G}{\partial n}$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}}$$

μ_i depends on $p, T, n_1, n_2 \ldots n_{i-1}, n_{i+1} \ldots$

$\bar{V}_i$ volume of species i per mol

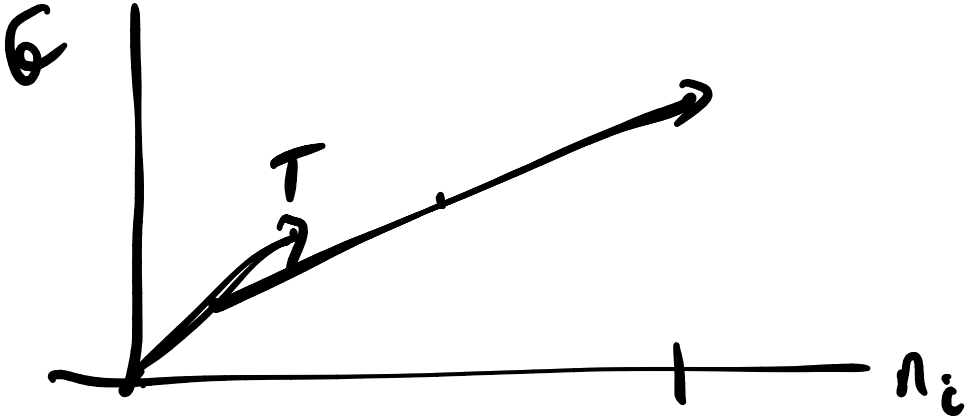
$$V_{tot} = \bar{V}_1 n_1 + \bar{V}_2 n_2 + \dots$$

$$G_{total} = \bar{G}_1 n_1 + \bar{G}_2 n_2 + \dots$$

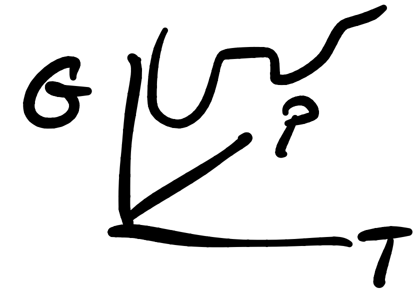
$$\mu_i = \bar{G}_i = G_i / n_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j \neq n_i}}$$

$G_i \leftarrow$ contribution of speices i to the free-energy

go from 0 moles to n_i moles



const $P, T, n_{j \neq i}$



$$\int_0^{n_i} \underbrace{\frac{\partial G}{\partial n_i}}_{\mu_i} dn_i = G_{syst} - G(n_i = 0) = G_i$$

$$\mu_i n_i = G_i \Rightarrow \mu_i = G_i / n_i$$

$$G = \sum_{i=1}^{species} \mu_i n_i$$

$$dG = -SdT + VdP + \sum_{i=1}^{n \text{ species}} \mu_i dn_i$$

$$G = \sum \mu_i n_i$$

$$dG = \sum (\mu_i dn_i + n_i d\mu_i)$$

$$\boxed{SdT - VdP + \sum n_i d\mu_i = 0}$$

Gibbs-Duhem relation

at const T, P $\leftrightarrow dP = dT = 0$

$$\sum n_i d\mu_i = 0$$

chemical potentials not independent

2 species

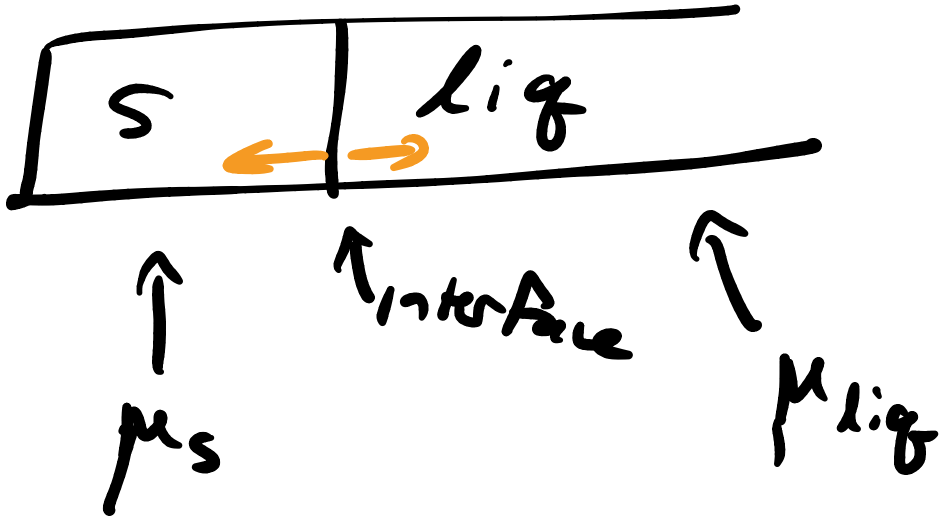
$$n_A d\mu_A + n_B d\mu_B = 0$$

divide by n_t $= n_A + n_B$

$$x_A d\mu_A + \underbrace{x_B}_{= (1-x_A)} d\mu_B = 0$$

$$x_A \, d\mu_A + (1-x_A)\, d\mu_B = 0$$

$$d\mu_B = \underbrace{\frac{-x_A}{1-x_A}}_{<0} d\mu_A$$



@ const T, P

$$dG = \mu_l dn_l + \mu_s dn_s \leq 0$$ for spontaneous process

$$n_t = n_l + n_s = \text{const}$$

$$dn_l + dn_s = 0, \quad -dn_l = dn_s$$

$$dG = \underbrace{dn_s(\mu_s - \mu_\ell)}_{\text{if } \mu_s > \mu_\ell} \quad \text{or} \quad = dn_\ell(\mu_\ell - \mu_s)$$

< 0 if

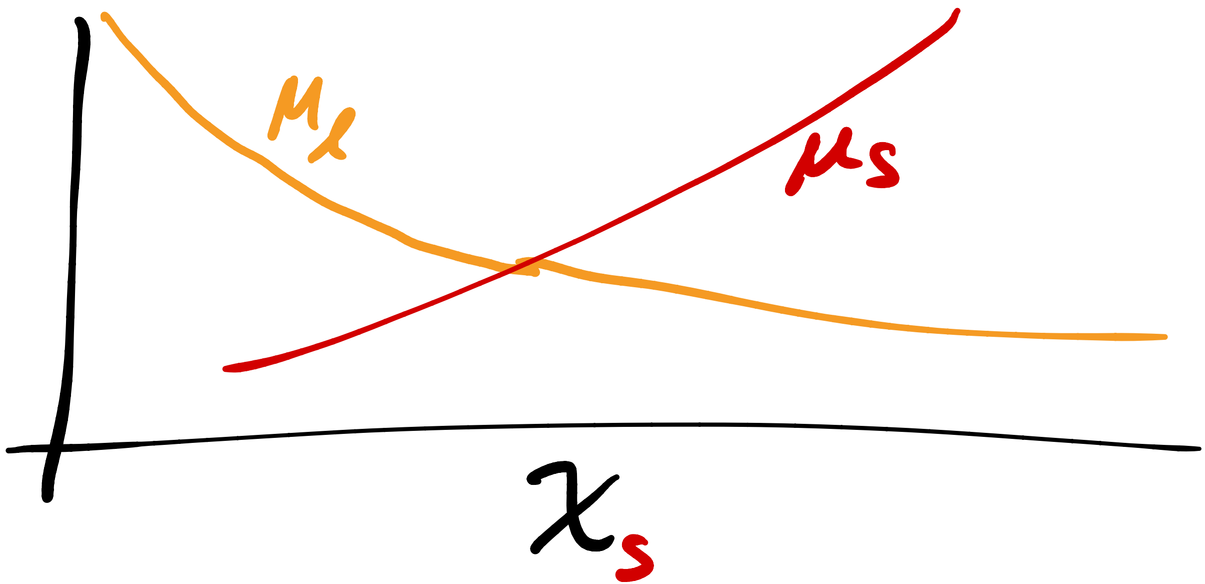
if $\mu_s > \mu_\ell$ $\quad dn_s < 0$ $\quad$ less solid

$\mu_s < \mu_\ell$ $\quad dn_s > 0$ $\quad$ more solid

move from high to low

if $dG = 0$ $\quad \cancel{dn_s, dn_\ell = 0}$ $\quad$ or

$\mu_s = \mu_\ell$



$G(n_\ell, n_s)$

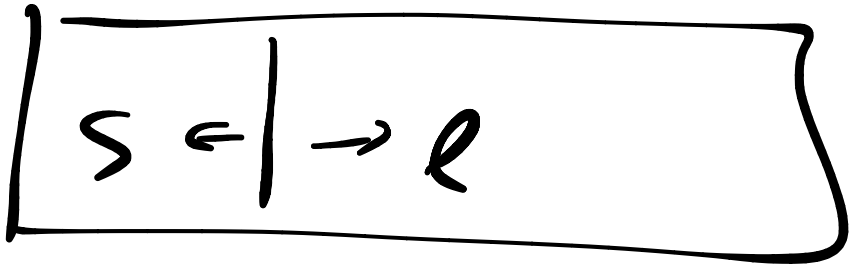
$$dG = \left(\frac{\partial G}{\partial n_\ell}\right)_{n_s} dn_\ell + \left(\frac{\partial G}{\partial n_s}\right)_{n_\ell} dn_s = \mu_\ell \, dn_\ell + \mu_s \, dn_s$$

Takeaways:

μ change in free energy with amount of something

"stuff" moves from high to low chem pot

equilibrium between phases, $\mu_A = \mu_B$



$$\Delta V = (\bar{V}_s - \bar{V}_l)\, dn_s$$

normally melting $\Rightarrow$ higher volume

except H_2O

$$dq = (\bar{H}_s - \bar{H}_l)\, dn_s$$