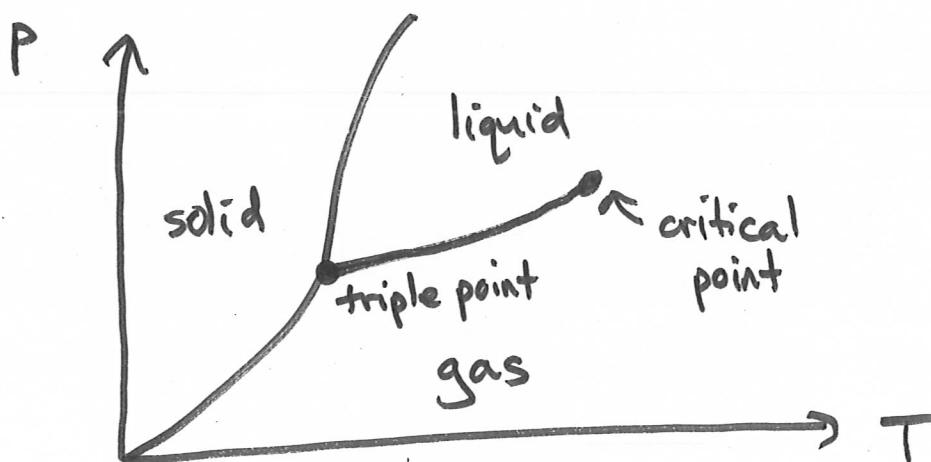# PHASES OF MATTER & PHASE CHANGES

We have largely concentrated on gases. But solids & liquids exist too! The transitions between them are important too!

Since normally work in open systems different phases compete to be lowest free energy at some T & P.

A typical phase diagram:

- High P tends to form liquids & solids as interatomic forces important

- High T ⇒ gas

- At T > critical point the distinction between liquid & gas is lost - we'll see an example model soon.

- Solid ⇒ gas is <u>sublimation</u>

- The three lines meet at a "triple point".

POSITION OF A PHASE BOUNDARY

The natural ~~free~~ energy depending on P, T is

$$G = U - TS + PV$$

$$dG = -SdT + VdP \quad \text{(after using central equation)}$$

Let's assume we are sat on a phase boundary. We need to consider how the total mass $M = m_1 + m_2$ splits between the two phases. We can write G in terms of specific g per unit mass

$$G = m_1 g_1 + m_2 g_2$$

The system will choose m_1 & m_2 to minimize G... at the minimum

$$dG = 0$$

$$dm_1 g_1 + m_1 dg_1 + dm_2 g_2 + m_2 dg_2 = 0$$

However, we're at a fixed T, P point so g_i are fixed $dg_i = 0$

$$dm_1 g_1 + dm_2 g_2 = 0$$

Conservation of mass says $dm_1 = -dm_2$

$$\Rightarrow \boxed{g_1 = g_2}$$

The phase boundaries are where the specific Gibbs ~~free~~ energies are equal.

CLAUSIUS - CLAPEYRON EQUATION

Lets now compute the slopes of the phase boundaries in the P-T plane.

We are at a point on the phase boundary

$$g_1 = g_2$$

& we move in T,P but wish to stay on the boundary $\Rightarrow$ $dg_1 = dg_2$

writing $dg_i = s_i\, dT + v_i\, dP$

specific entropy & volume

gives $\quad -s_1\, dT + v_1\, dP = -s_2\, dT + v_2\, dP$

$$\Rightarrow \quad \frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$

For 1kg the heat released is $\quad dQ = L$

$\leftarrow$ latent heat

so $\quad dS = L/T$
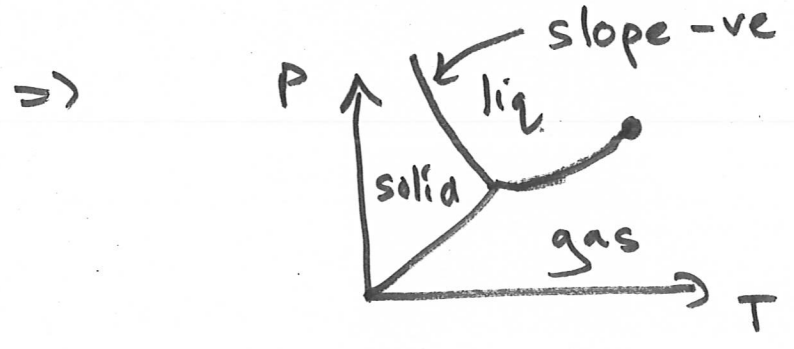
$$\Rightarrow \quad \boxed{\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)}}$$

MELTING ICE

$$\frac{dP}{dT} = \frac{L \leftarrow 335 \times 10^3 \, J kg^{-1}}{T(V_2 - V_1)}$$

$273K \qquad (1.00 - 1.09) \times 10^3 \, m^3 kg^{-1}$

$$= -13.6 \times 10^6 \, Nm^{-2} K^{-1}$$

Note here, and specially for water, $V_2 < V_1$ ie ice is less dense than water

$\Rightarrow$

Our calculation shows at $P = 136$ atmospheres the melting point drops by $1°$.
This has been proposed to play a role in ice flow in glaciers.

BOILING WATER

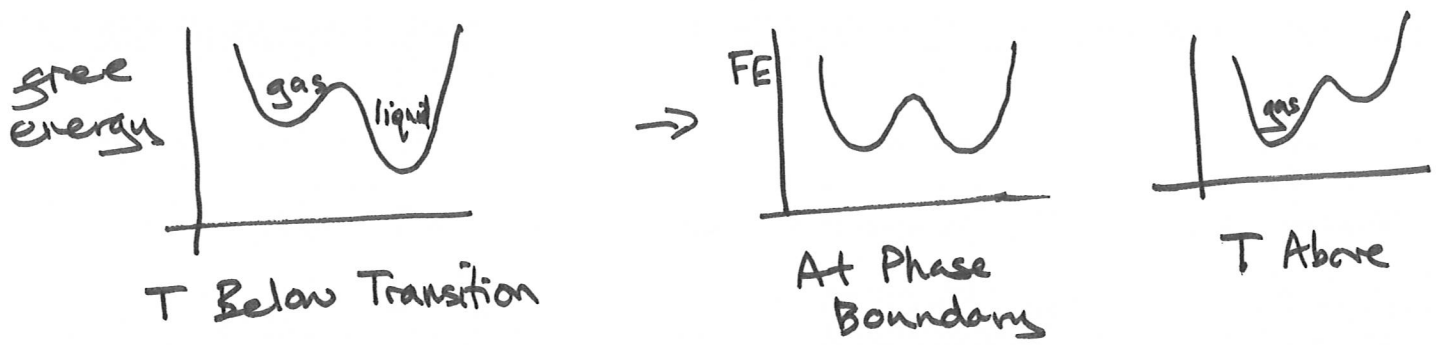$$\frac{dP}{dT} = \frac{L \leftarrow 2.257 \times 10^6 \, J kg^{-1}}{T(V_2 - V_1)} \qquad = 3619 \, Nm^{-2} K^{-1}$$
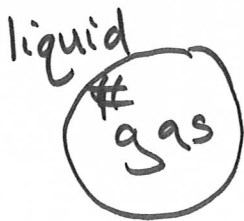
$373K \qquad (1.673 - 1.043) \times 10^{-3} \, m^3 kg^{-1}$

So at the top of Everest where $\Delta P = 66,000 \, Nm^{-2}$

$$\Delta T \sim 18°C.$$

SUPERSATURATION

As one crosses the phase boundary:

free energy — gas, liquid — **T Below Transition**

FE — **At Phase Boundary**

gas — **T Above**

Naively you might think the transition occurs everywhere as soon as one phase moves to lower FE than the other... there's an "activation energy" though... in practice thermal fluctuations nucleate bubbles in small patches of space... which naively should expand & trigger the transition....

liquid / # gas

Between the phases though the material has to cross the barrier at higher FE

$$\rightarrow \underline{\text{surface tension}} \quad F \sim 2\pi r \gamma$$

This opposes the pressure that wants to make the bubble expand

$$\pi r^2 \Delta P = 2\pi r \gamma$$

$$\Rightarrow \Delta P = 2\gamma/r$$

Now $\quad dG = -SdT + VdP$

$$\downarrow \qquad \nwarrow \frac{2\gamma}{r}$$

both phases
at same T
$\Rightarrow dT = 0$

This e̶f̶f̶e̶c̶t̶i̶v̶e̶ contribution to the FE can stop the expansion. The substance can get stuck in the wrong phase

→ <u>supersaturation</u>

 stays here

In̶ ̶f̶a̶c̶t̶ impurities typically change the interactions or provide e̶x̶t̶r̶a̶ energy & trigger bubble formation $\qquad$ e.g. $\quad$ beer glass
cloud chamber

MODELLING INTER-ATOMIC FORCES

To see solids & liquids we need to consider inter-atomic forces

repulsion as +ve nuclei & Pauli Exclusion forbids e^- accumulating between nuclei

r_0

attraction due to mutual polarization of e^- shells.

$$F = -\frac{dV}{dr}$$

VAN DER WAALS GASES

In this modification of the Ideal Gas:

- we remove the volume of the N atoms
  (b)

$$\Rightarrow \quad P(V - Nb) = NkT$$

- attractions between molecules tend to reduce the speed of those hitting the wall as they are pulled back into the gas $\Rightarrow$ reduced pressure

  number of collisions $\propto$ density N/V

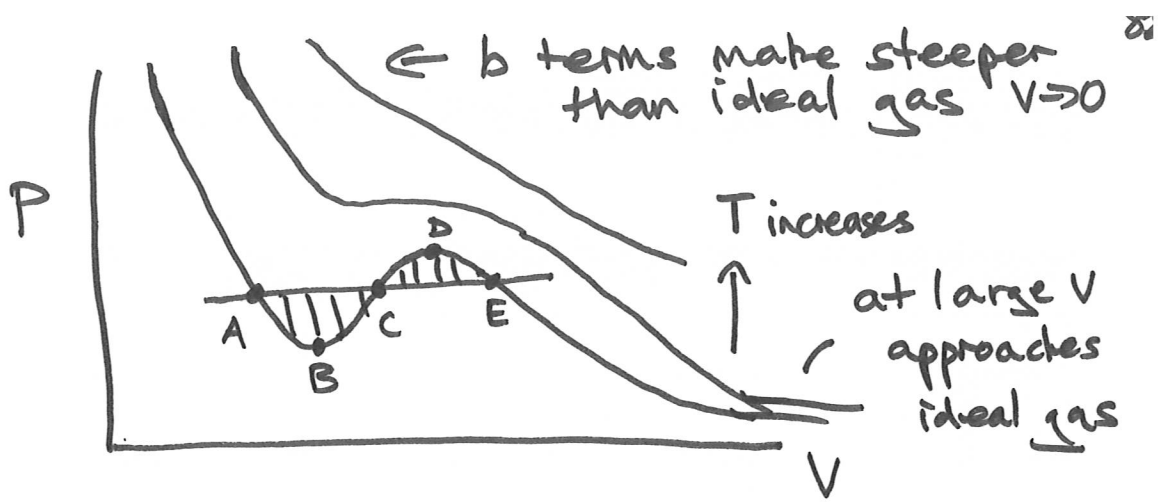 attractive force $\propto$ density too

  $$\Rightarrow \quad \Delta P \propto N^2/V^2$$

$$\Rightarrow \quad \boxed{\left(P + \frac{N^2 a}{V}\right)(V - Nb) = NkT}$$

or $\quad \left(P + n_M^2 \, \tilde{a}/V^2\right)(V - n_M \tilde{b}) = n_M RT$

here a & b are rescaled

Isotherms:

← b terms make steeper than ideal gas $V \to 0$

T increases

at large V approaches ideal gas

There are new structures at low T.

Consider fixed P, T — horizontal line

A & E are two different V ie different density states

→ liquid & gas

To find the phase boundary between them look for $g_A = g_E$

$$dg = -S\,dT + V\,dP$$

? zero on isotherm

? area under curve

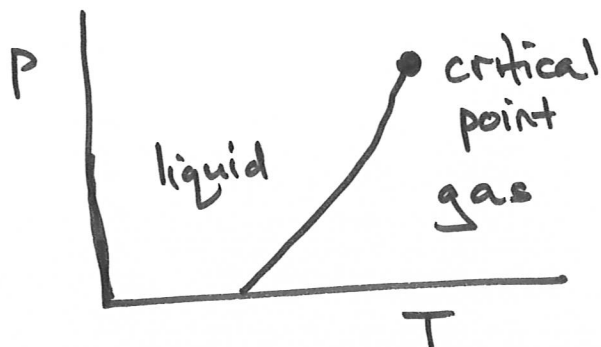$$\Rightarrow \quad g_E = g_A + \int_A^E V\,dP$$

$$\overset{||}{0} \quad \text{when shaded areas are equal ie move P line until they are.}$$

At higher T there is a critical point where

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \qquad \text{"point of inflection"}$$

then at higher T only one phase

which captures some of the observed phenomena

Near the critical point materials have domains (which can be quite large) of the two phases.

These scatter light & the material goes milky white ⟹ <u>critical opalescence</u>

<u>What about c?</u> In the region BCD as the ~~pressure~~ volume rises the ~~volume~~ pressure goes up. A bubble in this state will grow without limit until arriving at D - it's unstable.