Lecture 11 - Phase Transitions

Eg of combined quantities in mixtures:

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

if ideal, $\bar{V}_i = \bar{V}_i^* = 1/\rho$ $\quad \rho = \frac{n}{V}$

$\left[P = \rho RT \right.$ (ideal gas)

$$\mathcal{E}_{tot} = \sum \bar{\mathcal{E}}_i n_i$$

★ $G_{total} = \sum \bar{G}_i n_i = \sum_i \mu_i n_i$

Aside Partial pressure

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

$$\chi_i = \frac{n_i}{\sum n_i}$$

for ideal gasses P_i = ideal gas pressure

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

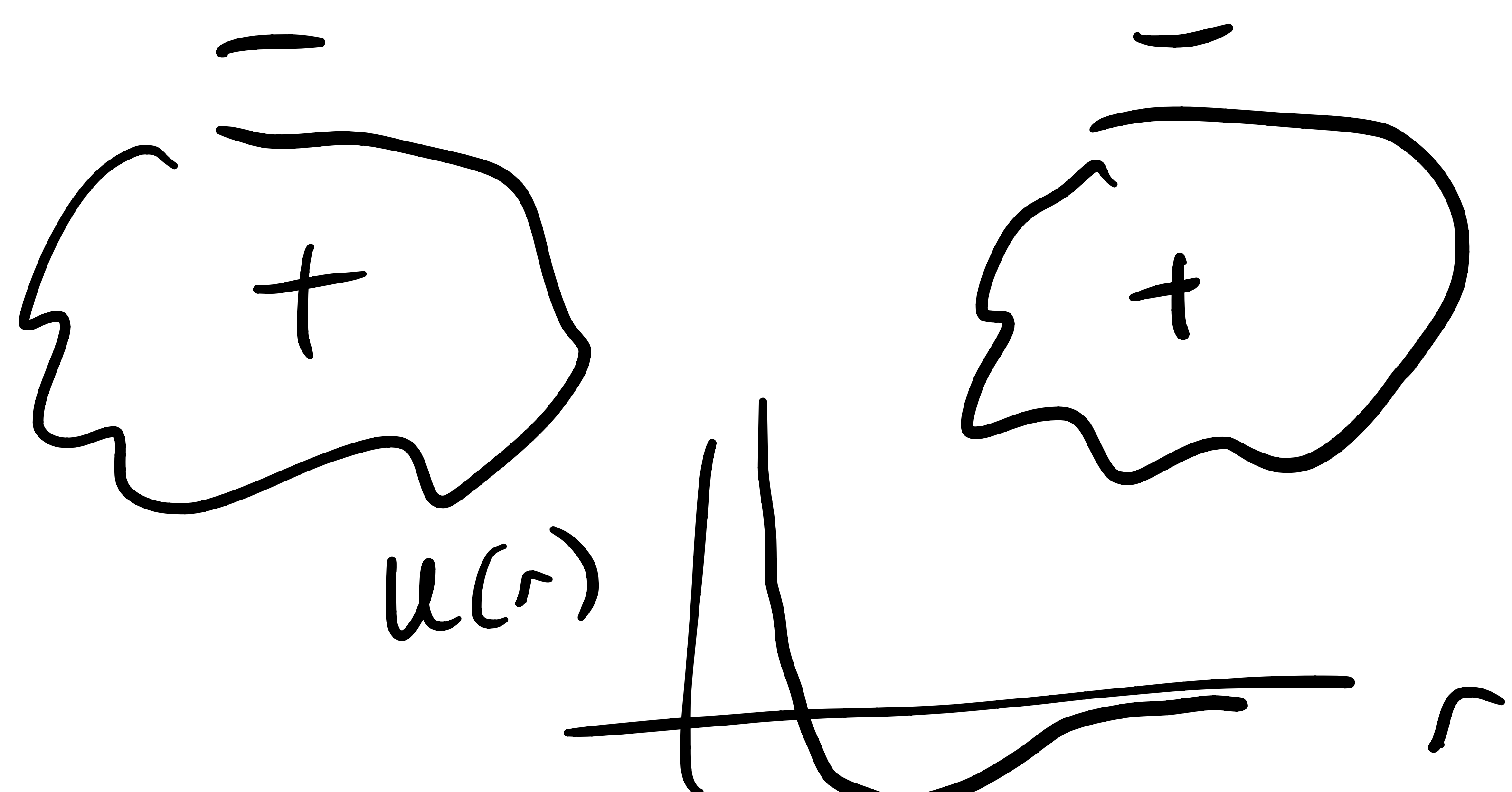
(Dalton's) $P_{total} = \frac{RT}{V} \sum_i n_i$

Non ideal gasses: (cf Van-der Waal's eqn of state)

2 contributions to interactions:

- "volume exclusion" ← pressure ↑ (relative to an ideal gas)
- attractions → pressure ↓ (relatively)

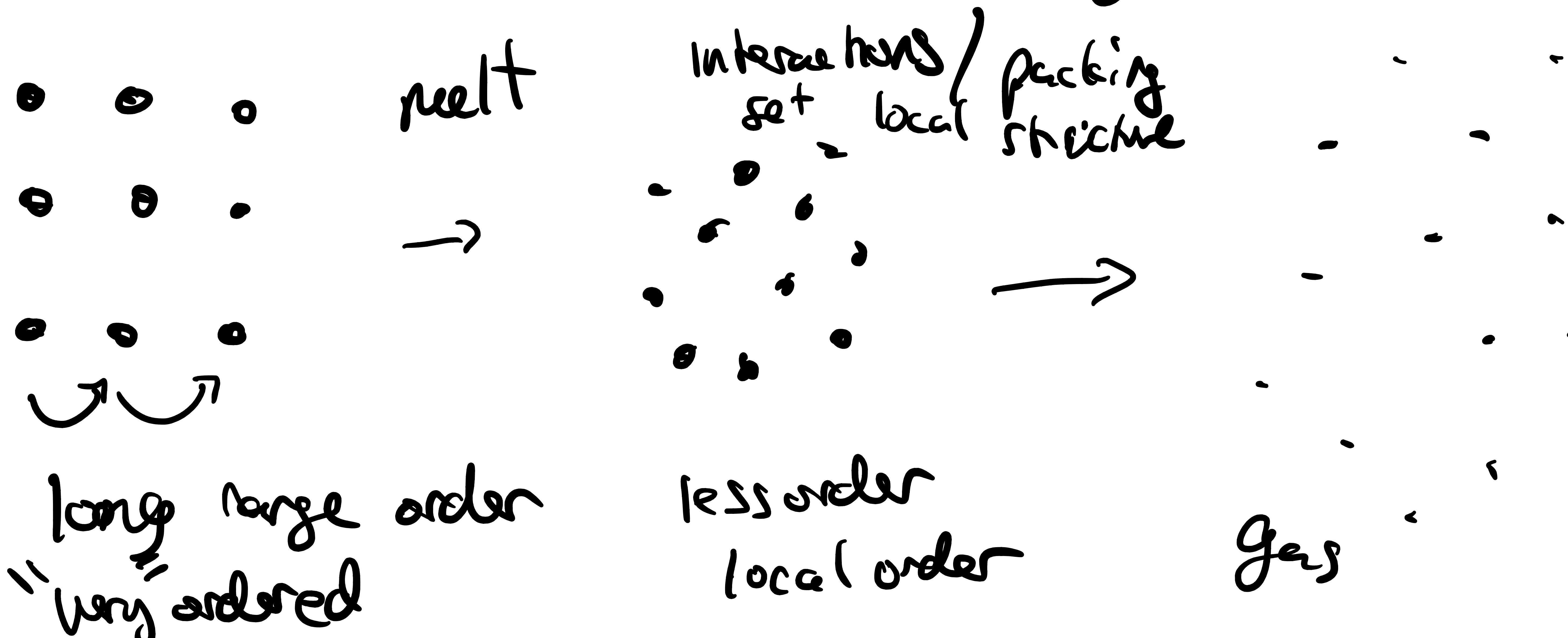
VdW:



Phase transitions

"Phases of matter": solids, liquids, gasses

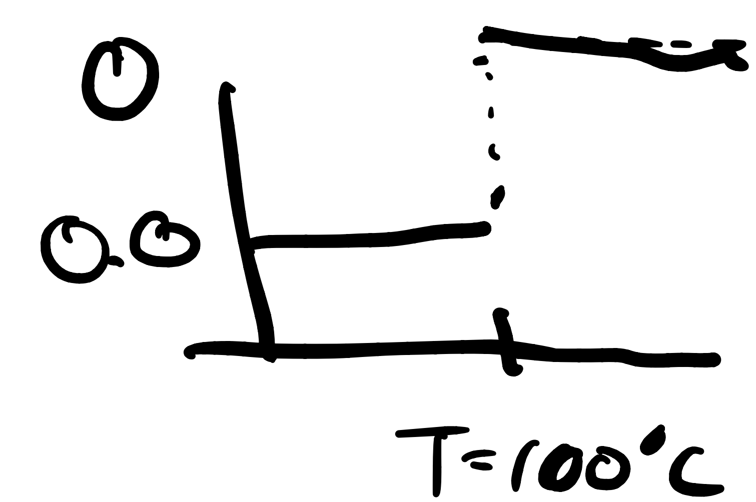
Difference: is about symmetry (order)



Define an "order parameter" that distinguishes different phases

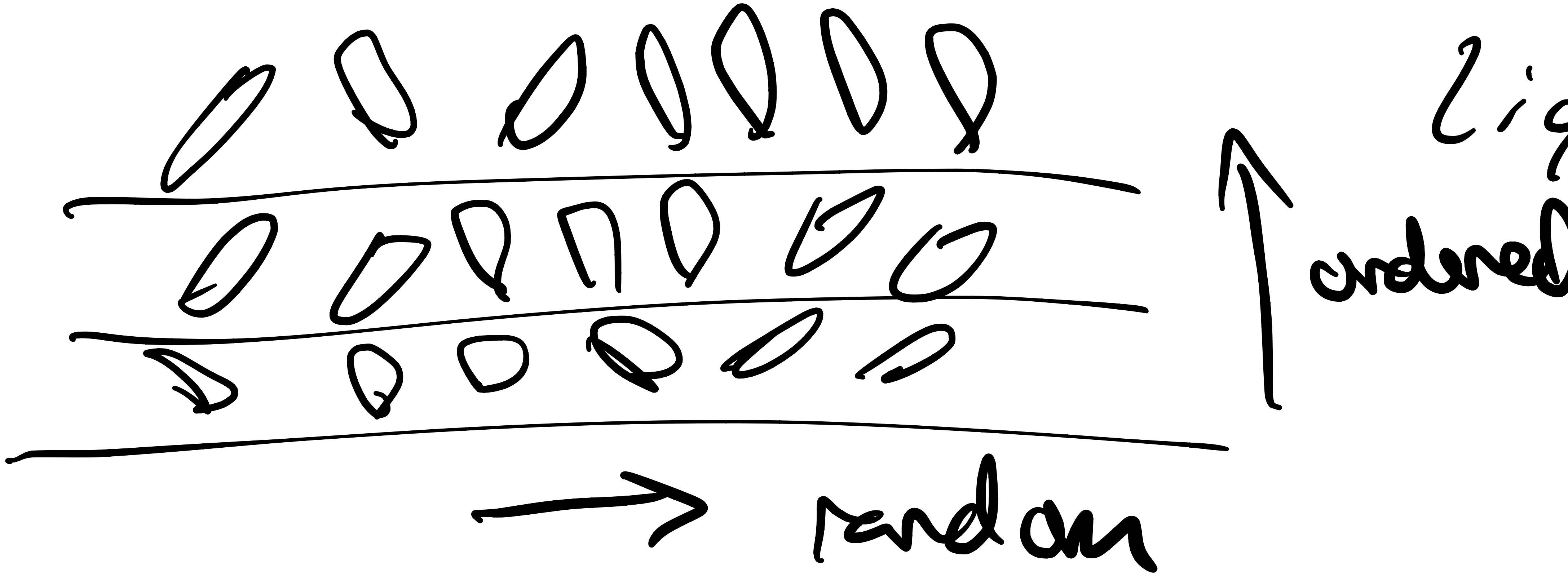
Eg liq/gas $O(\rho) = \dfrac{\rho - \rho_2}{\rho_2}$

$$O(\bar{v}) = \frac{\bar{v} - \bar{v}_2}{\bar{v}_2}$$



eg

Liquid crystals

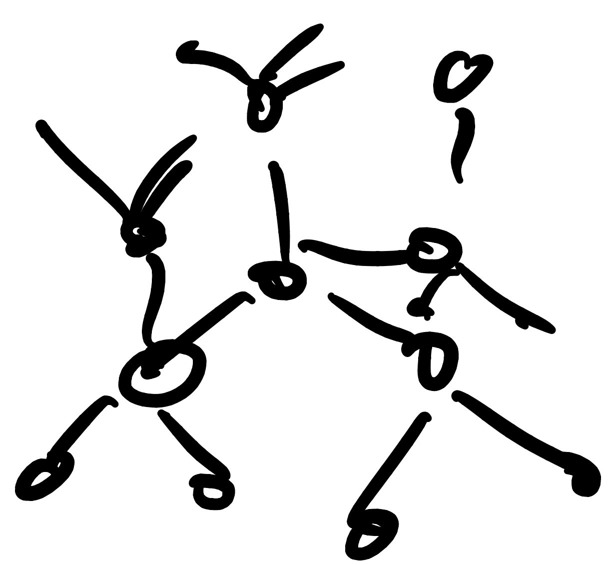


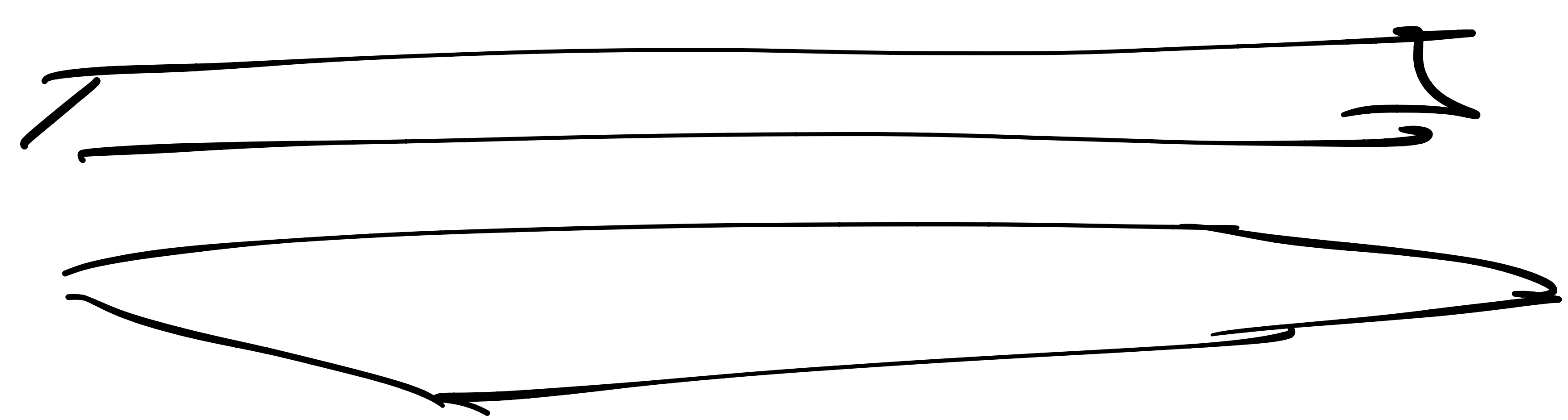
Differences between phases: density, compressibility, heat capacity, conductivity

Other kind of "phase": different arrangements of same atoms

Carbon: Diamond, graphite, → C_{60} ....
→ nanotubes

↑ more stable

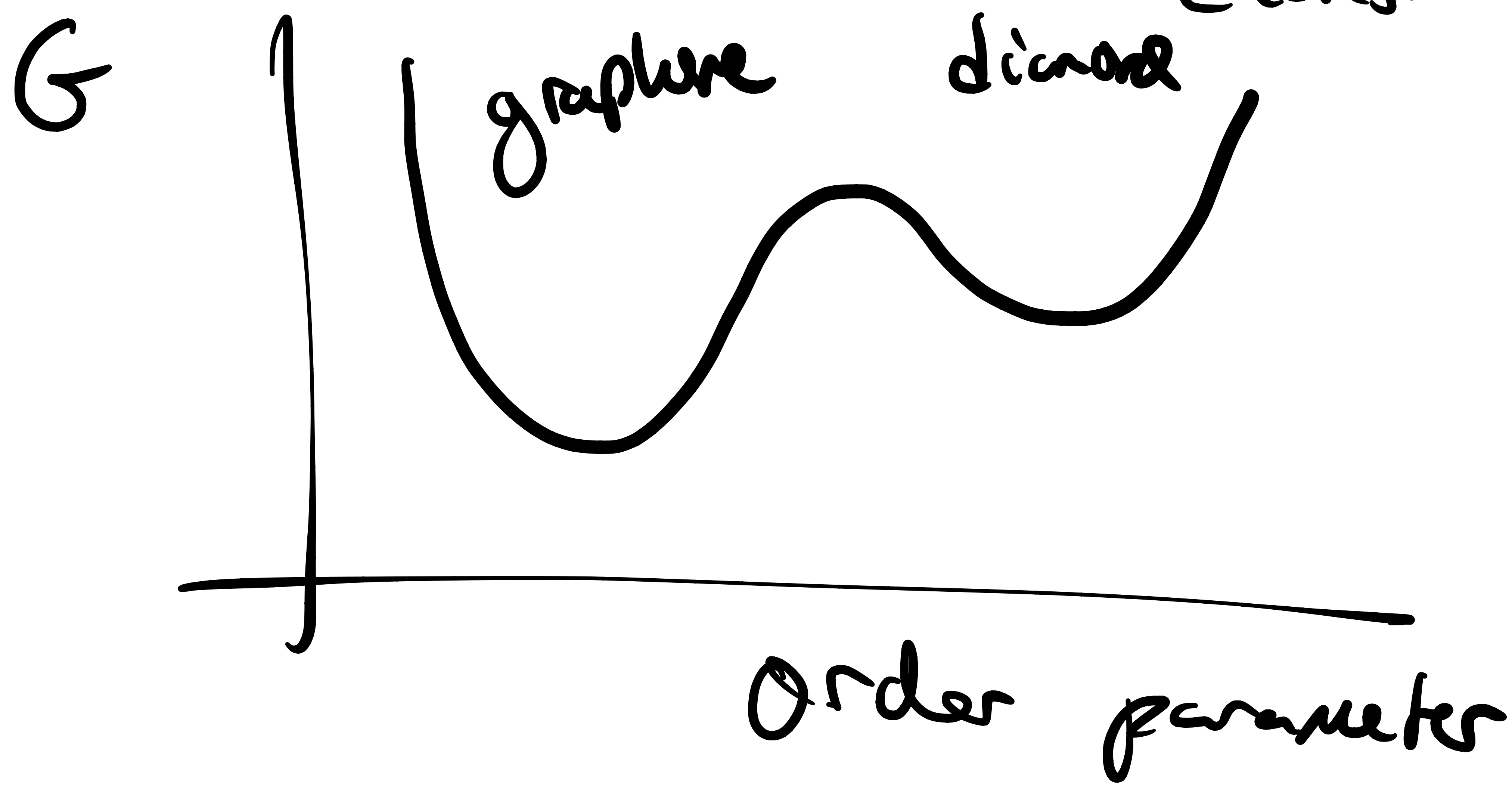




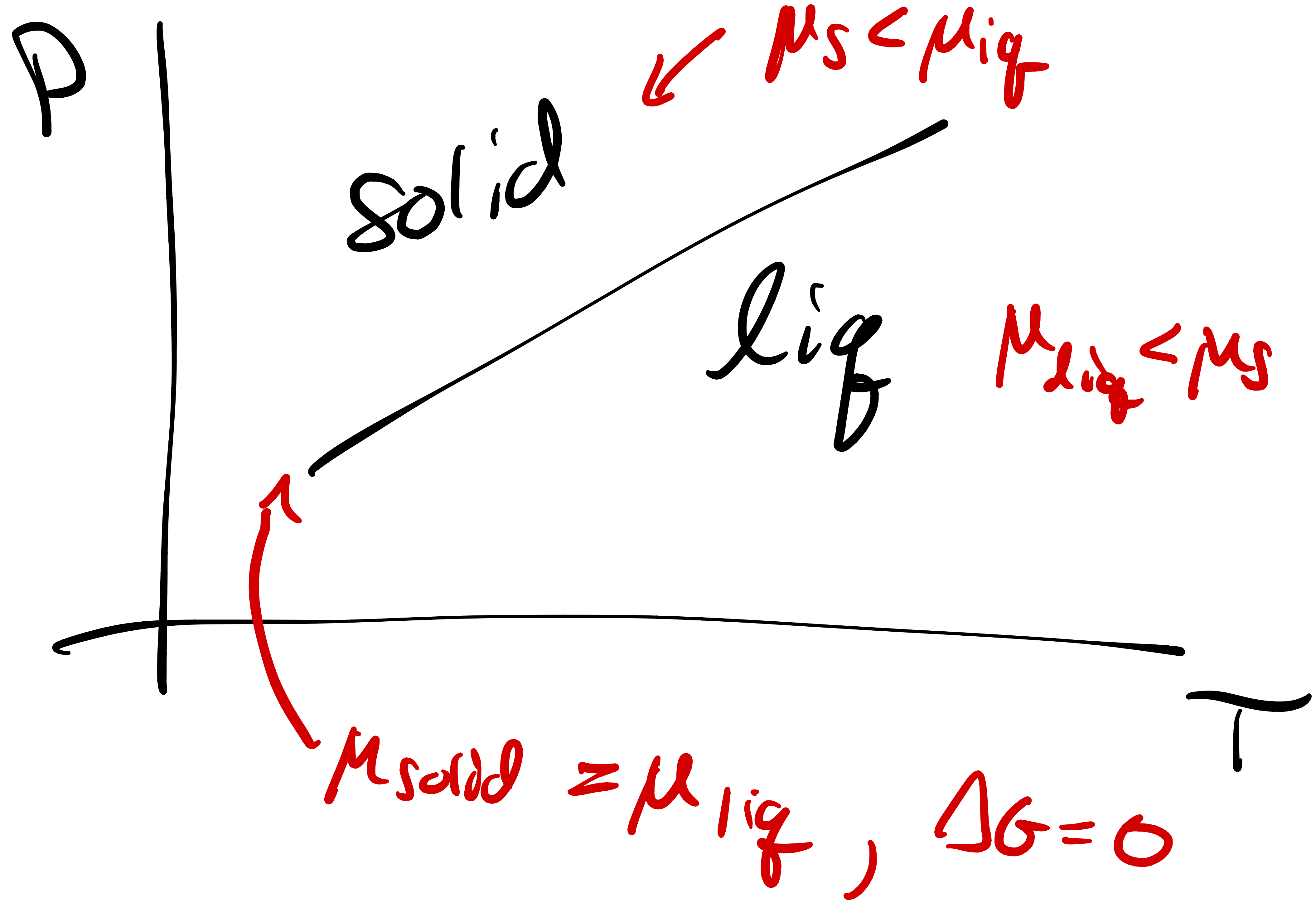
(TMD, magic angle graphene)

Stability

system is in a particular phase because G is lower (const T & P)



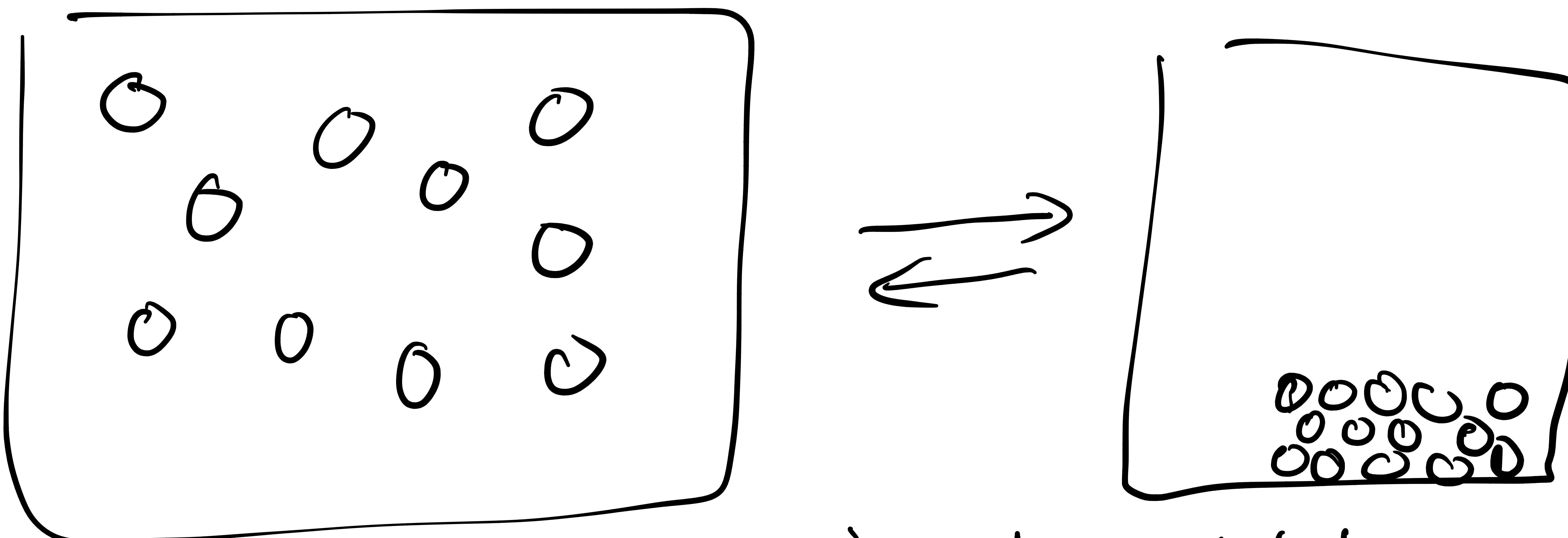
Phase diagram



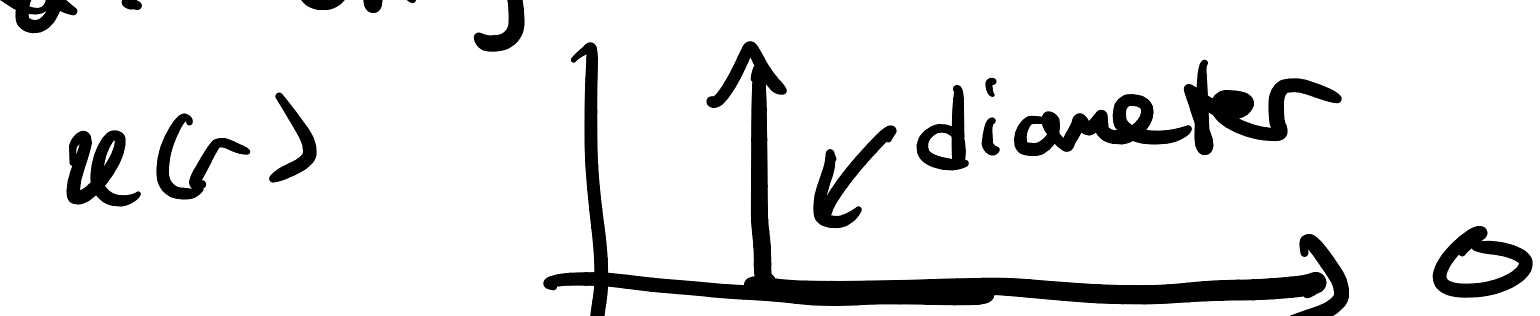
$$G = H - TS$$

↳ $\mu = \bar{H} - T\bar{S}$ @ T, P in a certain phase

Old Question: should hard spheres/disc crystallize



Hard: only interaction is volume exclusion



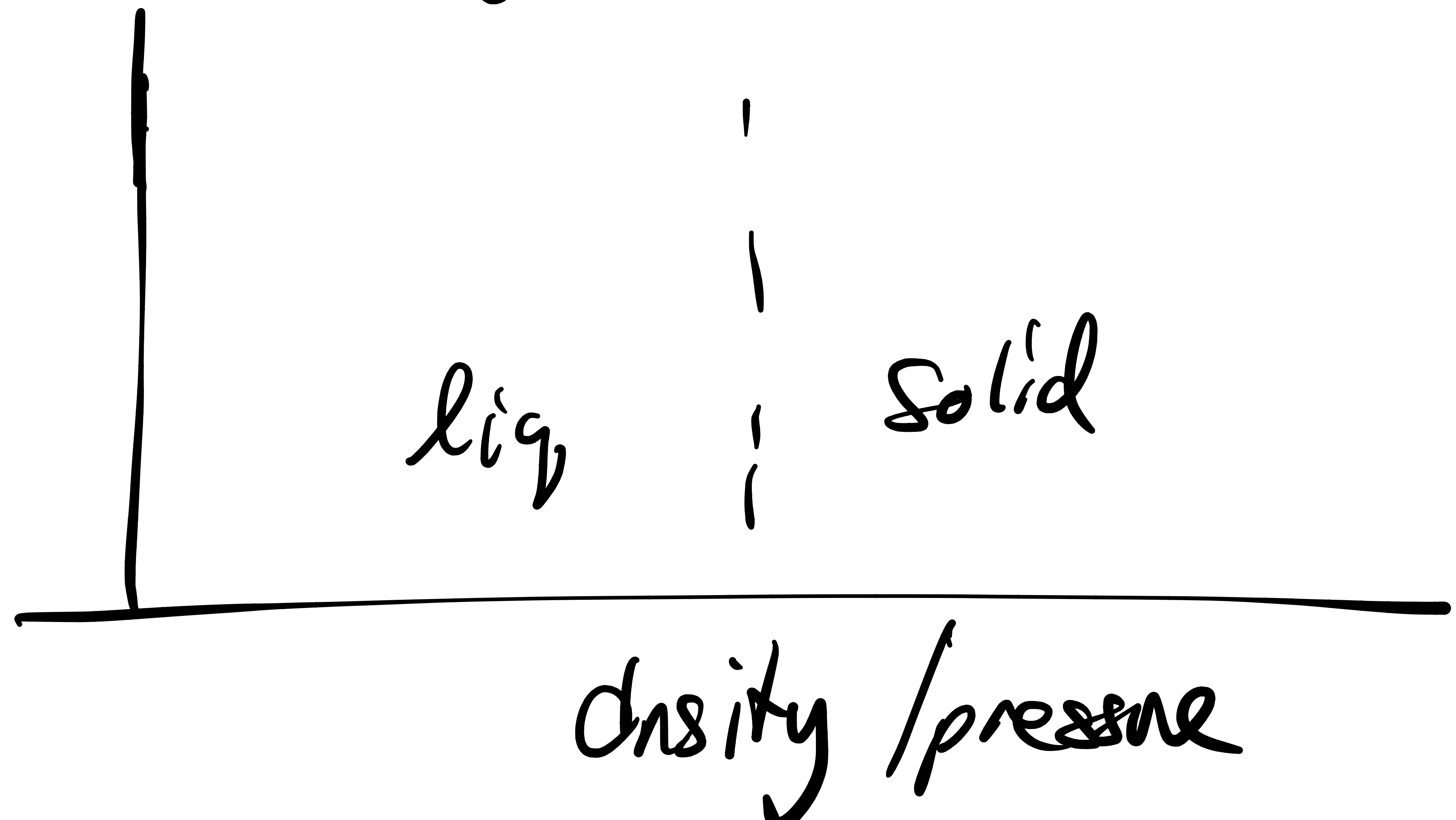
$$A = \mathcal{E} - TS$$

for hard spheres, $\mathcal{E} = 0$

$$A = -TS$$

crystallization means that the crystal has lower entropy

Hard particles crystallize at some density



at high density: reach random state where everything is touching

Non-equilibrum "phase"

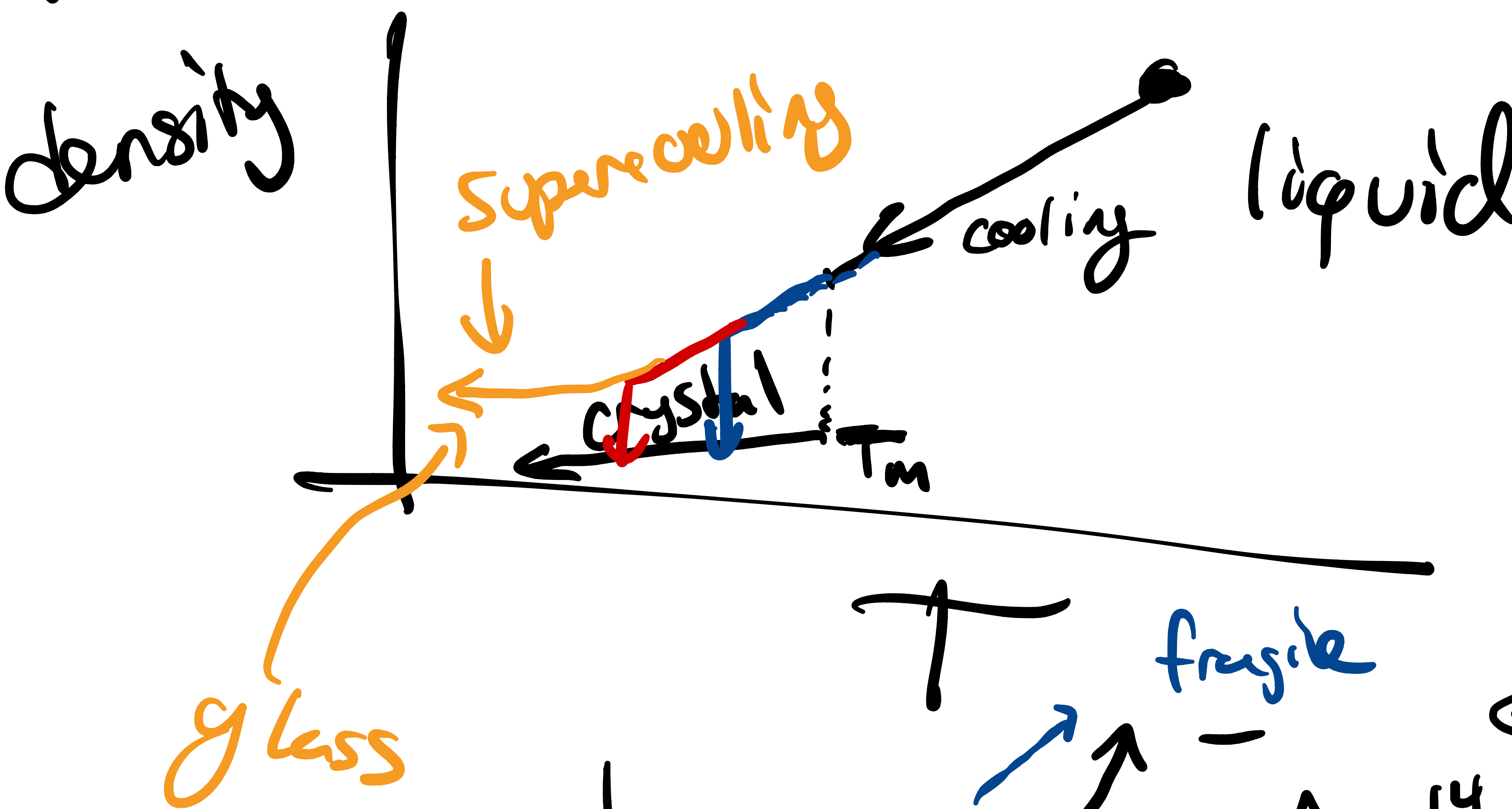
Can get stuck in a configuration that is not local free energy minimum

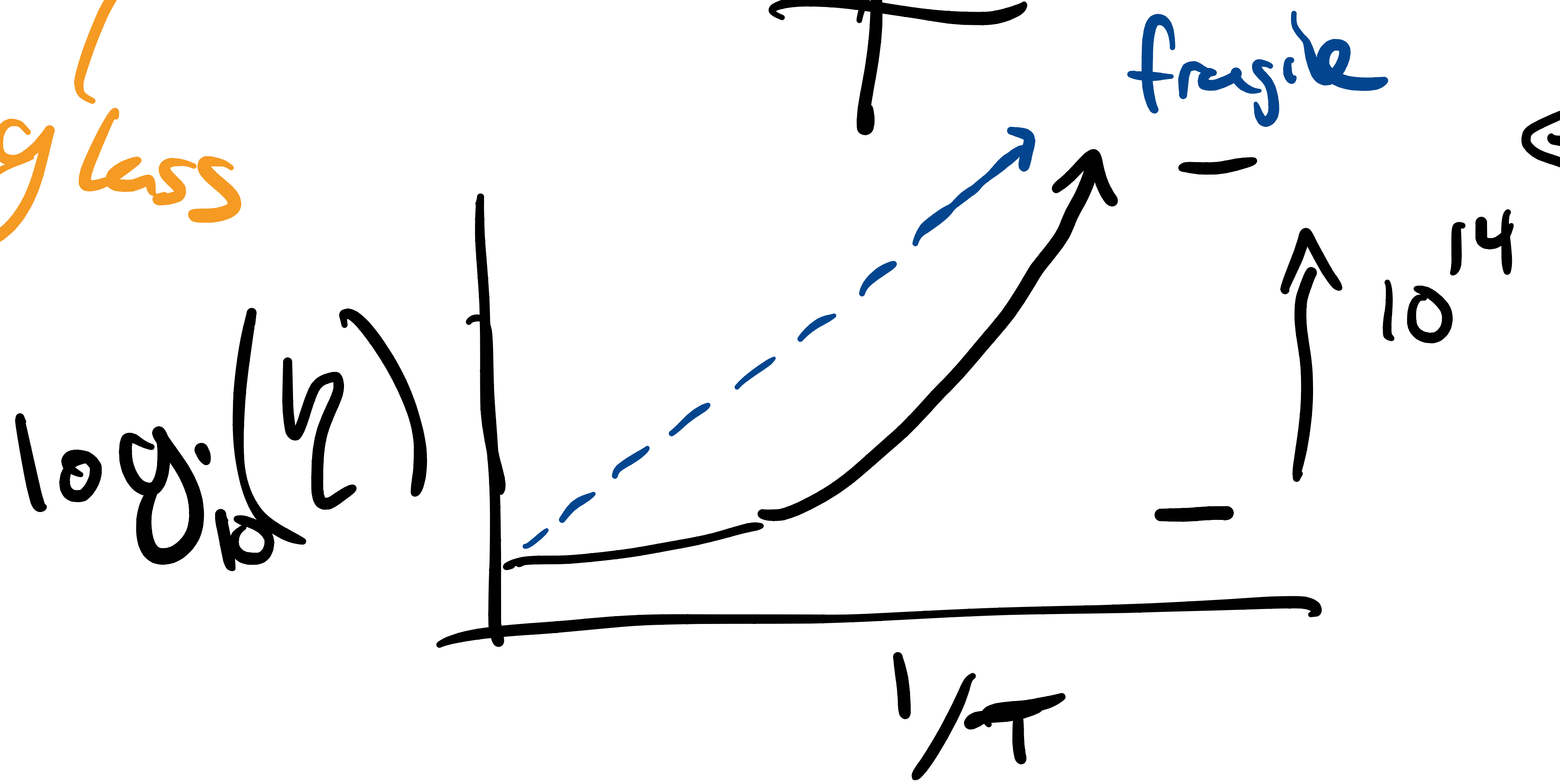
Change conditions "quickly", avoid phase change

Supercooled liquid - glass

Supercooled liquid

(glass is still a liquid





τ_α ← more Idiom

100 s

10^{-12} s → 100 s