I. Partition functions of systems that have distinguishable subsystems

II. Partition functions of systems that have indistinguishable subsystems

III. Example calculation of a partition function

I. Partition functions of systems that have distinguishable subsystems

Consider system S that has subsystems A and B

System S is in state s

System A is in state a

System B is in state b

The partition function for S is $Z = \sum_s e^{-\beta E_s}$

But energy is additive: $E_s = E_a + E_b$

and $\sum_s \; = \sum_{a,b}$

So $Z = \sum_a \sum_b e^{-\beta(E_a + E_b)}$

$$= \sum_a \sum_b e^{-\beta E_a} e^{-\beta E_b}$$

$$= \sum_a e^{-\beta E_a} \sum_b e^{-\beta E_b}$$

$$= Z_a \cdot Z_b$$

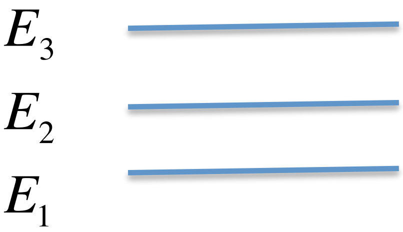
This can be generalized to >2 subsystems:

$Z_s = \prod_i Z_i$ if the subsystems are distinguishable.

How did the distinguishability enter? When we named them "A" and B."

II. Partition functions of systems that have indistinguishable subsystems

Consider 3 energy levels:



and three particles named A, B, and C.

How many ways are there to arrange the particles in the states, with no more than 1 particle per state? **Six.**

Arrangement #:	1	2	3	4	5	6
Energy Level						
E_3	C	B	C	A	B	A
E_2	B	C	A	C	A	B
E_1	A	A	B	B	C	C

IF the 3 particles are distinguishable (e.g., A = electron, B = proton, C = neutron), then each of the 6 arrangements may correspond to a different energy of the combined system. In that case 6 arrangments $\Rightarrow$ 6 energies.

$$\text{Then: } \sum_{s=1}^{6} \Rightarrow \sum_{\substack{a=1 \\ \text{(state of A)}}}^{3} \sum_{\substack{b=1 \\ \text{(state of B)}}}^{3} \sum_{\substack{c=1 \\ \text{(state of C)}}}^{3}$$

(with the constraint that no 2 particles can be in the same state)

IF the particles are indistinguishable (e.g., replace A, B, and C all with "D"), then there is only 1 arrangement (all 6 arrangements become equivalent) so there is only 1 system energy.

$$\text{Then } \sum_{\substack{s=1 \\ \text{(no sum} \\ \text{actually} \\ \text{needed)}}}^{1} \neq \underbrace{\sum_{\substack{a=1 \\ \text{(state of A)}}}^{3} \sum_{\substack{b=1 \\ \text{(state of B)}}}^{3} \sum_{\substack{c=1 \\ \text{(state of C)}}}^{3}}$$

because doing all these sums would overcount the number of distinct system energies.

Now suppose there are 2 levels and 2 particles.

Arrangement#	1	2
E_2	B	A
E_1	A	B

We see that the # of arrangements = # of distinct system energies

= 2 if the particles are distinguishable

and =1 if the particles are indistinguishable

Notice: $6=3!$

$2=2!$

And in general, # arrangements (=# distinct system energies)

$=(\#\ \text{particles})! = N!$ if the particles are distinguishable

and =1 if the particles are indistinguishable.

Now recall the partition function for a system S that has subsystems A, B, C, ...

This could be an atom. These could be the electrons, which are indistinguishable.

Suppose it has energy E_s. Name their energies E_a, E_b, E_c,...

The **definition** of Z_s is $\sum_s e^{-\beta E_s} = \sum_s e^{-\beta(E_a+E_b+E_c+\ldots)}$

This sum over s is NOT the same as a sum over $(a, b, c....)$ if A, B, C,... are indistinguishable.

If the subsystems are indistinguishable, $\sum_s = \frac{1}{N!}\sum_{a,b,c\ldots}$

So for S, which has N indistinguishable subsystems,

$$Z_s = \sum_s e^{-\beta E_s} \Rightarrow \frac{1}{N!}\sum_a e^{-\beta E_a}\sum_b e^{-\beta E_b}\ldots\sum_n e^{-\beta E_n} = \frac{1}{N!}Z_A \cdot Z_B \cdot \ldots \cdot Z_N$$

If $Z_A = Z_B = \ldots = Z_N$, call them all "$\mathbb{Z}$".

Then $Z_s = \frac{1}{N!}\mathbb{Z}^N$

This is the partition function if system S has N indistinguishable subsystems. We will use this in Chapter 24.

III. Example calculation of a partition function

Goal: find Z for a gas of N diatomic molecules in a field-free region

Interpret this as:

A system "s": the gas

with N identical subsystems: the molecules

This should take the form $\mathrm{Z}_s = \dfrac{1}{N!}\mathbb{Z}^N$.

We need to find $\mathbb{Z}$, the partition function of one diatomic molecule.

$$\mathbb{Z} = \sum_s e^{-\beta E_s}$$

Sum over all energy levels

E_s is the sum of the energies stored in all dof's:

$$E_s = E_{\substack{\text{translation}\\ \text{of molecule}}} + E_{\substack{\text{rotation}\\ \text{of molecule}}} + E_{\substack{\text{vibration}\\ \text{of molecule}}} + E_{\substack{\text{excitation of}\\ \text{molecule's electrons}}} + E_{\substack{\text{excitation of}\\ \text{molecule's nucleons}}}$$

For now, ignore $E_{\substack{\text{excitation of}\\ \text{molecule's electrons}}} + E_{\substack{\text{excitation of}\\ \text{molecule's nucleons}}}$, as they only contribute for $T >> 1000\,K$.

Then $\sum_s e^{-\beta E_s} = \sum_{translation} \sum_{rotation} \sum_{vibration} e^{-\beta(E_t+E_r+E_v)} = \mathbb{Z}_t \mathbb{Z}_r \mathbb{Z}_v$

To find $\mathbb{Z}_t = \sum_{translation} e^{-\beta E_t}$:

Plug in $\mathrm{E}_t = \dfrac{p^2}{2m}$

Make the approximation: $\sum_{translation} \Rightarrow \iint_{r,p} \dfrac{d^3p\, d^3r}{h^3}$

Then $\mathbb{Z}_t = \dfrac{1}{h^3} \iint d^3r\, \underbrace{d^3p\, e^{-\frac{\beta}{2m}p^2}}$

Call $\int d^3r = "V"$

Look this integral up in Stowe Equation 18.A.2.

Result:

$$\mathbb{Z}_t = \frac{V}{h^3} \cdot \left(\frac{2m\pi}{\beta} \right)^{3/2} = \frac{V \cdot (2m\pi kT)^{3/2}}{h^3}.$$

Note: $\mathbb{Z}_t \propto T^{3/2} = T$ raised to the power (# translational dof / 2)

To find $\mathbb{Z}_r = \sum_{rotation} e^{-\beta E_r}$:

Plug in $E_r = \frac{L^2}{2I}$. This is true for a dumbbell (diatomic) shape.

Recall from QM that the eigenvalues of the L^2 operator are $\ell(\ell+1)\hbar^2$, $\ell \in \{0,1,2...\}$.

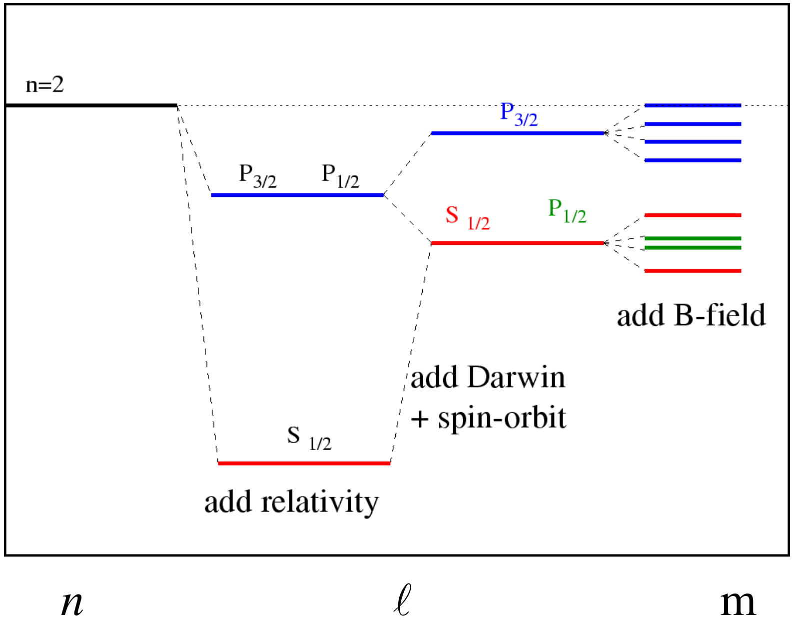
But also: each ℓ level has sublevels reflecting the eigenvalues of the L_z operator.

These are $m\hbar$, $m \in \{0,\pm1,\pm2,...,\pm\ell\}$.

So each ℓ level has $2\ell+1$ m-type sublevels.

Or: each angular momentum L state has

$2\ell+1$ allowed L_z states.



When we write $\sum_{rotation}$ we mean:

$$\sum_{\substack{\text{all levels that}\\ \text{can contribute}\\ \text{to rotational}\\ \text{energy}}} \Rightarrow \sum_{\ell}(2\ell+1)$$

$$\text{So } \mathbb{Z}_r = \sum_{\ell}(2\ell+1)e^{-\frac{\beta\hbar^2}{2I}\ell(\ell+1)} = \sum_{\ell}(2\ell+1)e^{-\frac{\hbar^2}{2kTI}\ell(\ell+1)}$$

Notice: these levels are discrete, so the sum is needed. But when temperature T is high $\Rightarrow$ energy E is high $\Rightarrow$ high ℓ states are populated $\Rightarrow$ many m states are populated.

The m states are very close together, separated by $\dfrac{1}{20000}$ of the energy splitting between the principal (n) levels.

So for high temperature T, it is reasonable to approximate $\sum_{\ell}$ as $\int d\ell$.

Here "high T" means $T >> T_{excitation}$:

$$kT >> \frac{\hbar^2 \ell(\ell+1)}{2I}.$$

So $\mathbb{Z}_r^{(high\ \mathrm{T})} \approx \int_0^\infty d\ell(2\ell+1)e^{-\frac{\beta\hbar^2}{2I}\ell(\ell+1)}$

To solve this integral, let $x = \ell(\ell+1) = \ell^2 + \ell$, so $dx = (2\ell+1)d\ell$

$$\mathbb{Z}_r^{(high\ \mathrm{T})} \approx \int_0^\infty dxe^{-\frac{\beta\hbar^2}{2I}x} = \frac{2I}{\beta\hbar^2} = \frac{2IkT}{\hbar^2}$$

Notice this $\mathbb{Z}_r \propto T^{2/2}$ = T raised to the power $(\#\text{ rotational dof } / 2)$.

To find $\mathbb{Z}_v = \sum\limits_{vibration} e^{-\beta E_v}$:

In QM, the paradigm for vibrational problems is the Simple Harmonic Oscillator.

For this, $E_v = \left(n + \frac{1}{2} \right) \hbar \omega_0, \quad n \in \{0,1,2,....\}$

So $\sum\limits_{vibration} \Rightarrow \sum\limits_{n}$

Then $\mathbb{Z}_v = \sum\limits_{n} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega_0} = \underbrace{e^{-\frac{\beta}{2}\hbar\omega_0}} \sum\limits_{n} e^{-n\beta\hbar\omega_0}$

We showed (lecture slide 278) that we can ignore energy offsets in the partition function.

So $\mathbb{Z}_v = \sum\limits_{n} e^{-n\beta\hbar\omega_0}$

Do the sum a la Appendix 21A:

$$\mathbb{Z}_v = \frac{1}{1 - e^{-\beta\hbar\omega_0}} = \frac{1}{1 - e^{-\frac{\hbar\omega_0}{kT}}}$$

If T is large (i.e., $kT >> \hbar\omega_0$), we can expand the exponent and truncate its series:

$$\mathbb{Z}_v^{(high\ \mathrm{T})} \approx \frac{1}{1-\left[1-\frac{\hbar\omega_0}{kT}+\underbrace{O\left(\frac{1}{T^2}\right)+\ldots}_{\text{neglect}}\right]} \Rightarrow \frac{1}{\frac{\hbar\omega_0}{kT}} = \frac{kT}{\hbar\omega_0}$$

Notice this $\mathbb{Z}_v \propto T^{2/2} = T$ raised to the power $\left(\#\ \text{vibrational dof} / 2\right)$.

Put these all together:

$$Z_{tot} = \frac{1}{N!}\left(\mathbb{Z}_t\mathbb{Z}_r\mathbb{Z}_v\right)^N = \frac{1}{N!}\left[\frac{V\cdot\left(2m\pi kT\right)^{3/2}}{h^3}\cdot\sum_{\ell}\left(2\ell+1\right)e^{-\frac{\hbar^2}{2kTI}\ell(\ell+1)}\cdot\frac{1}{1-e^{-\frac{\hbar\omega_0}{kT}}}\right]^N$$

...and at high temperature T, this approximates to:

$$\frac{1}{N!}\left[(const1)T^{3/2}\cdot(const2)T^{2/2}\cdot(const3)T^{2/2}\right]^N = \frac{(\text{constant})}{N!}\cdot\left(T^{\frac{\upsilon}{2}}\right)^N$$

where $\upsilon = \#\,dof\ /\ molecule$.

Recall $\mathbb{N}$ = # dof of the whole gas = $\mathrm{N}\upsilon$.

So $Z_{tot} = \frac{(\text{constant})}{N!} \cdot T^{\mathbb{N}/2}$ for an ideal diatomic gas at high temperature.

We could modify this formula for gases with # atoms $\neq 2$ or temperatures below $T_{excitation}$, for specific dof's.

I. Phases and phase changes

II. Phase stability

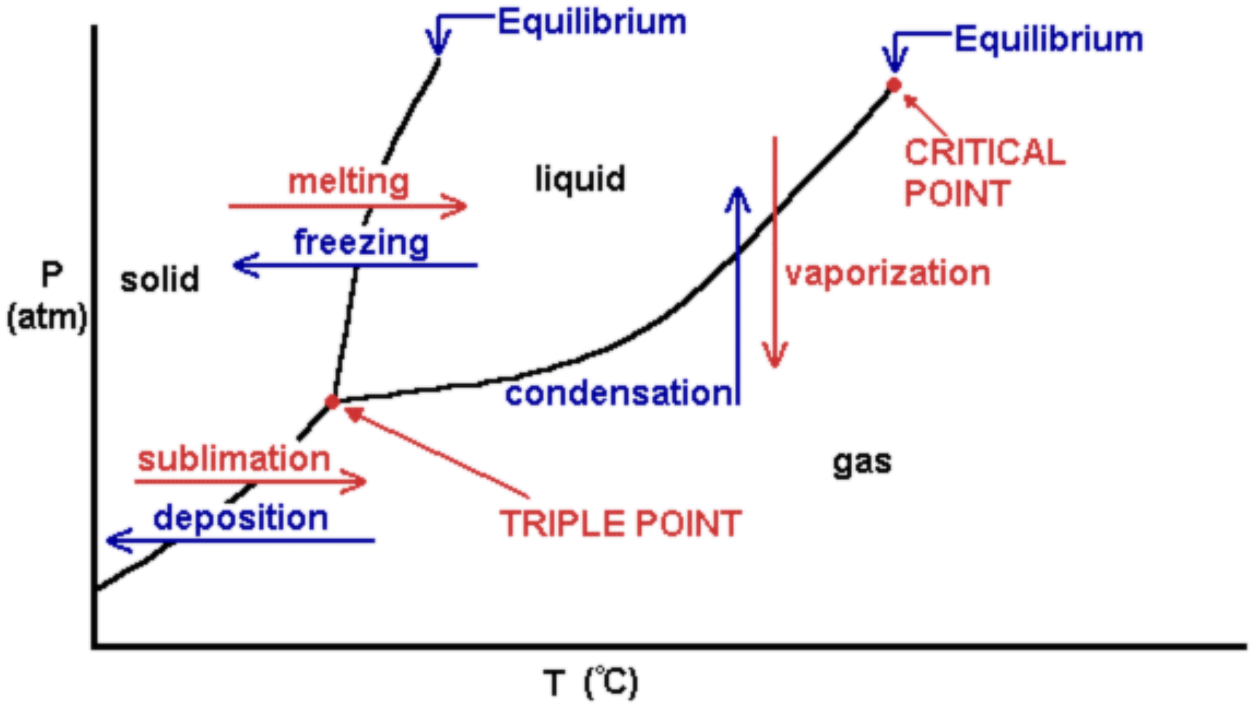
Please read Stowe chapter 24.

I. Phases and phase changes

Define:

Phase -- a single, spatially homogeneous state of aggregation;
this word characterizes the nature of a substance in a space of 2 independent variables, often $\left(pressure, Temperature\right)$.

Phase diagram -- a graph depicting the range of the 2 independent variables over which various phases are stable. Along the lines, the 2 phases are in diffusive equilibrium. Example:



Define:

Phase transition -- An onset of *collective behavior* among the constituents of a substance.

- Typically the response to an attractive force (e.g., if water freezes, it is because the temperature is low enough to allow electrostatic attraction to overcome thermal motion)
- Can be *induced by a change* in pressure or temperature.
- Is *characterized by a discontinuous change* in some property. Could be discontinuous in the 1st or 2nd derivative.

Examples:

Discontinuous in the 1st derivative:

Liquid-gas transition: discontinuous change in density

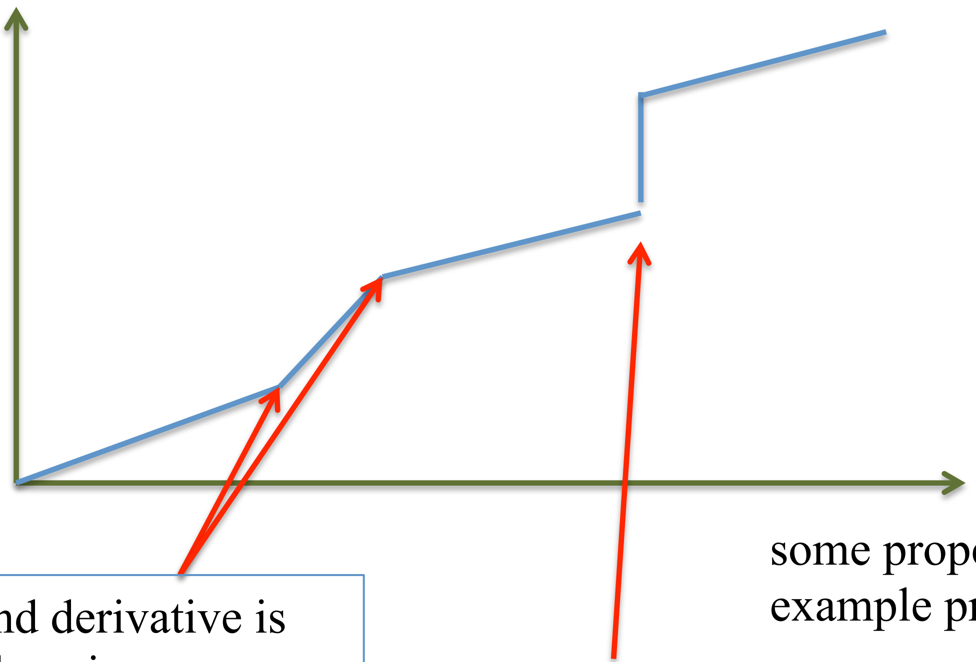
Liquid-superfluid transition: discontinuous in viscosity

Gas-plasma transition: discontinuous in conductivity

Discontinuous in the 2nd derivative:

Normal conductor - superconductor transition: discontinuous in conductivity

A graph that illustrates phase transitions:



Some property, for
example volume

some property, for
example pressure

At these points, the second derivative is undefined, because the slope is discontinuous. This is a second order phase transition.

Here the first derivative is undefined. This is a first order phase transition.

Define: critical point -- Beyond the critical point, the liquid and gas phases are indistinguishable, because the thermal motion of the fluid is so high that although it can be compressed to a density typical of a liquid, it does not *condense* there.

Condense -- exhibit collective behavior that results in a discontinuous volume change.

II. Phase stability

We study phase stability to understand why phase changes occur at the particular (p,T) points where they do.

Recall the Gibbs Free Energy. In differential form,

$$dG = -SdT + Vdp + \mu dN.$$

Use the First Law: $dE = TdS - pdV + \mu dN$,

to replace μdN with $dE - TdS + pdV$

Then,

$$dG = -SdT + Vdp + \left(dE - TdS + pdV\right)$$

$$= dE - \left(SdT + TdS\right) + \left(pdV + Vdp\right)$$

$$= dE - d\left(ST\right) + d\left(pV\right)$$

Infer:

$$G = E - ST + pV$$

Our goal: show that **stable equilibrium occurs for a system in which G is a minimum**.

Recall (lecture slide 201) that if a system "Δ" is in equilibrium with a reservoir "R", the probability P_s of finding the system to be in state "s" is proportional to Ω_R, the number of states of the reservoir that permit Δ to be in state s :

$$P_s \propto \Omega_R$$

But the reservoir's entropy, $\mathrm{S}_R = k \ln \Omega_R$,

so $\Omega_R = e^{S_R/k}$

$$P_s \propto e^{S_R/k}$$

Notice $\mathrm{S}_{tot} = S_\Delta + S_R$,

so $S_R = S_{tot} - S_\Delta$

$$P_s \propto e^{S_{tot}/k}.$$

Consider a nondiffusive $(\Delta N = 0)$ interaction between Δ and R.

Suppose Δ absorbs some heat Q from R to make its phase transition.

R's temperature T_0 and pressure p_0 do not change perceptibly, so

$$\Delta S_{tot} = \Delta S_\Delta + \Delta S_R = \Delta S_\Delta - \frac{Q}{T_0}$$

$$= \frac{1}{T_0}\left[T_0 \Delta S_\Delta - Q\right]$$

$$= \frac{1}{T_0}\left[T_0 \Delta S_\Delta - \left(\Delta E_\Delta + p_0 \Delta V_\Delta\right)\right]$$

$$= \frac{1}{T_0}\left[\Delta\left(T_0 S_\Delta - E_\Delta - p_0 V_\Delta\right)\right]$$

$$= \frac{1}{T_0}\left(-\Delta G_\Delta\right)$$

Suppose that the "Δ-R system" transitions from equilibrium to a combined state in which Δ is in state s.

Then: $\Delta S_{tot} = S_{\underset{(\Delta \text{ in s})}{tot}} - S_{\underset{equil}{tot}}$

and $\Delta G_\Delta = G_{\Delta \text{ in s}} - G_{equil}$

$$\Delta S_{tot} = S_{tot} - S_{\substack{tot \\ equil}} = \frac{1}{T_0}\left(G_{equil} - G_s\right)$$

$$\text{Therefore } S_{tot} = \underbrace{\frac{1}{T_0}G_{equil} + S_{\substack{tot \\ equil}}}_{\text{"some constant"}} - \frac{G_s}{T_0}$$

$$\text{So } P_s \propto \exp\left[\frac{S_{tot}}{k}\right] \Rightarrow \exp\left[\frac{1}{k}\left\{(\text{some constant}) - \frac{G_s}{T_0}\right\}\right]$$

$$\Rightarrow \underbrace{\mathrm{e}^{\text{some constant}/k}}_{\substack{\text{absorb this into} \\ \text{the proportionality}}} e^{-G_s/kT_0}$$

$$P_s \propto e^{-G_s/kT_0}$$

Evidently the probability is highest when G_s is minimum.

I. Why phase changes happen where they do in (p,T) space

II. The critical point

III. The Clausius-Clapeyron Equation

I. Why phase changes happen where they do in $\left(p,T\right)$ space

Recall the Equation of State is built from the relationship among 3 things:

- generalized forces (like pressure p). These are conditions imposed upon the system.
- macroscopic system parameters (like volume V). These are the system's *mechanical* response to external conditions.
- temperature. This is the system's *thermal* response to external conditions.

So an equation of state encodes much of the detail of a system's unique, specific structure. Thus it is natural to expect the eq. of state to provide the foundation for understanding the system's phase changes.

Example: consider the liquid-gas phase transition for a van der Waals gas.

Eq. of state: $\left(p+\dfrac{a}{v^2}\right)\left(v-b\right)=RT$.

$p =$ molar pressure

$v =$ molar volume

Solve for *p*:

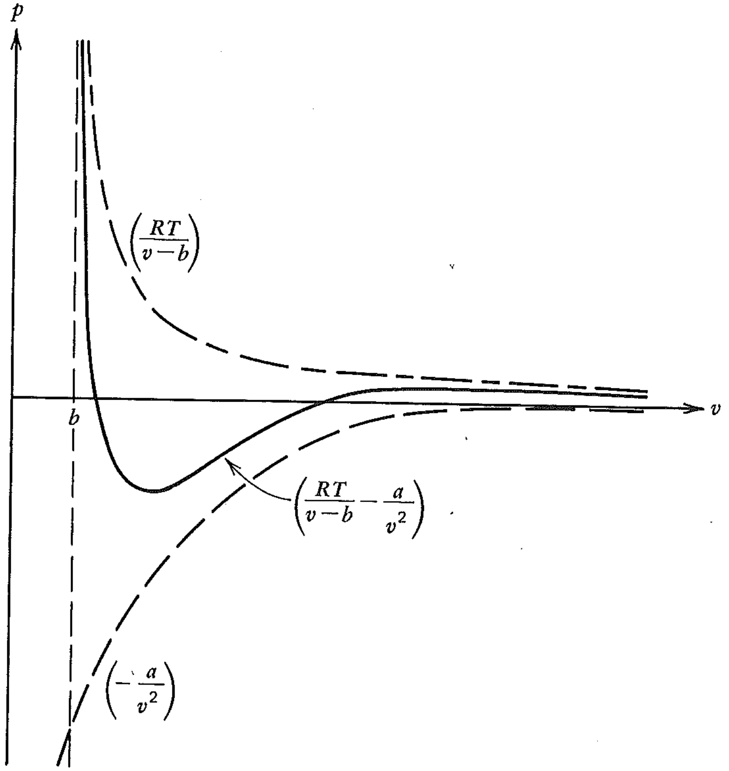
$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

"mutual attraction term" reflects polarizability, tendency of particles to aggregate

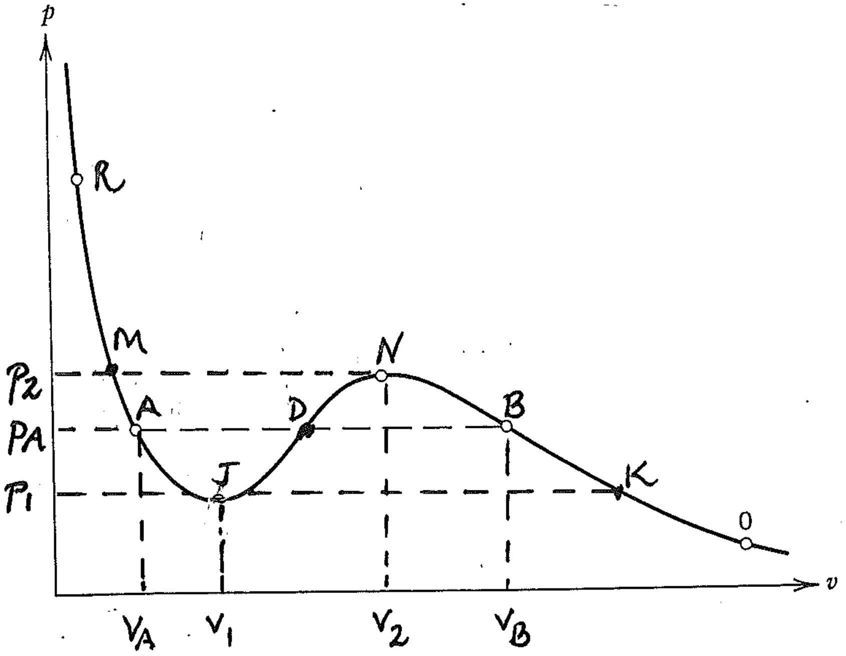
"thermal pressure term" reflects motion that keeps particles separated.

Graph both terms for some choice of *T* (i.e., *T* is some constant):

Notice the slope has different signs at different *v*'s.



Redraw with more labels:



We assert: the system will exist in those (p, v) configurations that are stable.

Which regions of this diagram indicate stability?

i) $p < p_1$ is stable. The slope $\dfrac{dp}{dv}$ is negative, so increased pressure means decreased volume.

Notice that the slope $\left|\dfrac{dp}{dv}\right|$ is small, as would be expected for a gas.

ii) $p > p_2$ is stable. The slope $\dfrac{dp}{dv}$ is negative. Notice $\left|\dfrac{dp}{dv}\right|$ is large, indicating a liquid phase.

iii) In the range $p_1 < p < p_2$, three v's are possible for each p. Which v corresponds to the maximum stability?

Conditions in which $v_1 < v < v_2$ correspond to instability, because here $\frac{dp}{dv} > 0$.

So the question reduces to a choice of 2 v's per p.

Consider 2 points: $\left(p_A, v_A\right)$ and $\left(p_A, v_B\right)$. When the system has pressure p_A, which volume does it choose?

It chooses the volume for which the Gibbs Free Energy G is minimized.

We now show this.

Recall the differential $dG \equiv -SdT + Vdp + \mu dN$ (lecture slide 299)

Define the molar form of dG:

$dg \equiv -sdT + vdp + \mu dn$. All of the lower case variables are "per mole."

Recall that the curve on slide 305 is for a fixed temperature, so $dT = 0$.

Additionally choose an isolated system, so $dN = 0$.

Then $dg = vdp$.

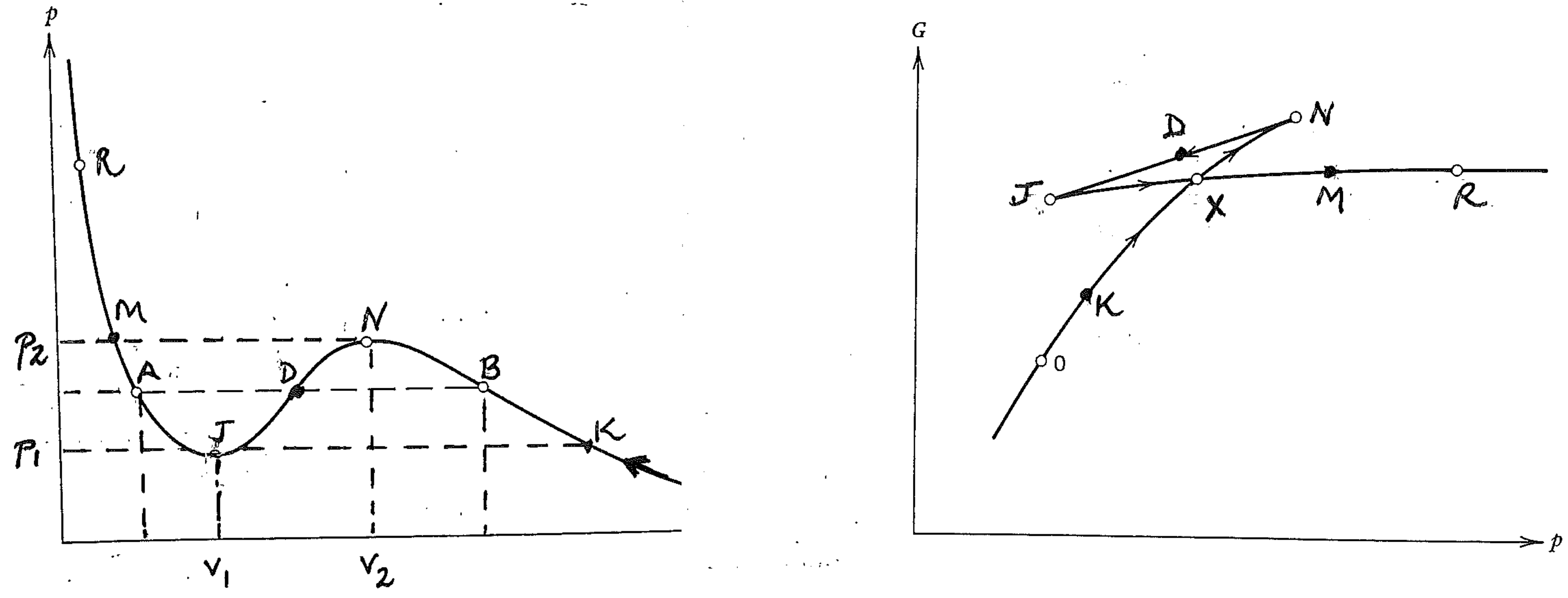
Integrate to get:

$$g - g_{init} = \int_{p_{init}}^{p} v\,dp'$$

Choose "init" to be point O.

Notice the RHS of this equation is the area between the curve and the p-axis.

Carry out the integral and plot the results:



What does the system do as it evolves in g - p space?

At O, it has no choice: it is a gas.

On line O-K-X-N: gas phase, large values of $v > v_2$, high compressibility

On line J-X-M-R: liquid phase, small values of $v < v_1$, low compressibility

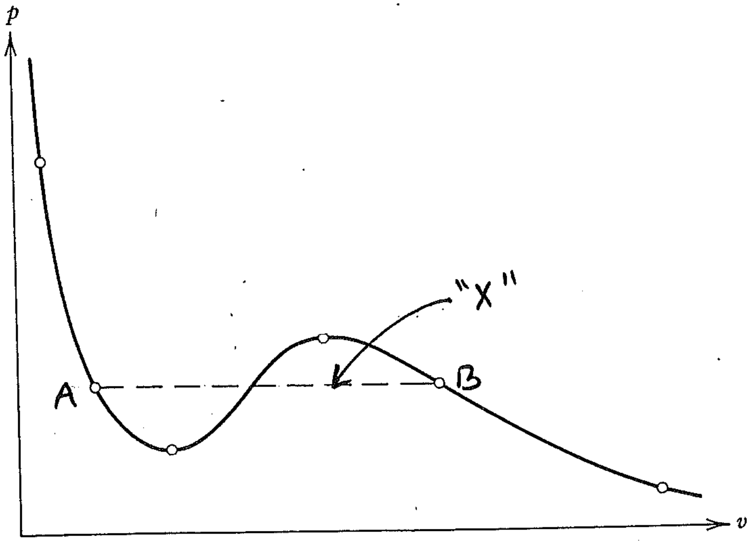
On line N-D-J: this is the intrinsically unstable range $v_1 \leq v \leq v_2$.

The system is a gas; it travels O-K-X.

At X, gas and liquid can coexists: this is the phase transition point.

To the right of X, the system's g will be minimized if it transitions to liquid rather than remaining gas, so it condenses to liquid and evolves to line M-R.

Where is X on the p-v curve?



"X" corresponds to the whole line from A to B. This is the path that the system actually traverses while it is condensing during the phase transition.
Recall "condensing" means V decreases while p stays constant.

So "X" is always associated with a horizontal line.
What determines the value of p_A?
By the definition of X,
$g(A) = g(B)$.

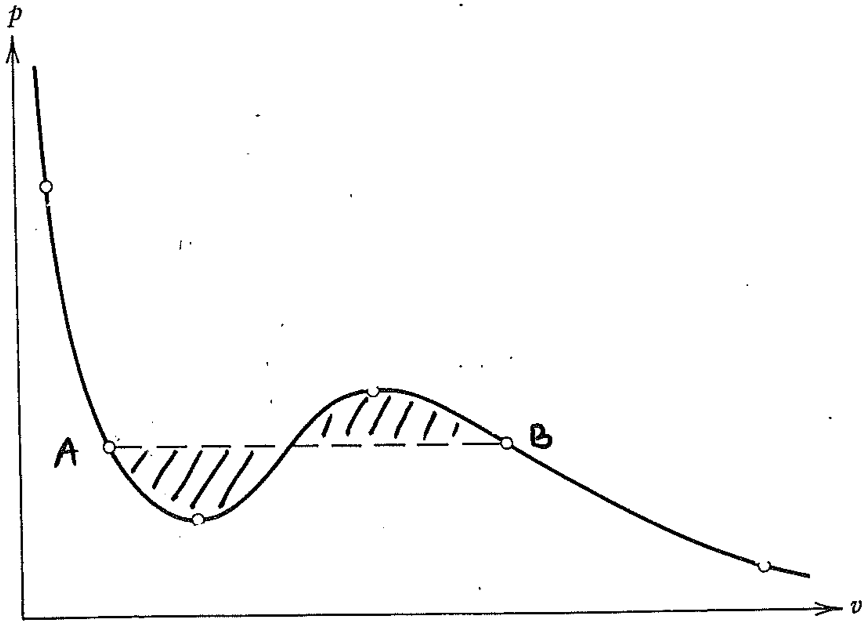
Recall $g - g_{init} = \int_{p_{init}}^{p} v\,dp'$.

$$\text{Call } B = init$$
$$A = \text{upper limit}$$

Then $\underbrace{g(A) - g(B)}_{} = \underbrace{\int_B^A}_{} v\,dp'$.

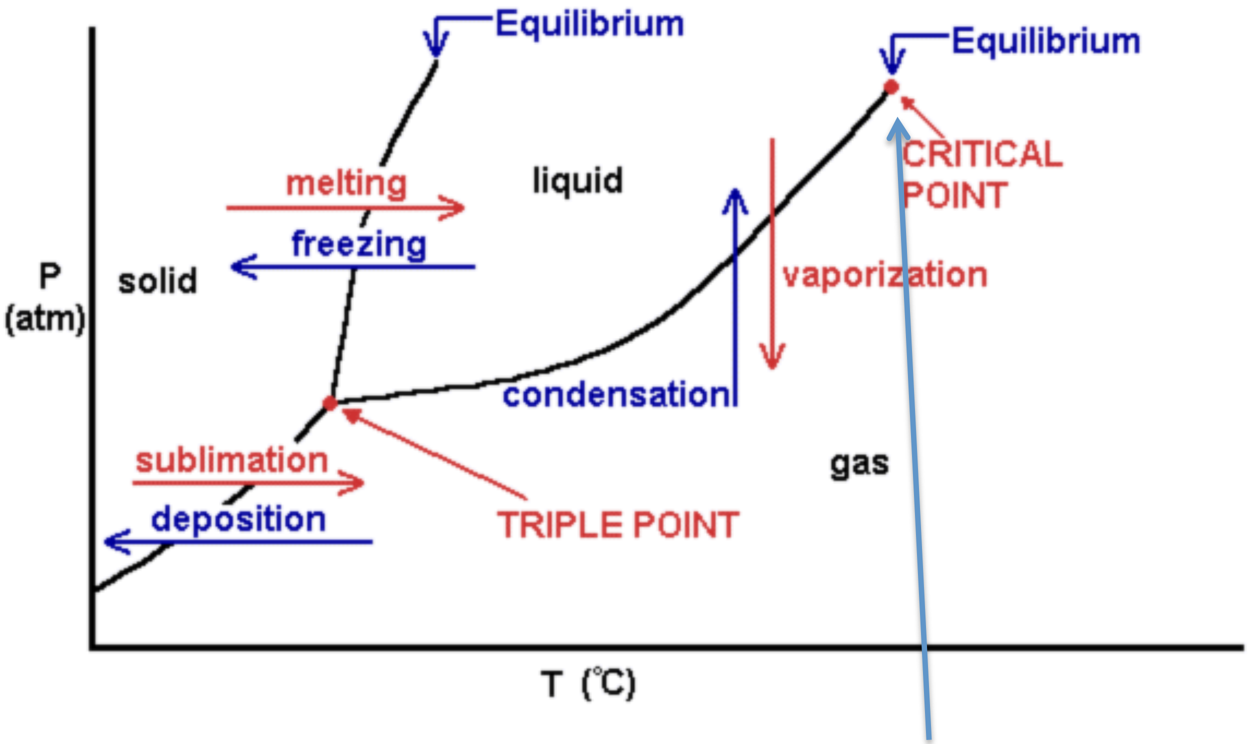
$$0 \quad = \int_{B-N-D-J-A} v\,dp'$$

As the line A-B must be horizontal, this fixes A and B so that the shaded areas below are equal:



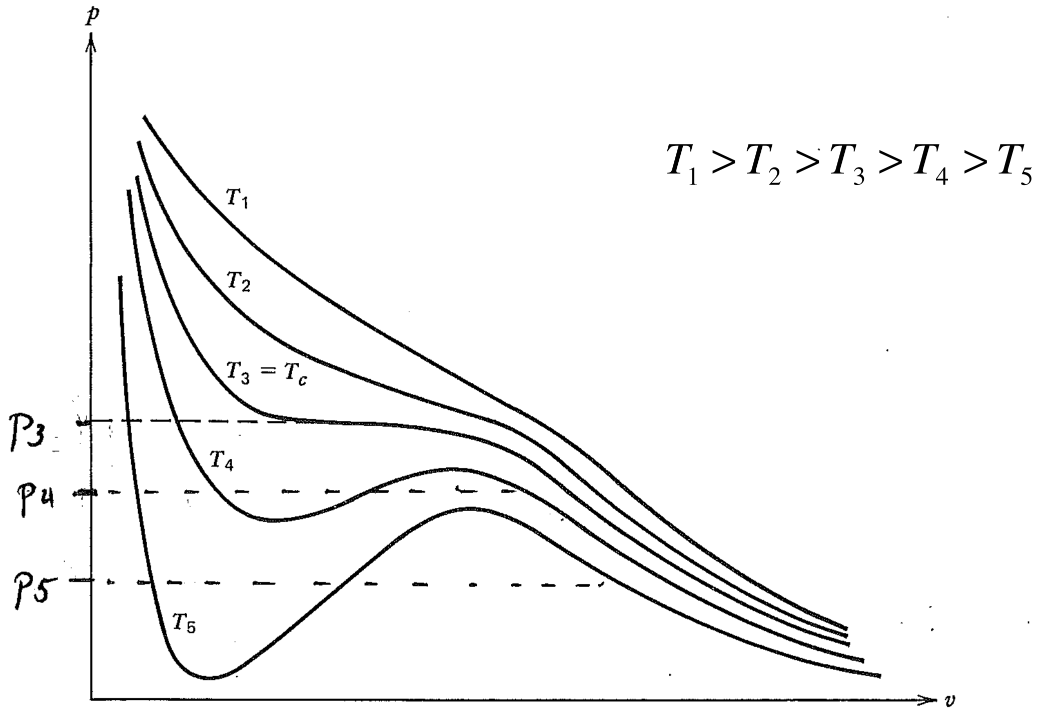
II. The critical point

Recall the p - T diagram:



This line ends here. Why here?

Plot p versus v for various temperatures. We get:



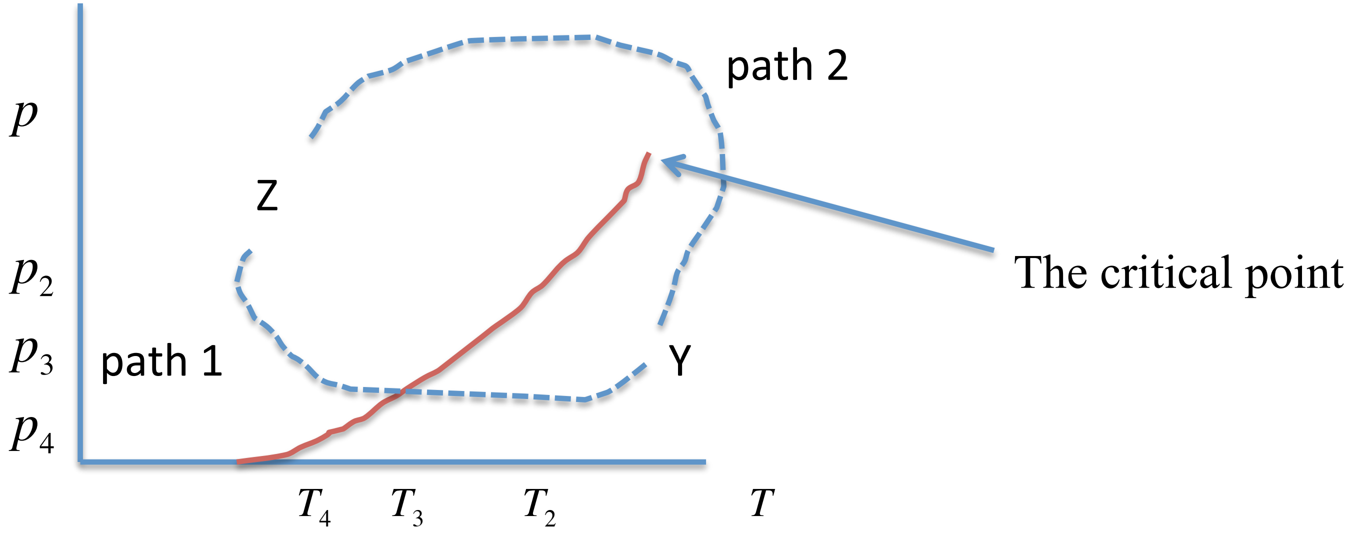
Recall: if the slope goes positive, there will be a phase change.

Each of these will have its own horizontal "X" line whose p-intercept is unique.

Notice:

- The X line for T_3 is not a line: it has shrunk to a point
- The T_1 curve has no X at all.

Plot the p-intercepts versus the T-values.



The critical point corresponds to the temperature line whose slope goes to zero but not positive: i.e., at $T_{critical}$, $\frac{\partial p}{\partial v} = 0$ and $\frac{\partial^2 p}{\partial v^2} = 0$

Suppose a system evolves from Y to Z.

If it takes path 1, it undergoes a phase change.

If it takes path 2, it does not.

When a substance has a (p,T) in the neighborhood of the critical point, it undergoes large density fluctuations. This makes it opaque. This is called "critical opalescence."

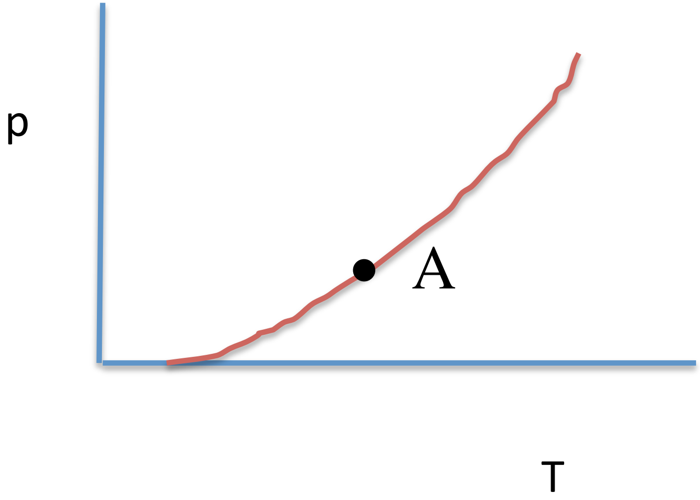
III. The Clausius-Clapeyron Equation

The question is: what is the equation for the line that separates the liquid and gas phases?

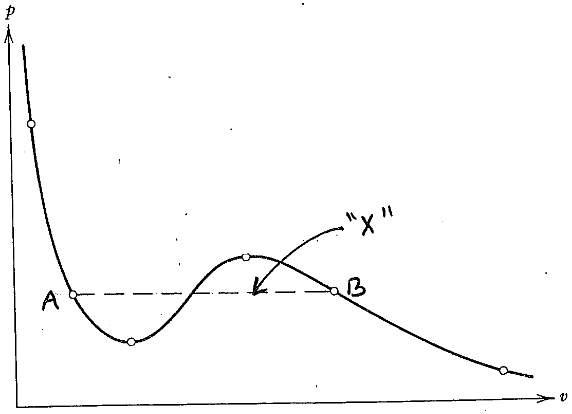
Another way to say this is: Given a known p_1 and T_1, how can we find the T_2 associated with another p_2, or the p_2 that goes with another T_2?

Yet another way to say this is: What is the equation for the vapor pressure of a substance?

To answer this, consider any point "A" on the phase transition line:



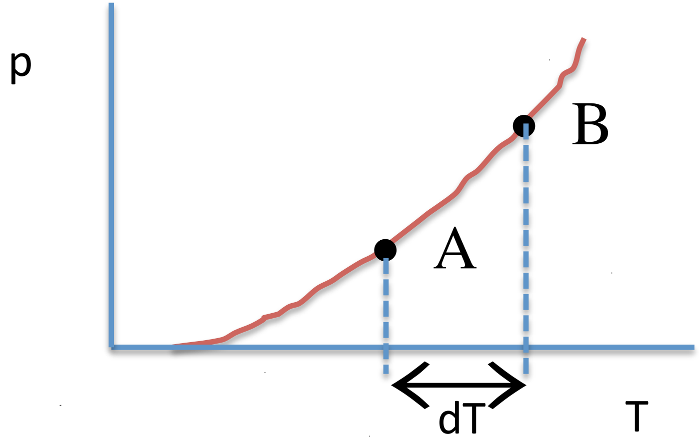
Recall that any point (including "A") has a p-V diagram like this:



On this p-V diagram,

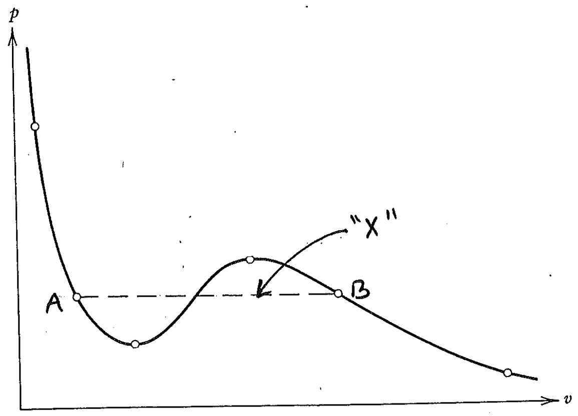
$$g_1(T,p)=g_2(T,p) \qquad \text{"Eq 1"}$$

Now consider a point "B" on the p-T diagram:



It too has a p-V diagram, located at $(T+dT,\ p+dp)$ with respect to point A.

B's graph:



For point B, $g_1\left(T+dT,p+dp\right)=g_2\left(T+dT,p+dp\right)$, which we rewrite as:

$$g_1\left(T,p\right)+\left.\frac{\partial g_1}{\partial T}\right|_p dT+\left.\frac{\partial g_1}{\partial p}\right|_T dp=g_2\left(T,p\right)+\left.\frac{\partial g_2}{\partial T}\right|_p dT+\left.\frac{\partial g_2}{\partial p}\right|_T dp \qquad \text{"Eq 2"}$$

Subtract: Eq 2 - Eq 1 to get:

$$\left.\frac{\partial g_1}{\partial T}\right|_p dT+\left.\frac{\partial g_1}{\partial p}\right|_T dp=\left.\frac{\partial g_2}{\partial T}\right|_p dT+\left.\frac{\partial g_2}{\partial p}\right|_T dp \qquad \text{"Eq 3"}$$

Now recall differential molar Gibbs Free Energy (lecture slide 308):

$$dg = -s\,dT + v\,dp \qquad \text{"Physics equation"}$$

Compare this term by term to:

$$dg = \left.\frac{\partial g}{\partial T}\right|_p dT + \left.\frac{\partial g}{\partial p}\right|_T dp \qquad \text{"Math equation"}$$

Infer that:

$$\left.\frac{\partial g}{\partial T}\right|_p = -s$$

$$\left.\frac{\partial g}{\partial p}\right|_T = v$$

Plug these into Eq 3 to get:

$$-s_1 dT + v_1 dp = -s_2 dT + v_2 dp$$

$$\left(s_2 - s_1\right) dT = \left(v_2 - v_1\right) dp$$

$$\Delta s \cdot dT = \Delta v \cdot dp$$

$$\frac{\Delta s}{\Delta v} = \frac{dp}{dT}.$$

This Clausius-Clapeyron Equation means: for any point on the p-T curve, the slope $\frac{dp}{dT}$ is given by the entropy change Δs and volume change Δv needed to "cross the line": i.e., needed to undergo a phase transition at that particular (p,T).

I. Latent heat and vapor pressure of an ideal gas

II. Quantum statistics

III. Fermions and bosons

Please read Stowe Chapter 25 (skip the Chapter 25 appendices).

I. Latent heat and vapor pressure of an ideal gas

Because there is a ΔS associated with a phase transition, there is a $\Delta Q = T\Delta S$.

Define L: The latent heat of transformation.

$$L \equiv T\,\Delta S_{\substack{phase\\transition}}$$

So $\Delta S_{\substack{phase\\transition}} = \dfrac{L}{T}$.

Plug this into the Clausius-Clapeyron Equation,

$$\frac{\Delta s}{\Delta v} = \frac{dp}{dT},$$

to get the vapor pressure equation:

$$\frac{1}{\Delta v}\cdot\frac{L}{T} = \frac{dp}{dT}$$

In general, $\Delta v = v_2 - v_1$, but for a liquid to gas transition, $v_2 >> v_1$,

So let $\Delta v \approx v_2$. Then:

$$\frac{1}{v_2}\cdot\frac{L}{T} \approx \frac{dp}{dT}$$

For an ideal gas, $pv = RT$, so $v_2 = \dfrac{RT}{p}$. Then,

$$\frac{dp}{dT} \approx \frac{L}{\left(\dfrac{RT}{p}\right)T} = \frac{Lp}{RT^2}$$

Rewrite:

$$\frac{dp}{p} = \frac{L}{R}\frac{dT}{T^2}$$

Integrate:

$$\ln p = -\frac{L}{RT} + const.$$

Name the *const* : "$\ln p_0$"

$$\ln p = -\frac{L}{RT} + \ln p_0$$

$p = p_0 e^{-L/RT}$. The equation for the vapor pressure of a liquid.

II. Quantum statistics

Recall the difference between classical and quantum statistics:

	Classical	**Quantum**
A "system" is:	A particle which can occupy various states.	A state (for example energy level) which can be occupied by various numbers of particles.
The probability eq. is:	$P_s = Ce^{-\beta E_s} = \dfrac{e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}$	$P_n = Ce^{-\beta n(\varepsilon_s - \mu)} = \dfrac{e^{-\beta n(\varepsilon_s - \mu)}}{\sum_n e^{-\beta n(\varepsilon_s - \mu)}}$
	This is the probability that the particle is in state s.	This is the probability that there are n particles in a state s whose energy is ε_s.

--Notice that the summation indices are different!--

We now focus on the Quantum Statistics column.

A commonly asked question is: What is the average number of particles occupying a given state?

The answer is known as: "the occupation number," $\bar{n}$.

Use the usual formula for averages:

$$\bar{n} = \sum_n P_n \cdot n$$

Plug in $P_n = Ce^{-\beta n(\varepsilon_s - \mu)}$:

$$\bar{n} = \sum_n Ce^{-\beta n(\varepsilon_s - \mu)} \cdot n = C\sum_n e^{-\beta n(\varepsilon_s - \mu)} \cdot n$$

Name $\beta(\varepsilon_s - \mu) \equiv x$

$$\bar{n} = C\sum_n e^{-nx} \cdot n$$

Math trick to convert this to an easy sum:

Notice $ne^{-nx} = -\frac{\partial}{\partial x}\left(e^{-nx}\right)$.

$$\bar{n} = -C\frac{\partial}{\partial x}\left[\sum_n e^{-nx}\right]$$

Plug in C :

$$\bar{n} = -\frac{1}{\sum_n e^{-nx}}\frac{\partial}{\partial x}\left[\sum_n e^{-nx}\right]$$

$$\bar{n} = -\frac{\partial}{\partial x}\left[\ln\left(\sum_n e^{-nx}\right)\right]$$

But what are the limits on the sum?