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Statistical Mechanics

CH. 7 CANONICAL ENSEMBLE AND GRAND CANONICAL ENSEMBLE LECTURE NOTES

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2-2-22

7.1 Canonical Ensemble

In the Canonical ensemble T, N, V are fixed and do not change

" Grand Canonical " T, μ, V " μ -chem E

We desire to find the thermodynamics of System A. We do this by looking at thermal equilibrium. We are not necessarily interested in System B

We put these two systems (A and B) together and we have one microcanonical ensemble. This is because we know how to treat the microcanonical ensemble.

We want to find an expression for $T'(E - E_A)$

$$k \log(T_B(E - E_A)) = S_B(E - E_A)$$

If we take the above and Taylor expand it we will get

$$T_B(E - E_A) = \exp\left(\frac{S_B(E)}{k}\right) \exp\left(-\frac{E_A}{kT}\right)$$

The ensemble density is then

$$\rho(p, q) = e^{-H(p, q)/kT} \Rightarrow \rho(p_A, q_A) = e^{-H(p_A, q_A)/kT_B}$$

To calculate the partition function we do

$$Q_N(V, T) \equiv \frac{1}{N! h^{3N}} \int e^{-\beta H(\vec{p}, \vec{q})} d^3 p d^3 q$$

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We calculate the number of microstates with

$$T'(E) = \frac{1}{N! h^{3N}} \int_{E < H + \Delta E} d^3 p d^3 q$$

Where the partition function is,

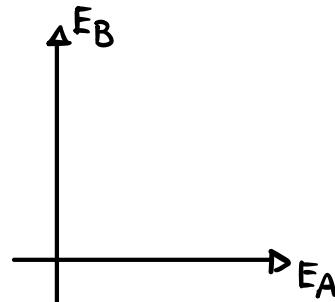
$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta H(\vec{p}, \vec{q})} d^3 p d^3 q$$

If we choose $N=1$, comparing the microcanonical and canonical ensemble

$$\text{Microcanonical : } P_{E_N} = 100\% , \text{ Canonical : } P_{E_N} = e^{-\beta E_N} / \sum_{j=1}^{\infty} e^{-\beta E_j}$$

When in the microcanonical ensemble, all allowed states are equally probable.

When we examined the energy the total energy is $E = E_A + E_B$



There are instances where $E_A > E$, this happens when $E_B < 0$. This is for the canonical ensemble

* we wish to find a connection between statistical mechanics and thermodynamics for the canonical ensemble

When we did (*) for the microcanonical ensemble we found the relationship to be

$$S = k \log(T'(E))$$

The connection between the canonical ensemble and thermodynamics is the Helmholtz free energy

$$A = U - TS$$

Where we define A to be

$$Q_N(V, T) = e^{-\beta A(N, V, T)},$$

Revisiting entropy, the entropy of an isolated system can never decrease,

$$\Delta S(E, V, N) \gg 0$$

Looking at the Helmholtz free energy $A = E - TS$ ($E \equiv \mathcal{U}$) we wish to express it in terms of $A(T, V, N)$

$$A = E - TS \rightarrow \text{Get rid of } S$$

└
 → Bring in temperature

$$dA = dE - Tds - SdT = -SdT - PdV + \mu dN$$

└
 → $dE = Tds - PdV + \mu dN$

We can proceed to say

$$dA(T, V, N) = \left(\frac{\partial A}{\partial T}\right)_{V, N} dT + \left(\frac{\partial A}{\partial V}\right)_{T, N} dV + \left(\frac{\partial A}{\partial N}\right)_{T, V} dN$$

We can then say that the Helmholtz free energy should always decrease, namely

$$\Delta A \leq 0$$

We now look at the Helmholtz free energy again. Summing individual systems¹ we have

$$Q_N(T, V) = e^{-\beta A(T, N, V)} = e^{-\beta A_1} e^{-\beta A_2}$$

Where we used the fact that $A(T, N, V) = A_1 + A_2 + \dots$. Using this we can proceed to show

$$A = \mu - TS = \langle H \rangle - T \left(\frac{\partial A}{\partial T} \right)_{V, N}$$

In this regime, the average value of the Hamiltonian is our energy.

Looking back at the partition function

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta \mathcal{H}(\vec{p}, \vec{q})} d^3 p d^3 q = e^{-\beta A(N, T, V)}$$

We can determine certain thermodynamic properties using $\partial/\partial \beta$.

In the microcanonical ensemble, the energy is fixed. In the canonical ensemble the temperature is fixed. This tells us that for the canonical ensemble the energy can fluctuate.

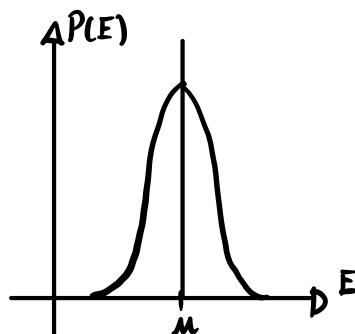
To calculate the fluctuation, we do

$$\sigma^2 = \sqrt{\frac{\langle \delta H^2 \rangle - \langle \delta H \rangle^2}{\langle \delta H \rangle}}$$

When worked out we find

$$\sigma^2 = \sqrt{\frac{K T^2 C_V}{\langle \delta H \rangle}} \quad \} \frac{1}{\sqrt{N}}$$

Typically we can say that as more particles are added the fluctuation is less and less.



Looking at energy levels with N particles we have,

_____ ε The microcanonical ensemble was $E = NE \frac{1}{1 + e^{\beta E}}$

_____ o The canonical ensemble is $E = \sum_{i=1}^N \epsilon n_i^{(0)}$

We can calculate our internal energy with

$$U = A - T \left(\frac{\partial A}{\partial T} \right)_{V,N}$$

We first need Q_N

$$Q_N = (1 + e^{-\beta E})^N$$

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Looking at the average energy,

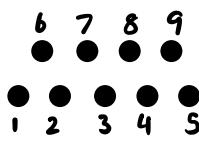
$$\langle \mathcal{H} \rangle = \frac{\int \mathcal{H} e^{-\beta \mathcal{H}} d^d \vec{p} d^d \vec{q}}{\int e^{-\beta \mathcal{H}} d^d \vec{p} d^d \vec{q}}$$

where "d" is the dimension we are working in. We now look at doing this in an easier way

$$\langle \mathcal{H} \rangle = \frac{-\frac{\partial}{\partial \beta} \int e^{-\beta \mathcal{H}} d^d \vec{p} d^d \vec{q}}{\int e^{-\beta \mathcal{H}} d^d \vec{p} d^d \vec{q}}.$$

We now go back to looking at our two-level system

_____ ε



$$\rightsquigarrow E_V = \sum_{i=1}^N n_i^{(v)} \epsilon$$

_____ o

$$v = (0, 0, 0, 0, 0, 1, 1, 1, 1)$$

where " v " is the v^{th} state configuration in our system. When we look at N particles the partition function is

$$Q_N = e^{-\beta A} = \sum_v e^{-\beta E_v} \Rightarrow \text{sum over all states} \Rightarrow Q_N = (1 + e^{-\beta E})^N$$

The above result tells us that the partition function for an N particle system is essentially the partition function of a single particle raised to N

We now examine a 3 particle system and how the configuration for these will look

$$N=3 \quad E=0 : (0,0,0)$$

$$E=E : (1,0,0), (0,1,0), (0,0,1)$$

$$E=2E : (1,1,0), (0,1,1), (1,0,1)$$

$$E=3E : (1,1,1)$$

We now expand our partition function

$$(Q_1)^3 = (1 + e^{-\beta E})^3 = 1 + 3e^{-\beta E} + 3e^{-2\beta E} + e^{-3\beta E}$$

We now examine molecules of hypothetical ideal gas with an internal energy level structure

$$E_n = E_n \text{ where } n = 0, 1, 2, \dots$$

The degeneracy of the n^{th} level is $(n+1)$. We now solve for our partition function

$$\begin{aligned} Q &= \sum_{\text{all states}} e^{-\beta E_j} = \sum_{n=0}^{\infty} (n+1) e^{-\beta E_n} = \sum_{n=0}^{\infty} (n+1) (e^{-\beta E})^n \xrightarrow{x = e^{-\beta E}} = \sum_{m=1}^{\infty} m x^{m-1} = \frac{d}{dx} \left(\sum_{m=1}^{\infty} x^m + 1 \right) \\ &= \frac{d}{dx} \left(\sum_{m=0}^{\infty} x^m \right) = (1-x)^{-2} = (1-e^{-\beta E})^{-2} \end{aligned}$$

We can continue to calculate the internal energy of one particle with

$$U_1 = \frac{1}{Q} \sum_{n=0}^{\infty} (E_n)(n+1) e^{-\beta E_n} = \frac{1}{Q} \left(-\frac{\partial}{\partial \beta} Q \right)$$

When this is calculated we find

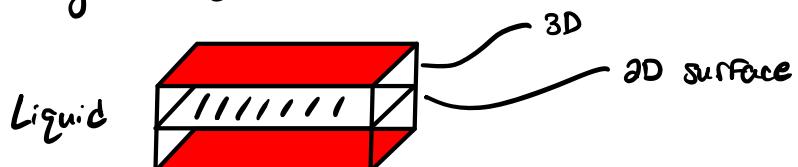
$$U_1 = 2E \frac{1}{e^{\beta E} - 1}$$

Now the internal energy for N particles will be

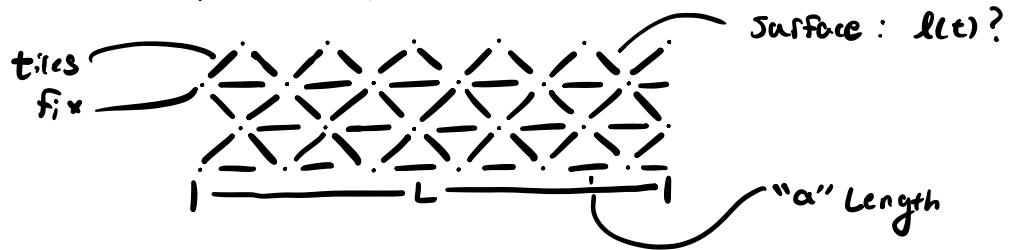
$$U_N = N U_1 = \frac{2NE}{e^{\beta E} - 1}$$

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We begin first by looking at a system like



Let's now take a closer look at this surface



From this we can say

N_+ tiles pointing up \sim Energy ϵ , N_- tiles pointing down \sim Energy ϵ

No tiles sitting flat \sim Energy ϵ

If we have a very low temperature, what would the arrangement of the surface be?
We use the micro-canonical ensemble

First we fix the energy:

$$E = \epsilon(N_+ + N_- + N_0) - \epsilon \frac{L}{a}$$

Next we put tiles straight $E=0$ ($E=0$ for $N_+ = N_- = 0$). $N_+ = N_-$ from one fixed point to another

$$E = \epsilon(2N_+ + N_0) - \epsilon \frac{L}{a}$$

We also know,

$$L = [N_0 + \frac{1}{2}(N_+ + N_-)]a = (N_0 + N_+)a, E = \epsilon(N_0 + 2N_+ - \frac{L}{a}), N_+ = \frac{E}{\epsilon}, N_0 = \frac{L}{a} - \frac{E}{\epsilon}$$

What about $\Gamma(E)$?

$$\Gamma(E) = \frac{(N_0 + N_+ + N_-)!}{(N_0!)(N_+!)(N_-!)} = \frac{(N_0 + 2N_+)!}{(N_0!)(N_+!)^2}$$

If we take the log of this,

$$\log(\Gamma(E)) = \log((N_0 + 2N_+)! - \log(N_0!) - 2\log(N_+!))$$

Using the above, we can calculate $(T)^{-1}$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial}{\partial E} k \log(\Gamma(E)) = k \frac{1}{\epsilon} \log \left(\frac{(L/a)^2 - (E/\epsilon)^2}{(E/\epsilon)^2} \right)$$

$$\Rightarrow \frac{\epsilon}{kT} = \log(\dots) \Rightarrow e^{\epsilon/kT} = (\dots) \Rightarrow l(T) = (N_+ + N_- + N_0)a = (2N_+ + N_0)a$$

7.3 Grand Canonical Ensemble

We first look at our 3 ensembles:

$$\text{Microcanonical: } E, N, V \longrightarrow S = k \log(\Gamma(E))$$

$$\text{Canonical: } T, N, V \longrightarrow A = -kT \log(Q_N)$$

$$\text{Grand Canonical: } T, \mu, V \longrightarrow \mu V = kT \log(Q_N)$$

For the Grand Canonical ensemble

$$Q_N(\mu, V, T) = \sum_{n=0}^{\infty} z^n Q_n(T, V) \quad \text{w/ } z = e^{-\beta \mu}$$

↳ Partition Fxn from canonical ensemble

We can calculate the mean number of particles with

$$\bar{N} = \langle N \rangle = \frac{\sum_{n=0}^{\infty} n z^n Q_n(T, V)}{\sum_{n=0}^{\infty} z^n Q_n(T, V)} = z \frac{\partial}{\partial z} \log(Q_N(\mu, V, N)) = \frac{\frac{\partial F(x)}{\partial x}}{f(x)}$$

The potential energy is then

$$U = \frac{-\frac{\partial}{\partial \beta} \left(\sum_{n=0}^{\infty} z^n Q_n(T, V) \right)}{Q_N(\mu, V, N)}$$

From this we can say: $U = U(\mu, T, V)$ and $\bar{N} = \bar{N}(\mu, T, V)$. Next we will re-write the internal energy as a function of \bar{N}, T, V .

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Grand Canonical Ensemble (T, μ, V)

Looking at an example: Ideal Gas

$$H_N = \sum_{i=1}^N \frac{p_i^2}{2m}$$

Which is the Hamiltonian for an N particle system. The partition function is then

$$Q_N = \frac{1}{h^{3N} N!} \int e^{-\beta H_N} d^3 p_1 d^3 p_2 \dots d^3 p_N$$

If we look at our example we see that our Hamiltonian is independent of q , therefore this will change our partition function to

$$Q_N = \frac{V^N}{h^{3N} N!} \left(\int e^{-\beta \vec{p}^2/\partial m} d^3 \vec{p} \right) \left(\frac{\partial m \pi}{\beta} \right)^{3N/2} = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N \Rightarrow \text{w/ } \lambda = \frac{h}{\sqrt{2\pi mkT}}$$

λ is referred to as the Thermal De Broglie wavelength. We can now calculate \tilde{Q} ,

$$\tilde{Q}(u, T, v) = \sum_{n=0}^{\infty} z^n Q_n(T, v)$$

For our example this is

$$\tilde{Q}(u, T, v) = \sum_{n=0}^{\infty} \left(\frac{zv}{\lambda^3} \right)^n \frac{1}{n!} = e^{zv/\lambda^3}$$

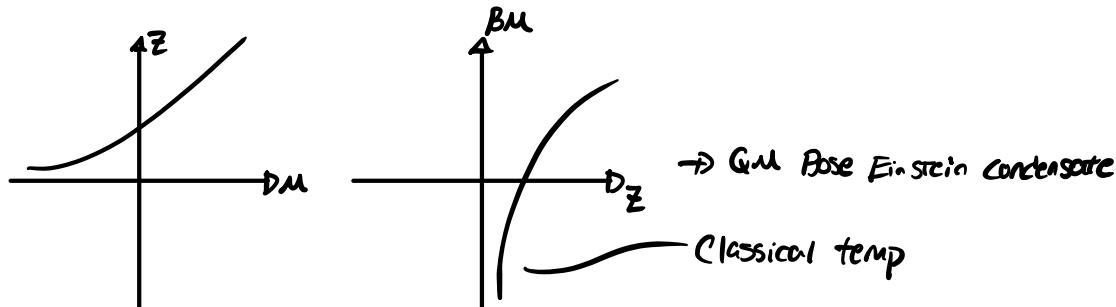
This then means,

$$PV = kT \log(\tilde{Q}) = kT \left(\frac{zv}{\lambda^3} \right) \rightarrow \langle n \rangle \therefore PV = \langle n \rangle kT$$

In the Grand Canonical ensemble $N \rightarrow \langle n \rangle$. Now looking at z

$$z = e^{\beta u} \Rightarrow u = \frac{1}{\beta} \log(z) = \frac{1}{\beta} \log \left(\frac{\lambda^3 \langle n \rangle}{V} \right) = \frac{1}{\beta} \left(\frac{\lambda^3 p}{kT} \right) \therefore u = \frac{1}{\beta} \log \left(\frac{\lambda^3 p}{kT} \right)$$

The chemical potential "u" is a macrovariable. $u \notin T$ determine the pressure of a system



Looking back at $\langle n \rangle$,

$$\langle n \rangle = \frac{zv}{\lambda^3} \rightarrow z = \frac{\lambda^3 \langle n \rangle}{V} \Rightarrow \bar{n} = \frac{\langle n \rangle}{V} = \frac{z}{\lambda^3} = \text{Average density}$$

Can T be negative? No (under fictitious scenarios yes). This means

$$u = \left(\frac{\partial V}{\partial N} \right)_{S,V} \rightarrow \left. N^{\frac{1}{V}} \right|_{S,V} \notin \text{if } u(\cdot)$$

The energy will go down. For the canonical ensemble this looks like



We know that the area of the top slab is the same as the bottom. ($v_L = v_u$) $\therefore (T_L = T_u)$
 The chemical potentials are

$$\mu_L = \left(\frac{\partial A_L}{\partial N_L} \right)_{T_L, V_L}, \quad \mu_u = \left(\frac{\partial A_u}{\partial N_u} \right)_{T_u, V_u}$$

We then ask:

Q: What happens to chemical potentials in equilibrium?

A: $\mu_L = \mu_u$

The Helmholtz free energy can of course be calculated with

$$A_L \rightsquigarrow Q_L = \frac{1}{N_L!} \left(\frac{V_L}{\lambda^3} \right)^{N_L}$$

$$A_u \rightsquigarrow Q_u = \frac{1}{N_u!} \left(\frac{V_u}{\lambda_u^3} \right)^{N_u} e^{-mgyv_u/kT_u}$$

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Continuing from the previous example we find that area, temperature, and number of particles are the same for the upper and lower slab. We then find the chemical potential energies to be

$$\mu_u = \left(\frac{\partial A_u}{\partial N_u} \right)_{T_u, V_u} = -kT \log \left(\frac{V}{N_u \lambda^3} \right) + mgy$$

$$\mu_L = \left(\frac{\partial A_L}{\partial N_L} \right)_{T_L, V_L} = -kT \log \left(\frac{V}{N_L \lambda^3} \right)$$

We now let particles travel between lower and upper slabs. We first calculate the partition function

$$Q(N, T, V) = Q_u(N, T, V) Q_L(N, T, V)$$

We can now calculate μ by minimizing A

$$\left(\frac{\partial A}{\partial N_L} \right)_{T_L, V_L} \Rightarrow \frac{\partial}{\partial N_L} (-kT \log(Q_u Q_L)) \Rightarrow \frac{\partial}{\partial N_L} (-kT(\log(Q_u) + \log(Q_L)))$$

But because $N = N_L + N_u$

$$\frac{\partial}{\partial N_L} = -\frac{\partial}{\partial N_u}$$

This means μ becomes

$$\mu_L = \left(\frac{\partial A}{\partial N_L} \right)_{T_L, V_L} = -kT \left(-\frac{\partial}{\partial N_u} \log(Q_u) + \frac{\partial}{\partial N_L} \log(Q_L) \right)$$

But since μ is being minimized, this can in turn tell us

$$\mu_L = \mu_{\text{H}}$$

We then find from this

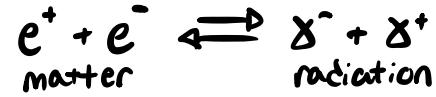
$$N_L = N_U e^{mgy/kT}$$

Where the above tells us that this is the condition for equilibrium.

We now look at 3 different viewpoints of chemical potential

- Thermodynamics view point
- Particle # conservation view point
- Chemical Equilibrium view point

Looking at the Particle # conservation view point

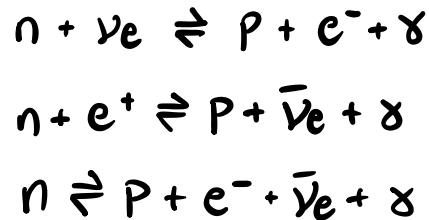


We know that charge and energy must be conserved. This tells us that if we lose an electron we must also lose a positron. We can then write the Hamiltonian as

$$\mathcal{H} = \mathcal{H}_{e^-} + \mathcal{H}_{e^+} - \mu(N_{e^-} - N_{e^+})$$

Looking at a similar scenario

ν ≈ neutrino
 n ≈ neutron
 γ ≈ photon
 P ≈ proton



These were the dominant processes in the Early Universe where the temperature was of the order $T \sim 10^4 \text{ K}$. When T falls below $T_{10} \text{ K}$ the weak interaction rate began to fall behind the cooling rate of the universe. \rightarrow Baryons fall out of equilibrium w/ neutrinos.

Equation of State

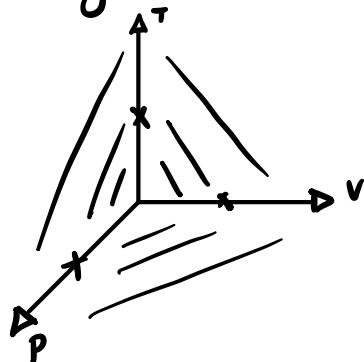
Looking at the ideal gas law

$$PV - NK T = 0$$

The above has 3 independent variables, we can make a substitution to make 2

$$P - \frac{N}{V} kT = P - \rho_N kT = 0$$

Looking at this graphically we have



\Rightarrow can be used to describe a phase

Given some function dependent upon (P, V, T) we have

$$f(P, V, T) = 0$$

The generic equations of state are

$$df = \left(\frac{\partial f}{\partial P}\right)_{T,V} dP + \left(\frac{\partial f}{\partial V}\right)_{P,T} dV + \left(\frac{\partial f}{\partial T}\right)_{V,P} dT = 0$$

This in turn means

$$\left(\frac{\partial f}{\partial V}\right)_{P,T} dV + \left(\frac{\partial f}{\partial T}\right)_{V,P} dT = 0$$

We can then say

$$\left(\frac{\partial V}{\partial T}\right)_P = \left[\left(\frac{\partial T}{\partial V}\right)_P\right]^{-1} = -\frac{\left(\frac{\partial f}{\partial T}\right)_{V,P}}{\left(\frac{\partial f}{\partial V}\right)_{P,T}}, \quad \left(\frac{\partial T}{\partial P}\right)_V = [\dots], \quad \left(\frac{\partial P}{\partial V}\right)_T = [\dots]$$

Taking all of these we find

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1}$$

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The Helmholtz free energy changes by μdN when the number of particles changes by dN

\hookrightarrow at constant $T \notin V$

We write the change in Helmholtz Free energy as

$$dA = -PdV - SdT + \mu dN$$

The internal free energy is

$$A = U - TS$$

We can then find

$$P = -\left(\frac{\partial U}{\partial V}\right)_{N,S}, \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}, \quad T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$$

Which quantities are extensive or intensive?

Extensive : Entropy (S), Energy (U) , Intensive : Pressure, Temperature

Extensive : These properties grow / shrink with the system linearly

Intensive : Opposite of extensive

Looking at the Gibbs Free Energy

$$G = A + PV, \quad dG = dA + PdV + Vdp$$

Inserting $dA = -SdT - PdV + \mu dN$,

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

In terms of A and G

$$A = A(T, N, V), \quad G = G(T, N, P)$$

Examining the partials for G

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dp + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN$$

Looking at another definition for G , we start with

$$dU = Tds - Pdv + \mu dN$$

Multiply all extensive quantities by λ

$$d(\lambda U) = Td(\lambda S) - Pd(\lambda V) + \mu d(\lambda N)$$

Going through this math we find

$$\lambda \underbrace{[dU - (TdS - PdV + \mu dN)]}_{=0} = -d\lambda \underbrace{[U - (TS - PV + \mu N)]}_{=0}$$

We can then say

$$\underbrace{U - TS}_{A} + PV - \mu N = 0$$
$$\underbrace{G}_{G}$$

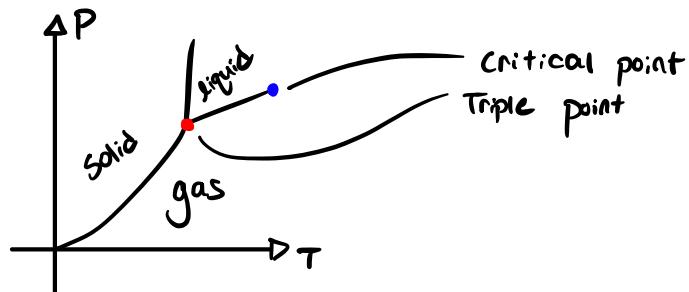
From this we can say

$$G = \mu N$$

Van der Waals Equation of State

To be on the black line

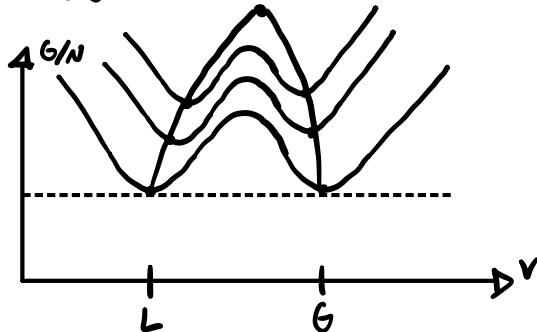
$$T_L = T_G, P_L = P_G, \mu_L = \mu_G$$



We are interested in understanding the critical points. Following the black lines, while present on these lines matter is in transition between the states of matter.

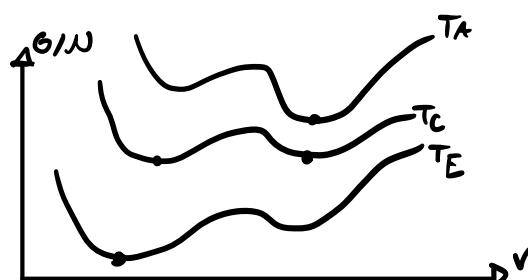
We ask if thermodynamics can tell us whether or not it can tell us the phase of matter. The answer is no.

Examining the Gibbs Free energy we have $G(T, P, N) = \mu N$



The above tells us that at critical points the phases become indistinguishable. In terms of Gibbs Free Energy it tells us that there is no longer two minima.

Looking at two separate systems

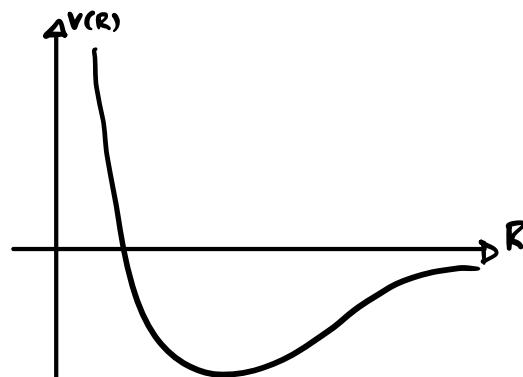


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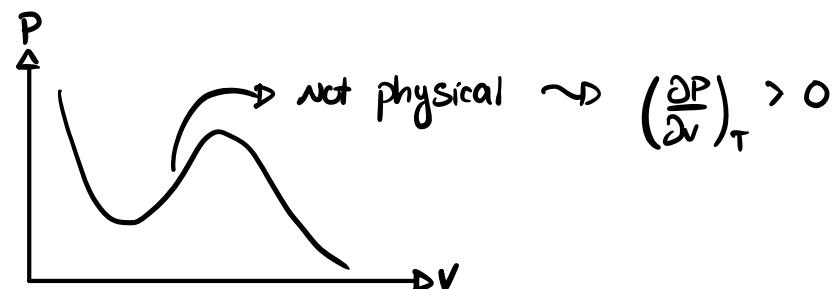
The Van der Waals equation of state

$$P = \frac{kT}{V-b} - \frac{a}{V^2} \rightsquigarrow VP \propto T \text{ if } a=b=0$$

We then look at plotting the potential as a function of distance for two Hydrogen molecules spaced a distance R apart



We have integrated out the electronic degrees of freedom. If we draw an isotherm in a PV diagram



where we can see that the point where the pressure is increasing is not physically possible.

For stability to happen we need

$$\left(\frac{\partial P}{\partial V}\right)_T < 0, \quad K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T > 0$$

where we are now interested in fixing the region where it is unphysical. This is formally called the Maxwell Construction. We then have

$$PV^3 - (P_b + kT)V^2 + aV - ab = 0$$

where we have a cubic equation in V with up to three terms. We choose to enforce two conditions

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

Enforcing these we find

$$(V_c, kT_c, P_c) = \left(3b, \frac{8a}{27b}, \frac{a}{27b^2} \right)$$

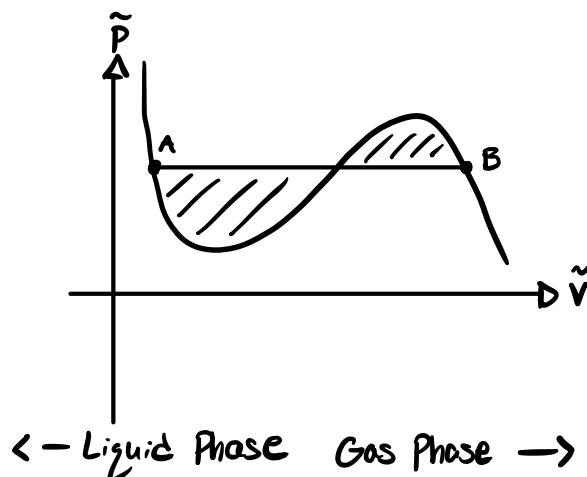
where we make a variable transformation of

$$\tilde{P} = \frac{P}{P_c}, \quad \tilde{T} = \frac{T}{T_c}, \quad \tilde{V} = \frac{V}{V_c}$$

We then have

$$\tilde{P} = \frac{8\tilde{T}}{3\tilde{V}-1} - \frac{3}{\tilde{V}^2}$$

We now continue with the Maxwell Reconstruction



We then have

$$P_A(V_B - V_A) = \int_A^B P(V, T) dV$$