H. Phase Transitions of H_2O (one species) as first encounter of Phase Transitions

Ideal Gas: $pV = NkT$ all temperatures (Gas phase Only)

↑ Won't go into a liquid and/or a solid as temperature lowers!

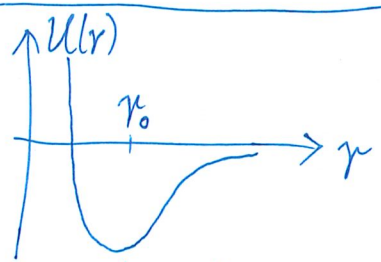
Key to have Phase Transitions

- What is missing in Ideal Gas?

No inter-particle interaction

Need inter-particle interaction for Phase Transitions Key Concept

e.g.



Typical interacting P.E. vs. inter-particle separation

Make Sense! $T = 0$, only Interacting P.E.

All particles sit at a distance r_0 from neighboring particles

lowest potential energy

What is it? A Solid! ($T = 0$, Minimize U)

Highly ordered

"TS" term has no effect at $T = 0$

Increasing T: Particles oscillate about equilibrium positions

still a solid [lattice vibrations]

Some $T_{melting}$: Oscillations big enough that we can't tell which particle is sitting at which place (a liquid) (disordered, S higher)

[Need energy (reluctant to happen), but $-TS$ term helps]

$G_{liquid} < G_{solid}$ at appropriate condition (melting)

$A \rightleftharpoons B$ (same species)

solid (ice) liquid (water)

Entropy $A \to B$ $\Delta S > 0$ (towards more disordered)

Energy $A \to B$ needs latent heat

$$\Delta H = \Delta U + \Delta(PV) \approx \Delta U > 0$$

[small volume change† in Solid/liq. transition]

$$\Delta G = \Delta H - T\Delta S$$

low temp: $\Delta G > 0 \Rightarrow$ melting won't go

high temp: $\Delta G < 0 \Rightarrow$ melting will go [$\Delta G < 0$ for processes to occur]

given T, p

$\Delta G = 0$ (atmospheric pressure at 0°C), ice and water co-exist

a point on transition curve

† Not so for liquid-vapour transitions, for which ΔV is huge.

For transitions for which ΔV is small, e.g. solid-liquid (but not liq-gas), can also consider $\Delta F = \Delta U - T\Delta S$

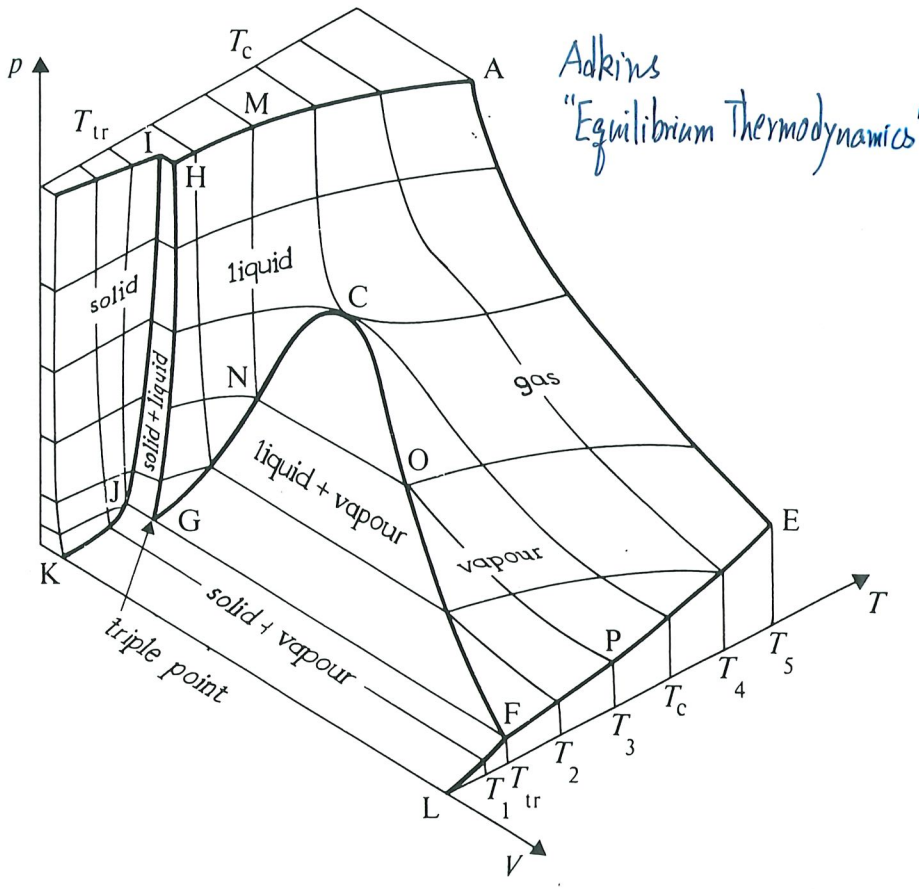
ΔU: important term at low temp.

$T\Delta S$: important term at high temp.

[Again, Competition between order and disorder!]

Typical PVT surface with Phase Transitions

The *p*–*V*–*T* relation of a pure substance.



Adkins "Equilibrium Thermodynamics"

- Follow constant temperature cut (isotherm) at T_3, for example, vapour → liquid → solid through compression

[Points P → O → N → M →]

vapour-liquid transition

liquid-solid transition

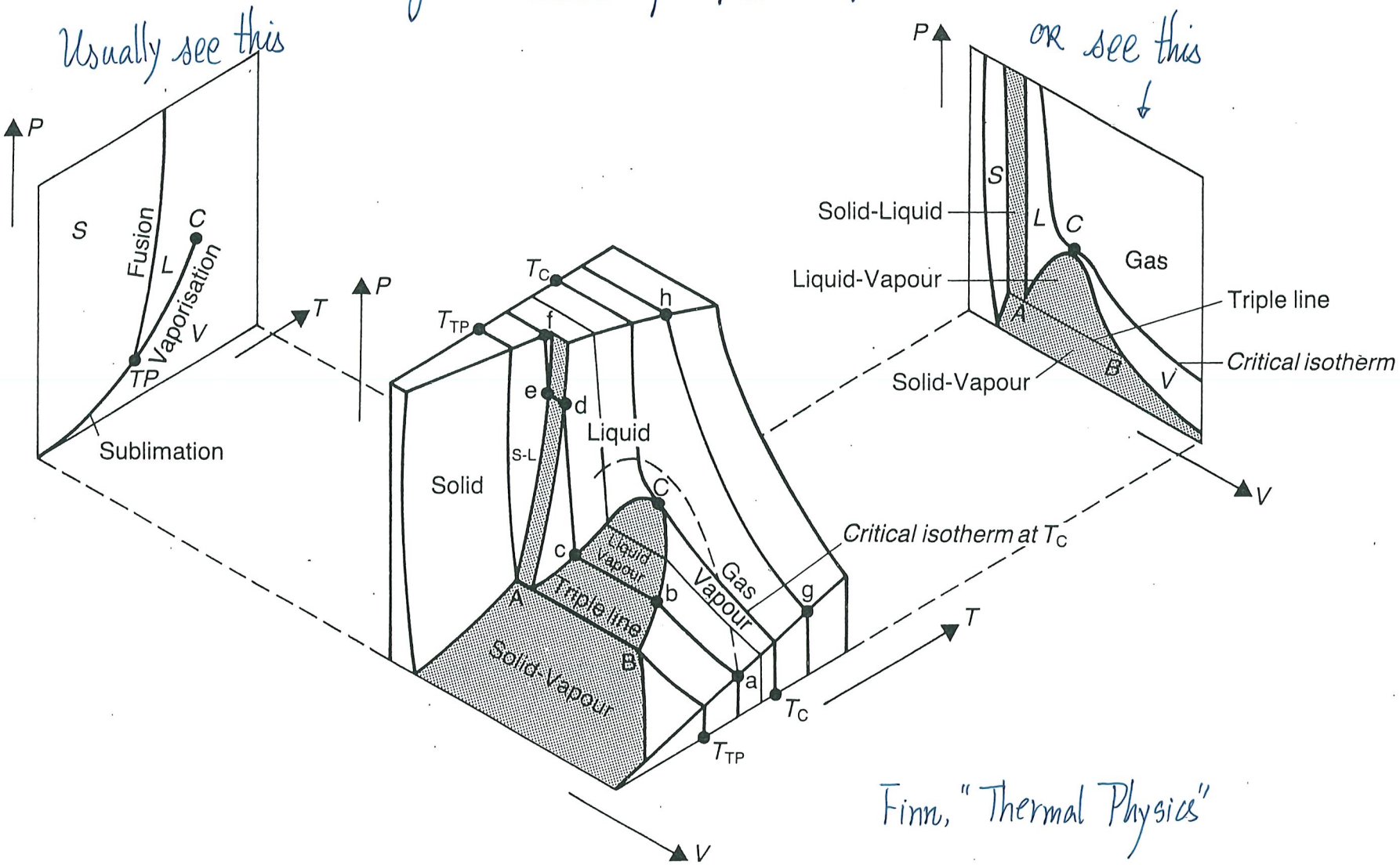
- One point C [critical point] on diagram above which there is no distinction between vapour and liquid [usually use the word "gas" to describe this part]

Phenomena around point C are called Critical Phenomena.

- One Point G (triple Point) at which vapour-liquid-ice coexist.

Projections onto P–T and P–V Planes

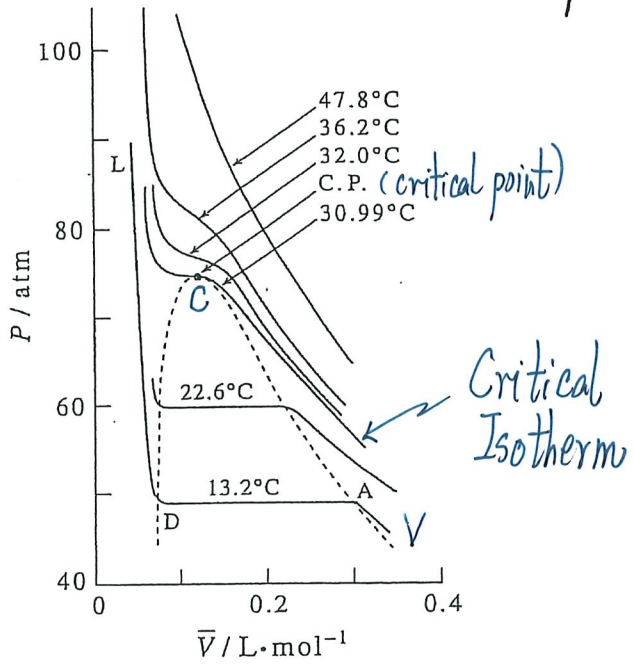
Usually see this



Finn, "Thermal Physics"

A typical *PVT* surface together with its *P*–*T* and *P*–*V* projections.

CO_2 Data p-V projection



Experimental pressure-volume isotherms

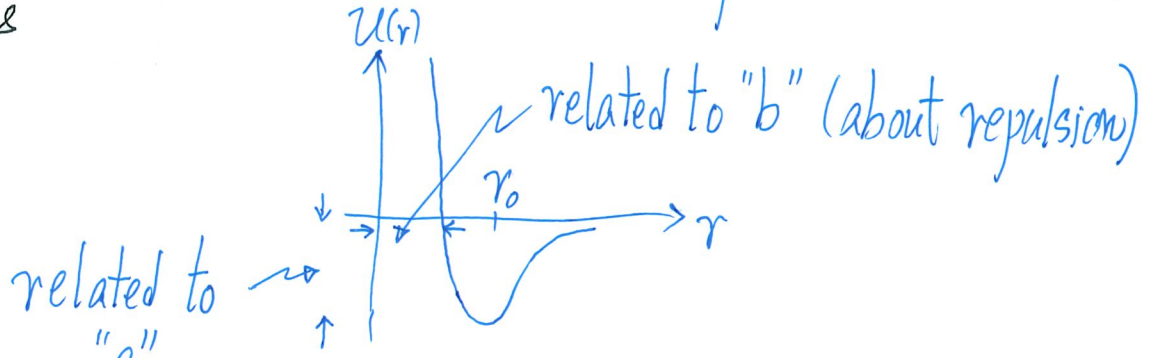
First theory that can give vapour-liquid transition

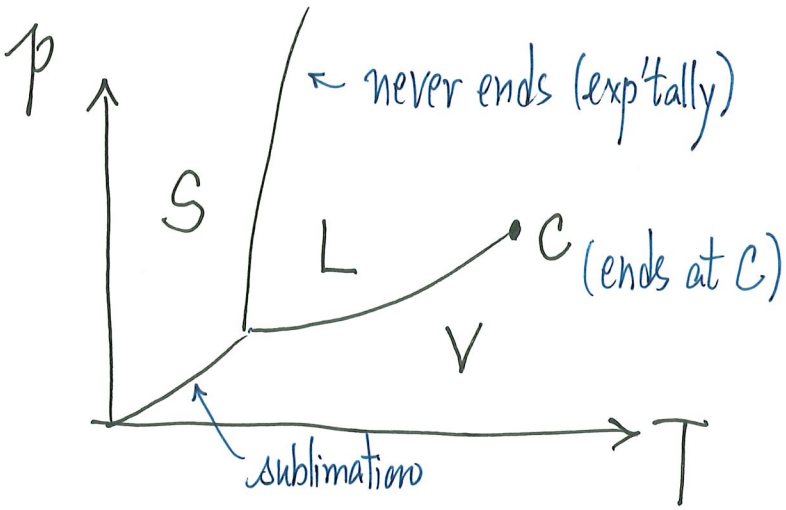
Van der Waals Equation (1910 Nobel Prize)

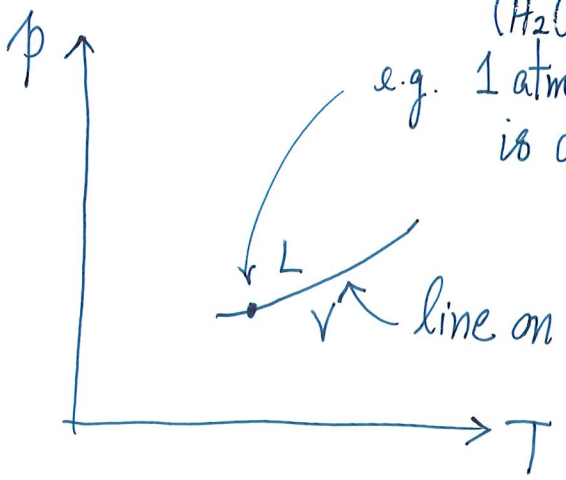
$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \qquad (19)$$

v: molar volume

Recall: Needs inter-particle interaction







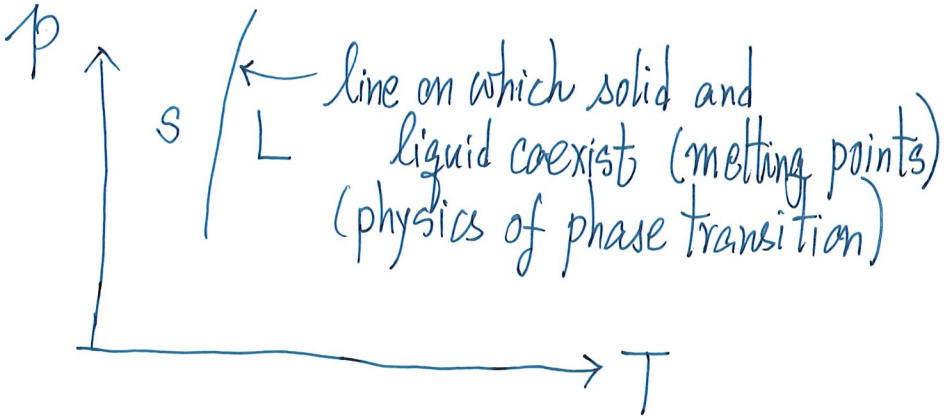
(H_2O)

e.g. 1 atm and 100°C is one point on line

line on which liquid and vapour coexist (boiling points)

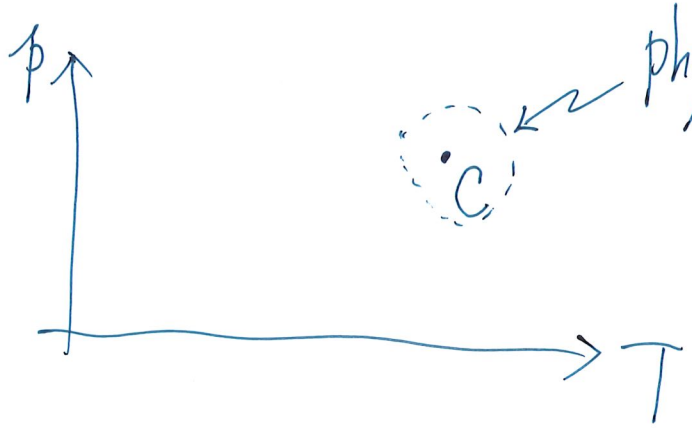
(physics of Phase transition)

相変 (相變)



line on which solid and liquid coexist (melting points)

(physics of phase transition)



physics around critical point C

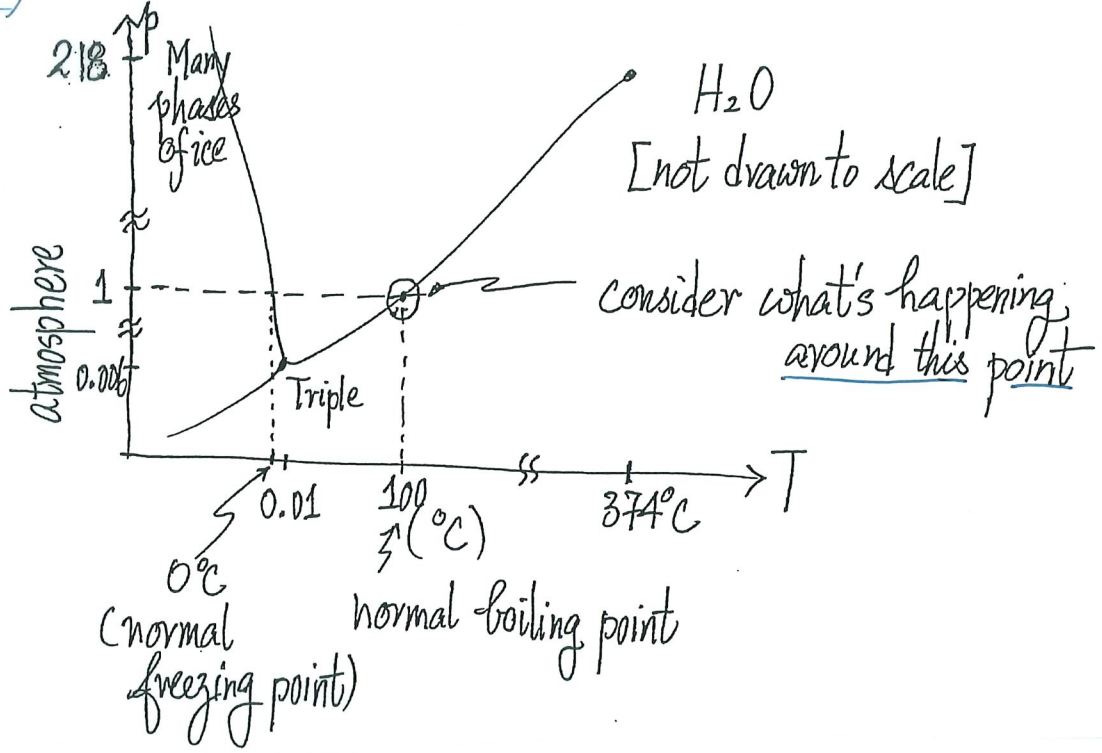
Critical Phenomena (臨界現像)

Physics at the boiling point (water)

- Same idea on competition between ΔH and $T\Delta S$
- 1 atm and 100°C

$(\Delta H)_{vap}$ for 1 mole $= Q_p = 40.65\ kJ/mole$

[This is the "latent heat of vaporization" usually cited as ~2265 $kJ\ kg^{-1}$ for H_2O.]



On the transition curve, vapour-liquid coexist. The phase transition is a good example of a reversible process, as a tiny change in temperature can reverse the process (vaporize vs condense).

$$(\Delta S)_{vap} = \frac{Q_p \leftarrow 40.65\ kJ/mole}{T_{vap} \leftarrow 373.15\ K\ (100°C)} = 108.9\ JK^{-1}mol^{-1}$$

(>0 ∵ Vapour phase is less ordered)

- If it is 1 atm and 363.15K (lower than 373.15K),
  then $(\Delta G)_{vap} = (\Delta H)_{vap} - T(\Delta S)_{vap} \cong +1\ kJ/mole > 0$
  (so vaporization of H_2O is NOT a spontaneous process at 1 atm and 363.15K)
  (remains in water phase)
- If it is 1 atm and 383.15K (higher than 373.15K)
  then $(\Delta G)_{vap} \cong -1\ kJ/mole < 0$
  (so vaporization is a spontaneous process at 1 atm and 363.15K)
  (it is in vapour phase)

Summary

- Ordinary experimental situation (T and P)

$$\underbrace{G_{T\ A\ phase}^{mole\ (or\ per\ kg)} = G_{T\ B\ phase}^{mole\ (or\ per\ kg)}}_{\text{condition}} \quad \text{for two phases coexist} \qquad (20)$$

[useful for determining the line: P ↑, T →]

At the point on curve : $(\Delta G_T)_{vap} = \Delta H - T_{vap}(\Delta S)_{vap} = 0$

(ΔG_T: liquid to vapour; ΔH: per mole; T_{vap}: per mole; $(\Delta S)_{vap}$: per mole)

$\therefore$ $\boxed{G_{T\,liquid}^{(per\ mole)} = G_{T\,vapour}^{(per\ mole)} \text{ at the point where liquid and vapour coexist}}$ (20)

equilibrium condition (key concept on handling phase transitions)

Important : (i) Comparing $G_T^{(per\ mole)}$ or $G_T^{(per\ kg)}$ or any specific† G_T

[not comparing G_T^{ocean} with $G_T^{tiny\ ice\ cube}$!]

(ii) Here, it is about a pure substance (H_2O)

(iii) Usually written as $g_{liquid} = g_{vapour}$ (with g being specific G_T — per mole, per mass, etc.)

† Following Euler's theorem, $\frac{G_T}{N} = \mu$, so μ is a specific G_T.

General Equilibrium Condition for 2 phases

Recall: For a system maintained at a constant temperature and pressure, G_T is a minimum (for equilibrium)

Phase A : Mass M_A ; Phase B : Mass M_B ; $M = M_A + M_B$

$G_T = M_A g_A + M_B g_B$ ← Gibbs function per mass in phase B

↑ Gibbs function per mass in phase A

On transition curve, the equilibrium state is Phase A and Phase B coexist

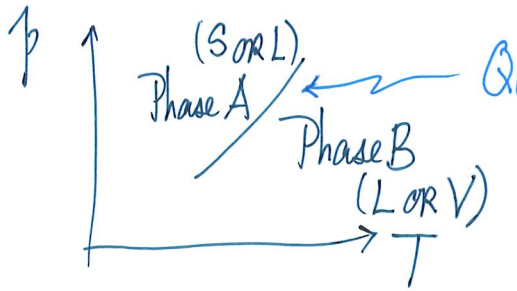
$dG_T = 0 \Rightarrow g_A dM_A + g_B dM_B = 0$; but $\underbrace{dM = 0}_{\text{total mass not changing}} = dM_A + dM_B$

$\Rightarrow (g_A - g_B) dM_A = 0$

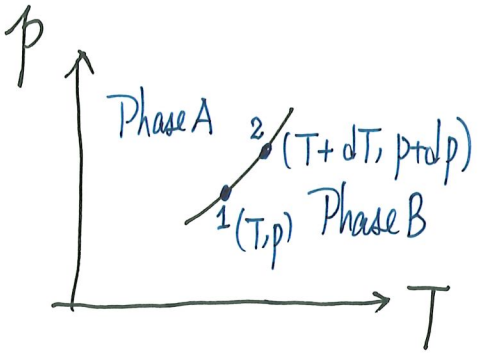
$\Rightarrow g_A = g_B$ (coexistence of two phases)

$\left[G_A^{\text{per kg}} = G_B^{\text{per kg}} \right]$

Equation Controlling the Phase Boundary



Question: How does this line look?



1 & 2 are nearby points on the boundary

Point 1: $g_A(T,p) = g_B(T,p)$ ($\because$ coexist)

pt. 1 pt. 1

Point 2: $g_A(T+dT, p+dP) = g_B(T+dT, p+dP)$ ($\because$ coexist)

pt. 2 pt. 2

$$g_A(T,p) + \left(\frac{\partial g_A}{\partial T}\right)_p dT + \left(\frac{\partial g_A}{\partial p}\right)_T dP = g_B(T,p) + \left(\frac{\partial g_B}{\partial T}\right)_p dT + \left(\frac{\partial g_B}{\partial p}\right)_T dP$$

Taylor expansion Taylor expansion

But $\left(\frac{\partial G_T}{\partial T}\right)_p = -S$ OR $\left(\frac{\partial g}{\partial T}\right)_p = -s$ ← entropy per mass (true for phases A and B)

$\left(\frac{\partial G_T}{\partial P}\right)_T = V$ OR $\left(\frac{\partial g}{\partial P}\right)_T = v$ ← volume per mass (true for phases A and B)

$$\therefore \quad -S_A\,dT + v_A\,dP = -S_B\,dT + v_B\,dP$$

[e.g. S_A is S in liquid, v_A is v in liquid]

[e.g. S_B is S in vapour, v_B is v in vapour (so $v_B \gg v_A$)]

$$(S_B - S_A)\,dT = (v_B - v_A)\,dP$$

$$\therefore \quad \boxed{\frac{dP}{dT} = \frac{S_B - S_A}{v_B - v_A}} \qquad (21)$$

Clausius-Clapeyron Equation

- Good for L-V, S-L, S-V (sublimation)
- Of course, needs $\underbrace{S_B - S_A \neq 0}_{\text{entropy change}}$ and $\underbrace{v_B - v_A \neq 0}_{\text{volume change}}$ > 1st order phase transition: $\left(\frac{\partial G_T}{\partial T}\right)_p$ and $\left(\frac{\partial G_T}{\partial P}\right)_T$ discontinuous

$$\frac{dP}{dT} = \frac{S_B - S_A}{v_B - v_A} = \frac{S_B - S_A}{V_B - V_A}$$

where S, V refer to same amount of matter (mole, kg, # particles) in A and B phases

L = Latent Heat (per "something")

$$T(S_B - S_A) = L$$

($\because \Delta S = \frac{Q}{T}$)

$$\therefore \boxed{\frac{dP}{dT} = \frac{L}{T(V_B - V_A)}} \quad (22)$$

Clausius-Clapeyron Equation

↑ slope of phase boundary

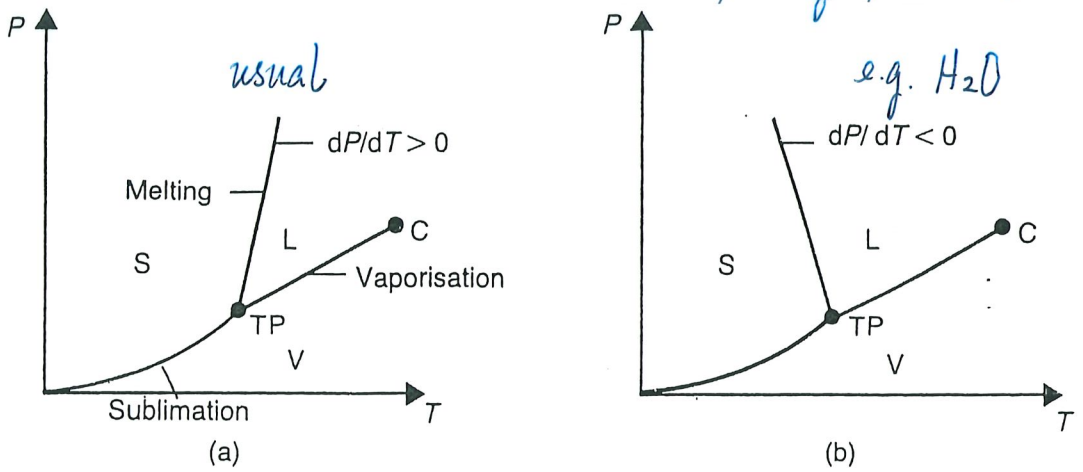
↑ Work for:

L-V : L (Latent Heat of vaporization)

S-L : L (Latent Heat of Melting)

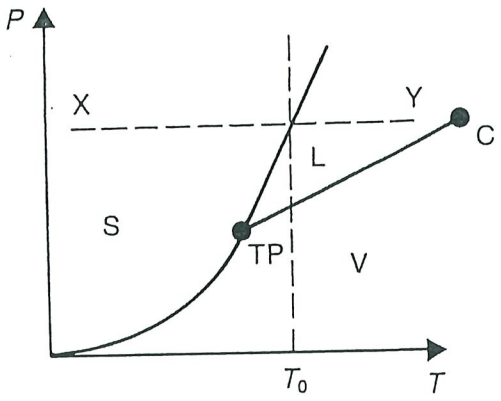
S-V : L (Latent Heat of Sublimation)

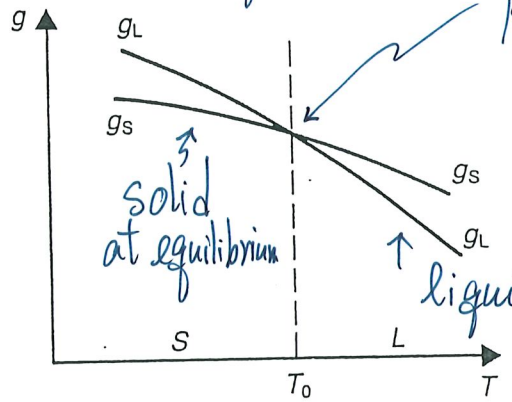
with corresponding ΔV



(a) A *P*–*T* projection for a typical substance which expands on melting. (b) A *P*–*T* projection for a substance which contracts on melting.

Putting information together





Along XY (T increases at fixed P)

point on phase boundary

$g_S = g_L$

↑ solid ↑ liquid

↑ solid at equilibrium

↑ liquid at equilibrium ($\because$ g is a minimum)

$$\left(\frac{\partial g}{\partial T}\right)_P = -S$$

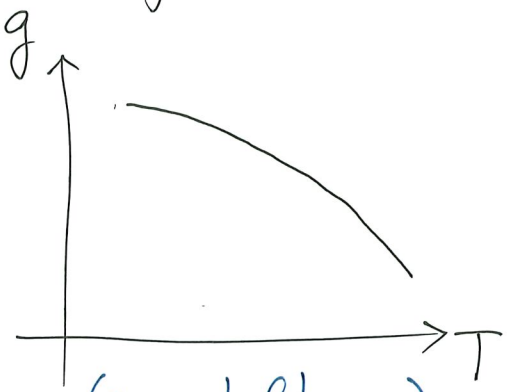
$S > 0$

negative slopes

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_P}{T} < 0$$

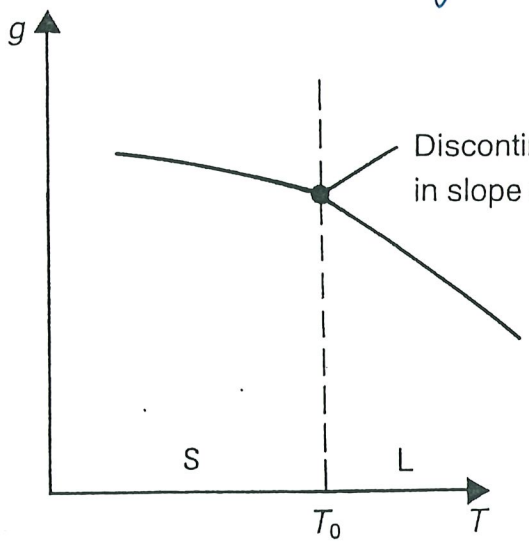
slope getting more negative as T increases

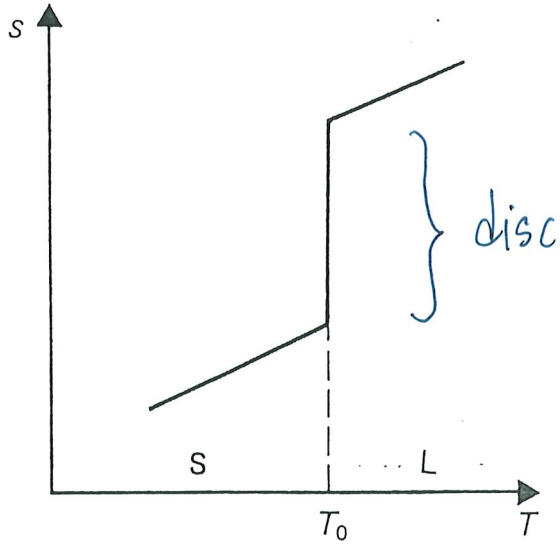
Therefore,



(general behavior)

Read out lower g





} discontinuity in S

$(S_L - S_S) \neq 0 \; (>0)$

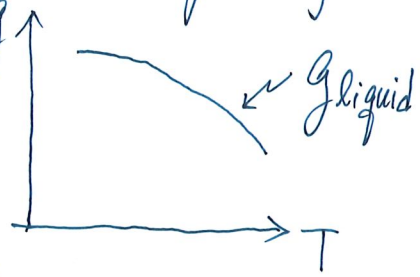
$\Rightarrow \left(\frac{\partial g}{\partial T}\right)_p$ discontinuous at phase transition point

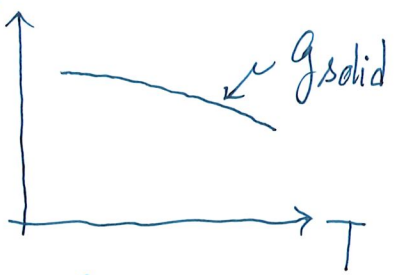
1st derivative(s) of g discontinuous

(1st order phase transition)

Note:

- Looks like the "surface" g now has a kink (not "nice surface" for derivatives)
- No!





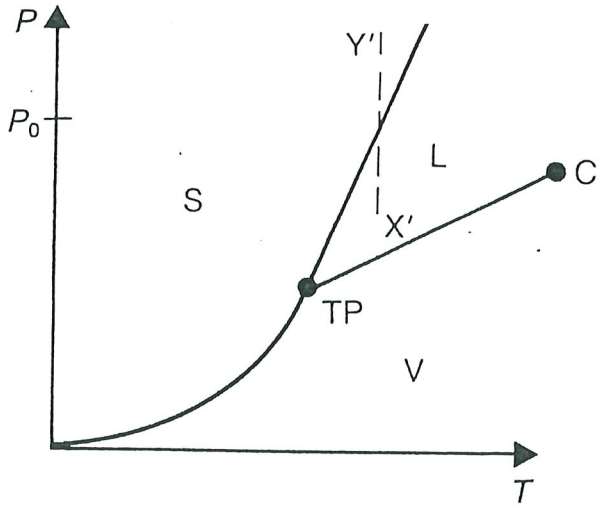
g_{liquid} is a nice surface

g_{solid} is a nice surface

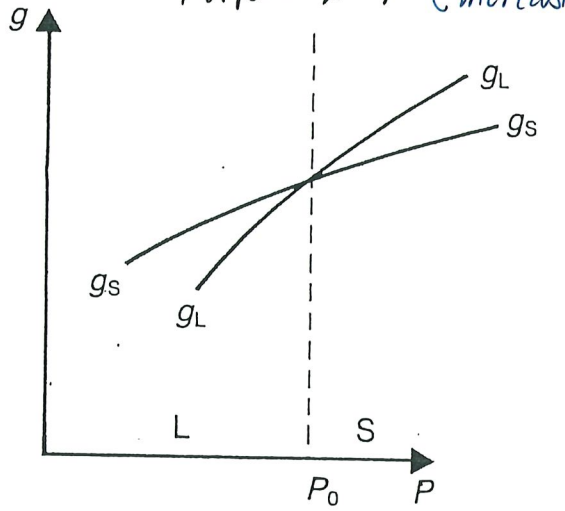
← This is why we can talk about $S_L - S_S = \Delta S$ at transition point

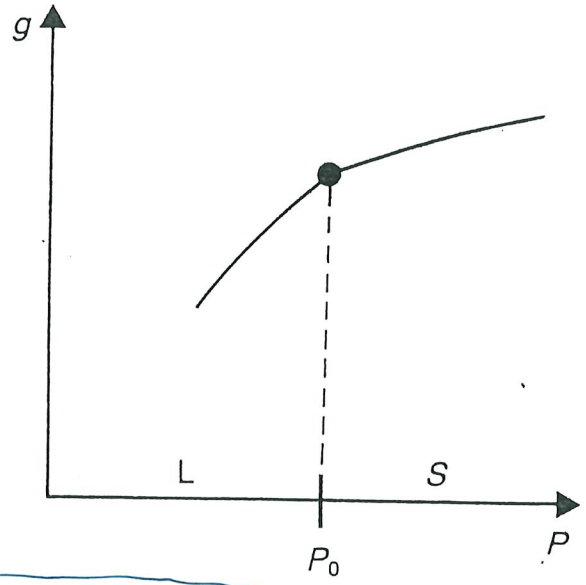
(similarly for $V_L - V_S = \Delta V$)

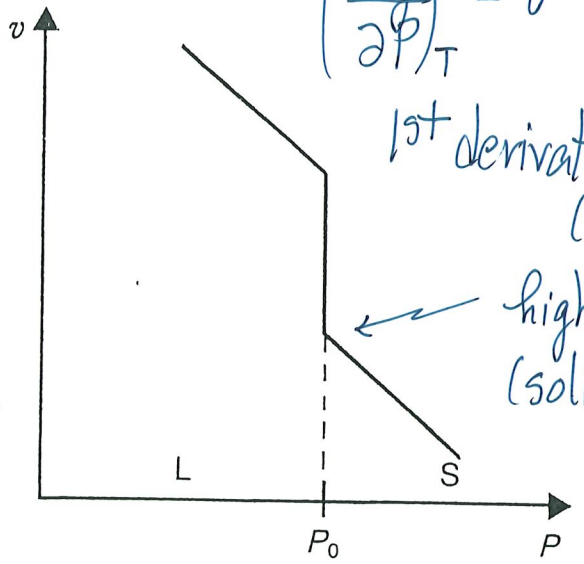
Similarly,



Follow X'Y' (increasing P at fixed T)†







$\left(\frac{\partial g}{\partial P}\right)_T$ = v discontinuous

1st derivative discontinuous (1st order phase transition)

← higher pressure phase (solid has a smaller volume)

† Why is g ↑ ⟶ P the general behavior?

First-order Phase Transitions Classified

- $g_A = g_B$, $\underbrace{v_A \neq v_B}$, $\underbrace{s_A \neq s_B}$ Phases A and B

$$v = \left(\frac{\partial g}{\partial P}\right)_T \qquad s = \left(\frac{\partial g}{\partial T}\right)_P$$

∴ First-order Phase Transitions are classified by

- g continuous across transition
- 1st derivatives of g w.r.t. T an P are discontinuous across transition

(23) Ehrenfest Classification of Phase Transitions

Second-order Phase Transitions?

- g continuous, 1st derivatives of g w.r.t. T and P continuous

  i.e. $V_A = V_B$ $(\Delta V = 0)$, $S_A = S_B$ $(\Delta S = 0,\ T_{transition}\,\Delta S = 0$ (no latent heat))

- But there are <u>discontinuities</u> in the <u>2nd derivatives</u> of g

  What are they? $\left(\frac{\partial V}{\partial T}\right)_P$, $\left(\frac{\partial V}{\partial P}\right)_T$, $\left(\frac{\partial S}{\partial T}\right)_P$, $\left(\frac{\partial S}{\partial P}\right)_T$ — 2nd derivatives

  $\left(\frac{\partial V}{\partial T}\right)_P$ related to β ← expansivity

  $\left(\frac{\partial V}{\partial P}\right)_T$ related to $-K$ ← compressibility

  $\left(\frac{\partial S}{\partial T}\right)_P$ related to C_P ← heat capacity at constant P

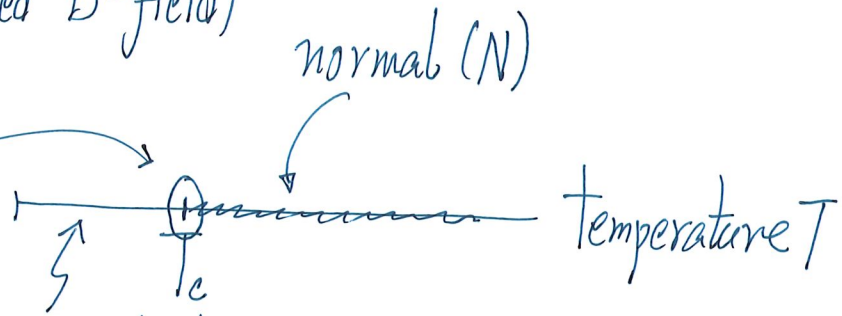
  $\left(\frac{\partial S}{\partial P}\right)_T \to -\left(\frac{\partial V}{\partial T}\right)_P$ (Maxwell Relation) thus β again

∴ expect discontinuities in β, K, C_P

Examples

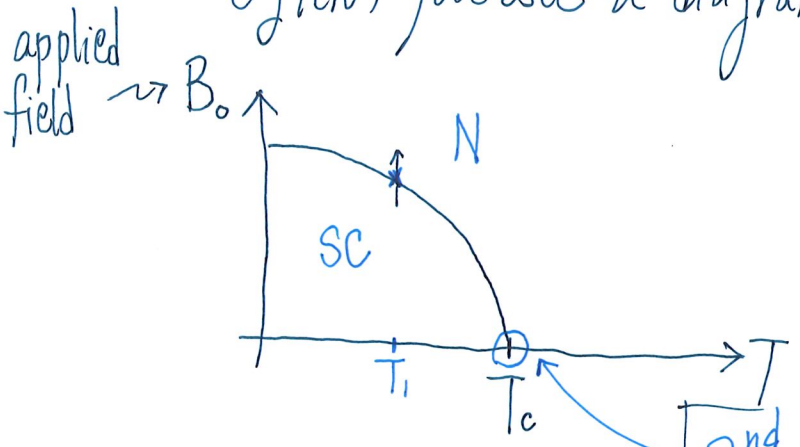
- Superconducting Transition (No applied B-field)

  e.g. Pb $T_c \sim 7K$



Transition at T_c is 2nd order

Often, you see a diagram

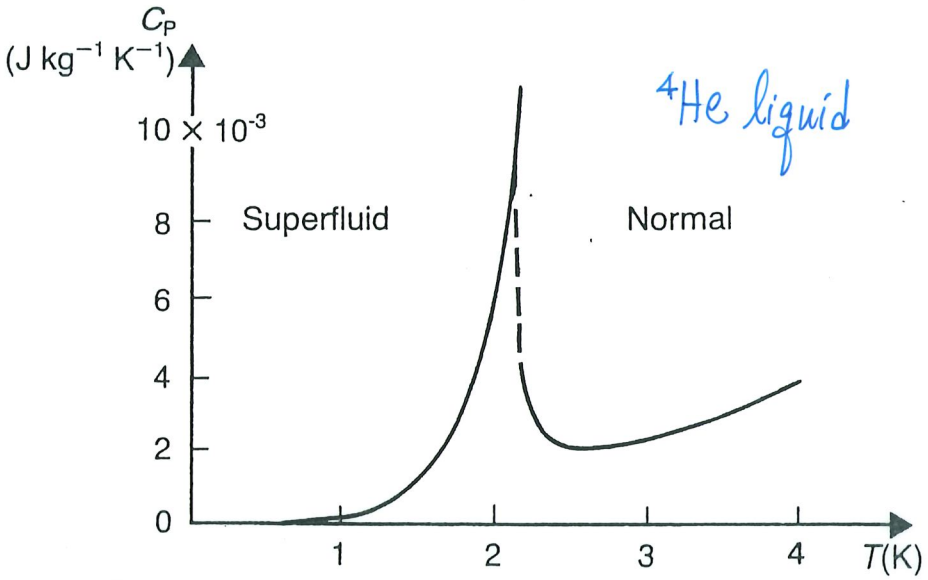


- At T_1 ($< T_c$), Pb is SC when $B_0 = 0$
- Apply small B_0, Pb remains SC
- But there is a critical value $B_{0c}(T_1)$ ["x"] above which Pb is N
- trace out $B_{0c}(T)$ for $T < T_c$

2nd order phase transition at $T \to T_c$ AND $B_0 = 0$ ← only that point (critical point)

The transition from SC to N across "x" (finite B_0) is a 1st order transition

- Liquid Helium ^4He (^{4} ← isotope): Normal fluid (viscosity $\neq 0$) to Superfluid (viscosity $= 0$) at $T_c \sim 2.2$ K



^{4}He liquid

Discontinuity of C_p at T_c

[Kapitsa (1938), Nobel Prize 1978]

^{4}He are bosons. The transition to superfluid is thought to be related to Bose-Einstein Condensation of ^{4}He atoms.

I. A few words on the Third Law of Thermodynamics

- It is about entropy at $T = 0\,K$
- $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$; $S(T) = S_0 + \int_0^T \frac{C_V}{T}\,dT$

What is S_0 (entropy at 0K)

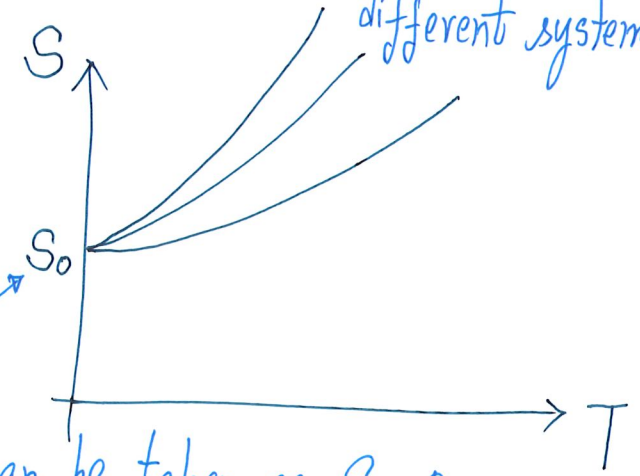
[Don't need S_0 in applying 1st and 2nd Laws as we only work with ΔS (change in entropy)]

∴ A "law" that fixes S_0 is beyond 2nd law (introduces ΔS)

Simply put: $\boxed{S_0 = S(T=0\,K) = 0}$ (24)

Planck's statement (3rd Law): The Entropy of all perfect crystals is THE SAME at the absolute zero, and may be taken as Zero (25)

It says



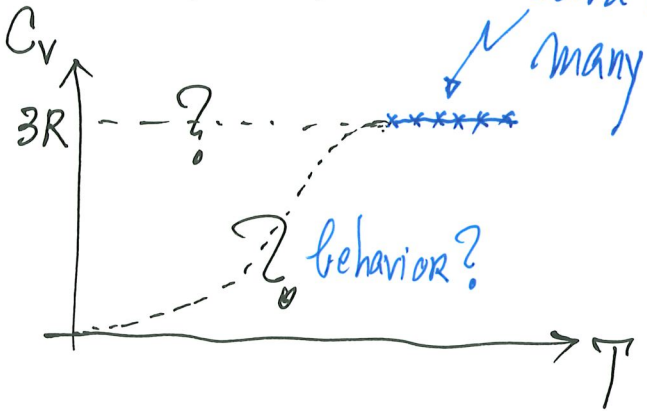
different systems / different exp'tal setups (e.g. $B=0$, $B\neq 0$)

Same S_0 and S_0 can be taken as $S_0 = 0$

Meaning: It is NOT

Impliciations

Solids' C_V



data show that many solids have $C_V = 3R$ (per mode) at high temperature

$$S = \int_0^T \frac{C_V}{T} dT$$

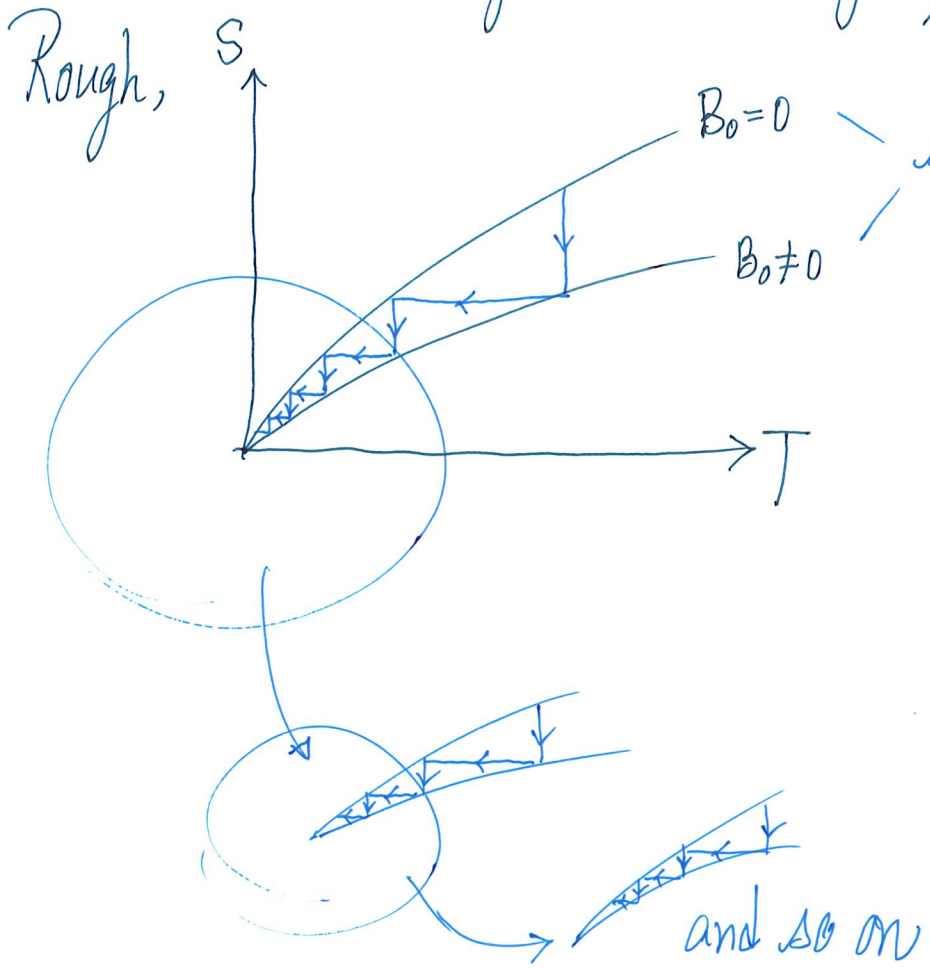
$\Rightarrow$ C_V must goes to zero as $T \to 0$ (at least as fast as $\sim T$)

This was a problem that Einstein and Debye picked up (1908~1911)

How $C_V(T)$ behaves in solids as $T \to 0$?

- Can't approach absolute zero using a finite number of processes

[We didn't discuss thermodynamics of paramagnetic salts and so we lacked the background on cooling by magnetizing and adiabatic demagnetizing.]



same substance

$B_0 \neq 0$, align magnetic moments (more ordered)
(S drops)

switch off B_0 ($B_0 = 0$) adiabatically ($Q = 0$, $\Delta S = 0$)

- This ends the Thermodynamics part of the course.
- We have the necessary background (and thermodynamics equations) to do statistical mechanics efficiently.

  i.e. Once we have $S(U, V, N)$, then what derivatives to do to get T, p, μ.

  Once we have $F(T, V, N)$, what derivatives to do for S, P, μ, U.