Recap

$$V = \sum_{i=1}^{k} \bar{V}_i n_i$$

$$\rho = \frac{n}{V}$$

$$P = \rho RT$$

$\bar{V}_i$ is not ideal $1/\rho$

$$\text{ideal} \updownarrow \text{isolated}$$

$$\mathcal{E}_{tot} = \sum_{i=1}^{k} \bar{\mathcal{E}}_i n_i$$

$$G_{tot} = \sum_{i=1}^{k} \bar{G}_i n_i = \sum_{i=1}^{k} \mu_i n_i$$

Partial pressures

$$P_i = \chi_i P_{total} \qquad \text{(definition)}$$

$$\sum_i P_i = \sum_{i=1}^{K} \chi_i P_{total} = P_{total} \sum_{i=1}^{K} \chi_i$$

$$= P_{total}$$

For an ideal gas

$$P_i = n_i \frac{RT}{V} = \rho_i RT$$

$$P_{total} = \frac{RT}{V} \sum_{i=1}^{K} n_i \qquad \text{(Dalton's law)}$$

what about non ideal gasses?

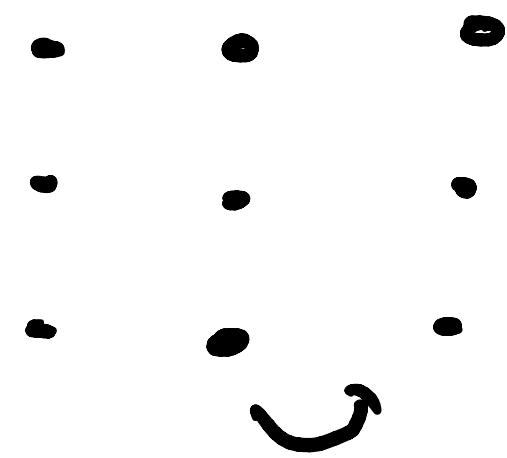Repulsive: increase pressure

Attractive: decrease pressure

↗ (for same mixture in same volume & temperature)
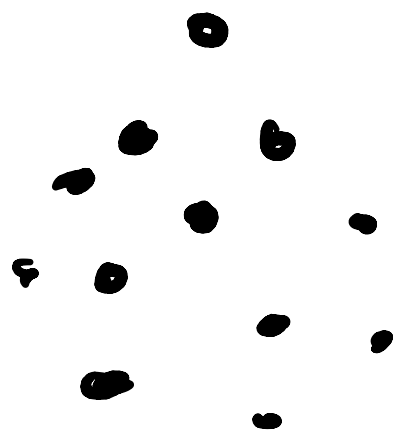
compared to ideal gas

Phase transitions

Phases of matter: solids, liquids, gas

Difference is $\sim$ symmetries
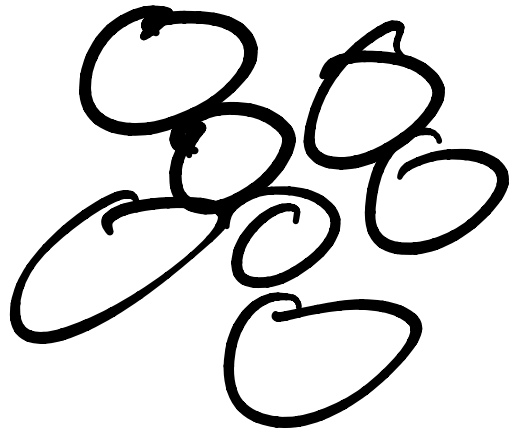
crystal

liq
(local order)

gas (no local order)

@ some T, P, ρ

$\leftarrow \dashv$
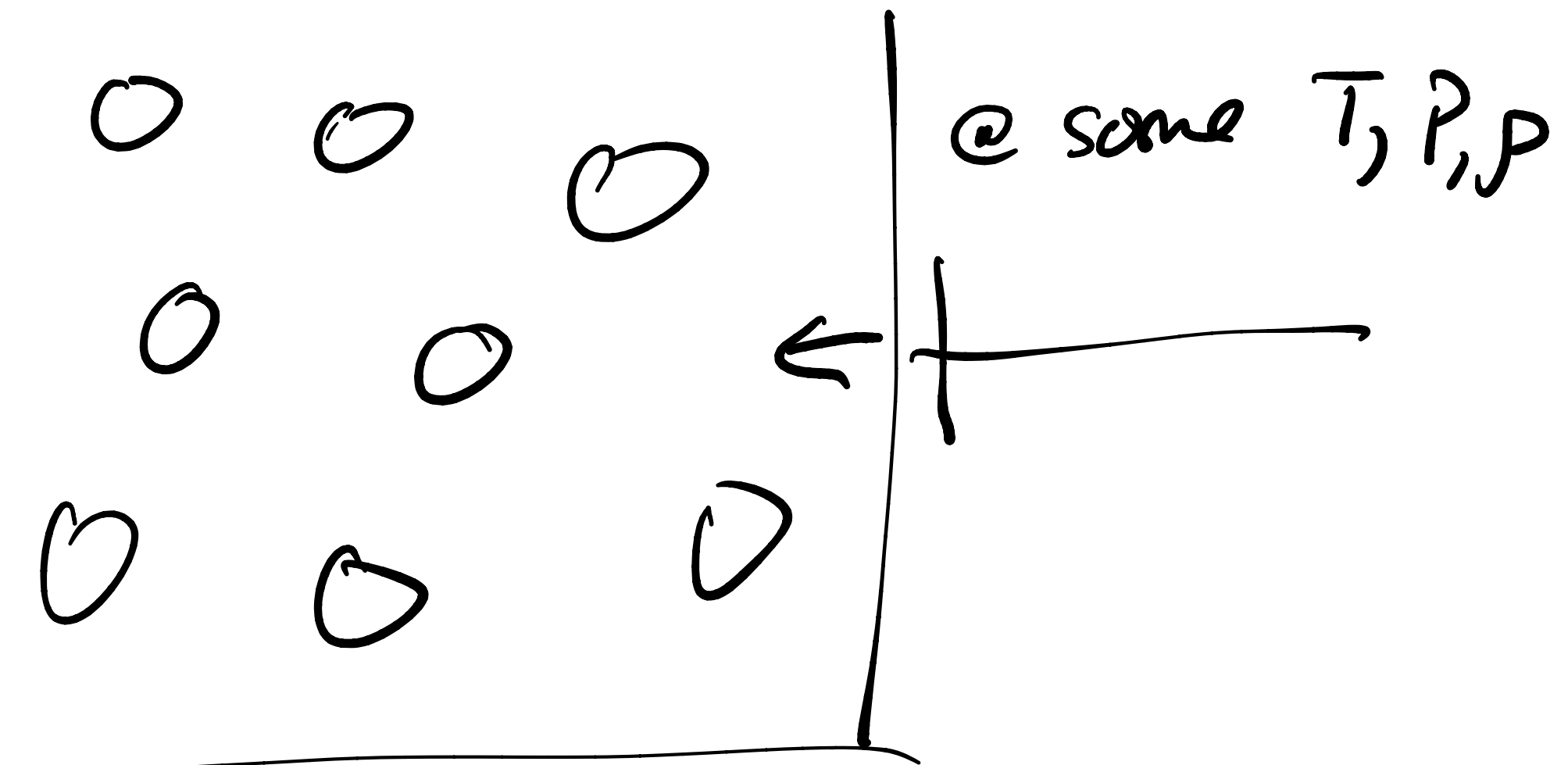
do hard particles crystallize
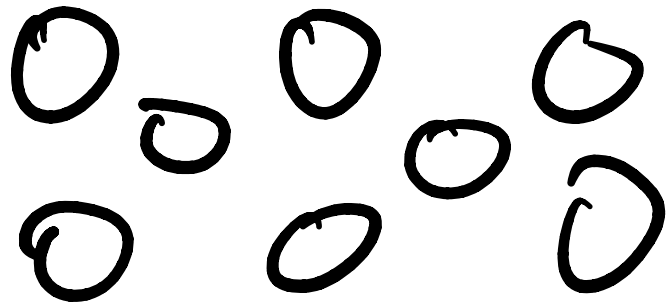
$A = \mathcal{E} - TS$

@ const volume

$\mathcal{E} = 0$ if no overlaps
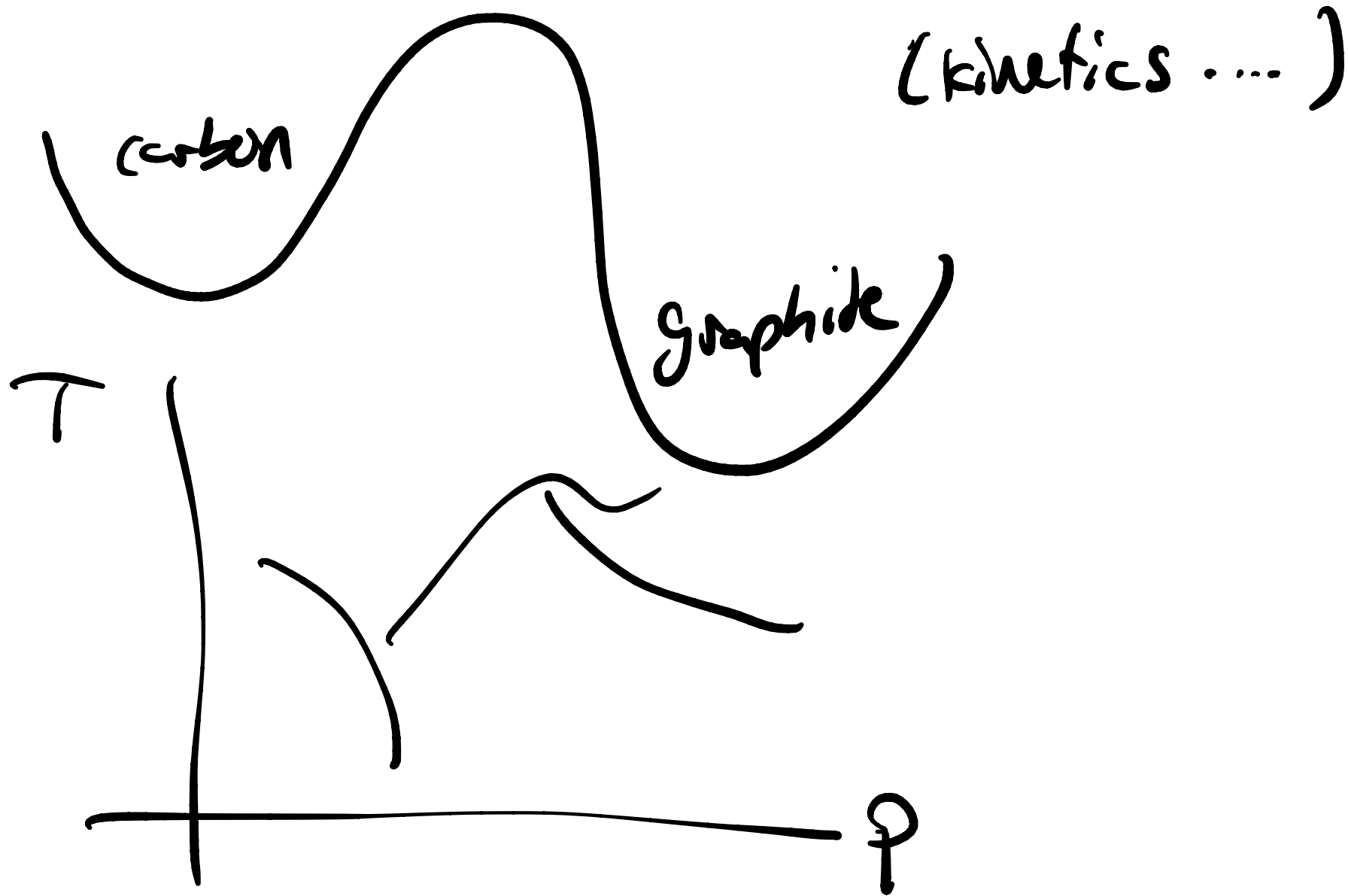
random close packing
less entropy at
same density

→ so, yes, crystalizes

Differences: density, compressibility
heat capacity, conductivity

Other "kinds" of phases

Diamond, Graphite, Nanotubes
C_{60}

if @ some T, P G is not
minimized, not a stable phase
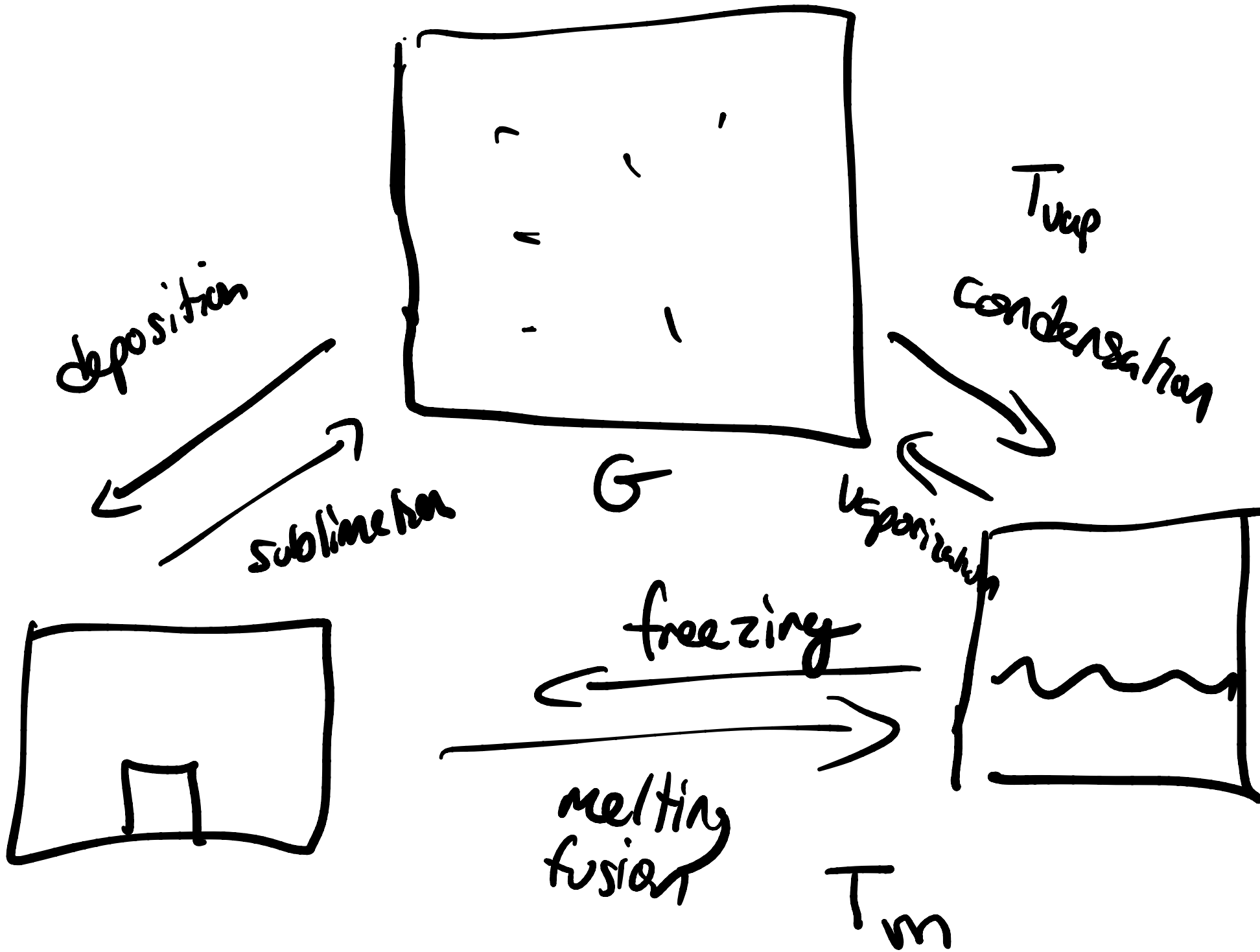
(kinetics ....)

carbon

graphite

T

P

Indicates lowest free energy structure

"Non equilibrium phase"
glass — effectively a solid
structure of a liquid

density

slower cooling

liquid

Crystal

T

Slow motion
→ no time to
crystallize

G

deposition

sublimation

T_{vap}

condensation

vaporization

freezing

melting
fusion

T_m

why is this a "mixture"
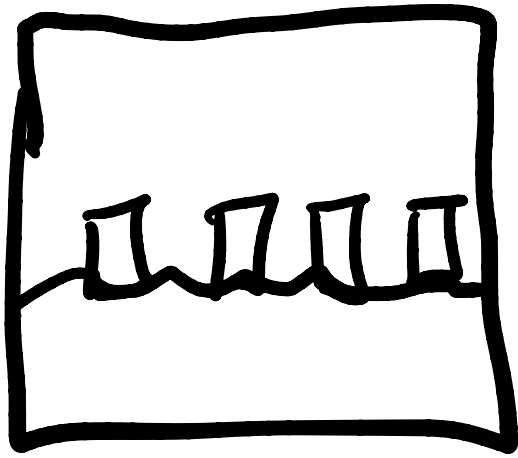
$$n_{liq} + n_{solid} + n_{gas}$$

Gibbs free energy is the thermodynamic potential for phase transitions @ const P, T

$$G(P, T, n_1, n_2, \ldots)$$

$\checkmark \mu_i$

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_1 \ldots} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_1 \ldots} dT + \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_{j \neq i}} dn_i + \ldots$$

$$= VdP - SdT + \sum_{i=1}^{K} \mu_i \, dn_i$$

also $G = \sum \mu_i n_i$

$$dG = \sum \mu_i \, dn_i + n_i \, d\mu_i$$

G.D. $SdT - VdP + \sum_{i=1}^{K} n_i \, d\mu_i = 0$

$$S dT - V dP + \sum_{i=1}^{k} n_i d\mu_i = 0$$
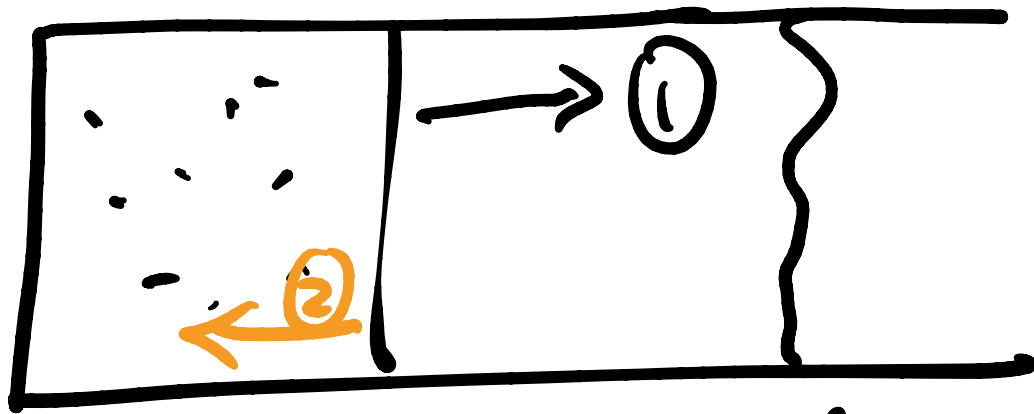
$$\underline{} \\ ||0$$

@ const T&P

$$\sum_{i=1}^{k} n_i d\mu_i = 0$$

only 2 things $n_1 d\mu_1 = -n_2 d\mu_2$

2 phase are in equilibrium when
$$\mu_i = \mu_j$$

Solid   liquid

$$T < T_m \quad \text{①}$$

$$T > T_m \quad \text{②}$$

@ const temp & pressure

$$dG = \mu^s \, dn^s + \mu^\ell \, dn^\ell \quad \curvearrowleft$$

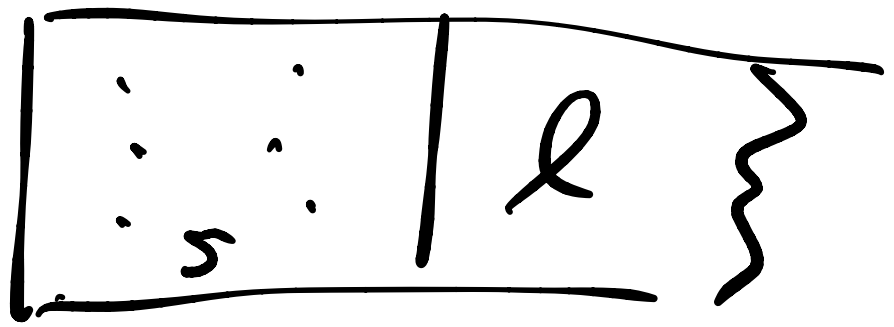$$n_{total} = n^s + n^\ell \Rightarrow 0 = dn^s + dn^\ell$$

$$dG = \mu^s dn^s + \mu^\ell dn^\ell \quad \hookleftarrow$$

$$n_{total} = n^s + n^\ell \Rightarrow 0 = dn^s + dn^\ell$$

$$dG = (\mu^s - \mu^\ell) dn^s$$
$$= (\mu^\ell - \mu^s) dn^\ell$$

Spontaneous change, $dG < 0$

$\mu^s > \mu^\ell$, $dn^s < 0$ for spontaneous

things go from high μ to low μ

Same setup

$$\Delta V = (\bar{V}^s - \bar{V}^\ell)dn^s$$

nomally $\bar{V}^s < \bar{V}^\ell$

when you melt, $dn^s < 0$
$dn^\ell > 0$

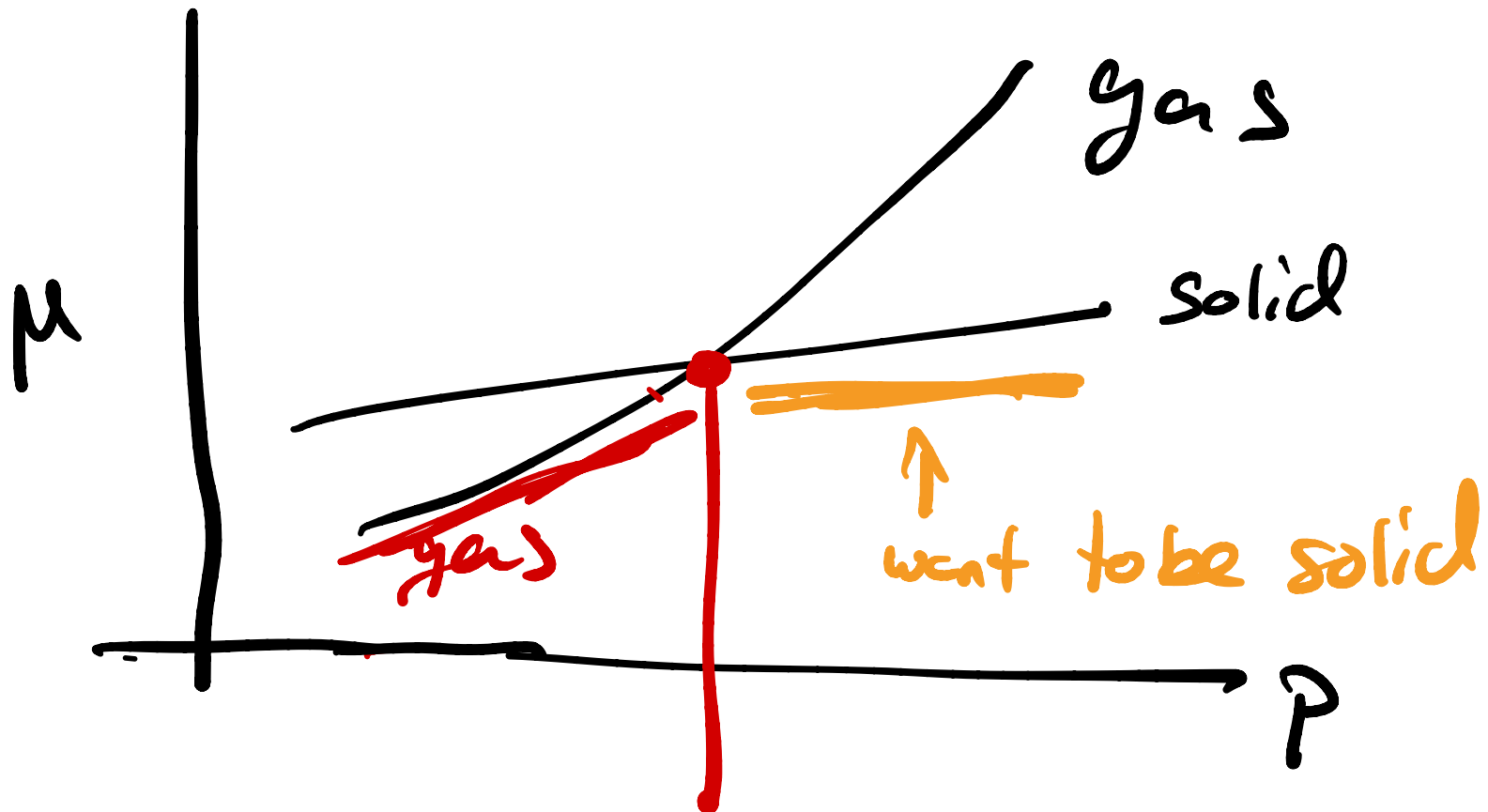[exception for water $\bar{V}^{ice} > \bar{V}^{water}$]

Heat flow...

$$dq = (\bar{H}^s - \bar{H}^\ell) \, dn^s$$

need to know molar enthalpies

$$\left[dH = T \, dS + V \, dP = T \, ds = dq = C_p dT \right]$$

When is a phase transition

$$\mu^\alpha = \mu^\beta \quad , \quad \text{how depend on } T, P$$

gas

imagine

μ

solid

@ fixed
T

gas

want to be solid

P

phase coexistence

ρ

P