

$$\frac{dP}{dT} = \frac{\Delta S_{l \rightarrow g}}{\Delta V_{l \rightarrow g}}$$

$$\Delta S = \frac{Q}{T}$$

$$\Delta S_{l \rightarrow g} = \frac{m L}{T}$$

$$\frac{dP}{dT} = \frac{m L}{T \Delta V}$$

Clausius-Clapeyron relation

Differential Eqn for phase boundary on a
PT diagram

Ex: Consider the transition from liquid to gas:

Assume: L does not vary with T

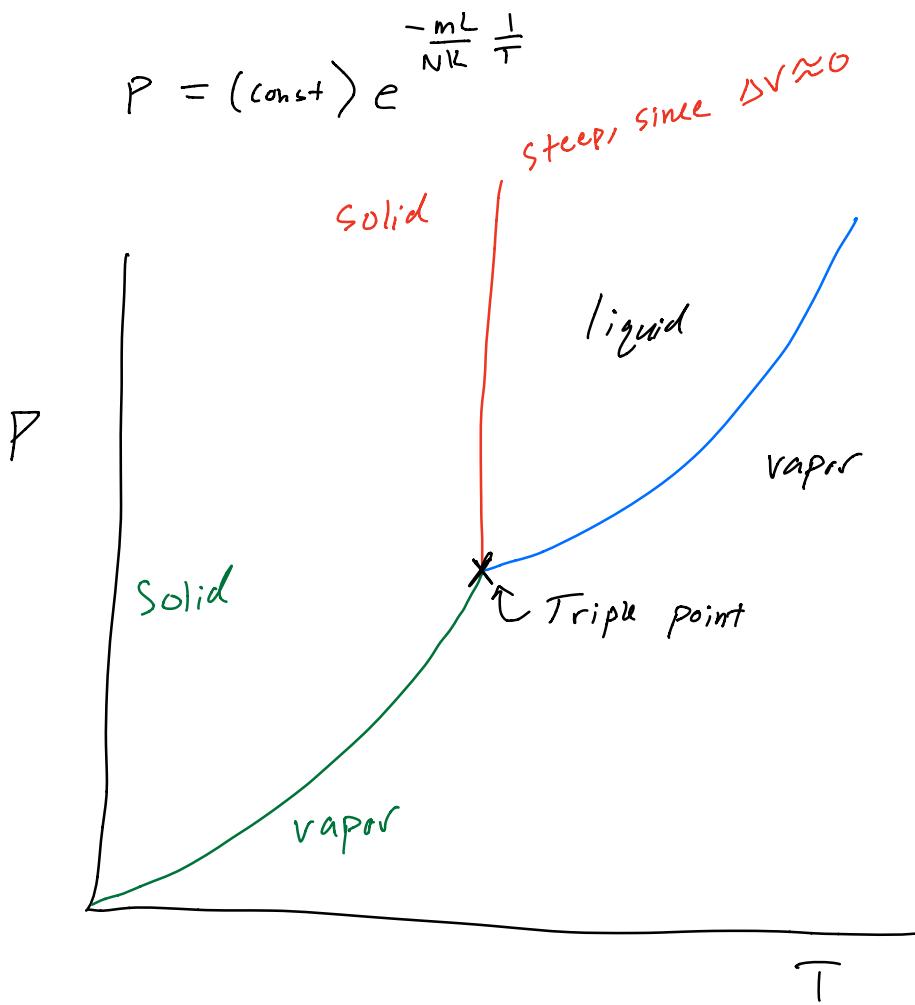
$$V_g \gg V_l \quad (\Delta V \rightarrow V_g - V_l = V)$$

$$\frac{dP}{dT} = \frac{m L}{T V} \qquad V = \frac{N k T}{P}$$

$$\frac{dP}{dT} = \frac{mL}{T \left(\frac{NkT}{P} \right)} = \frac{mL}{Nk} \frac{P}{T^2}$$

$$\frac{dP}{P} = \frac{mL}{Nk} \frac{dT}{T^2}$$

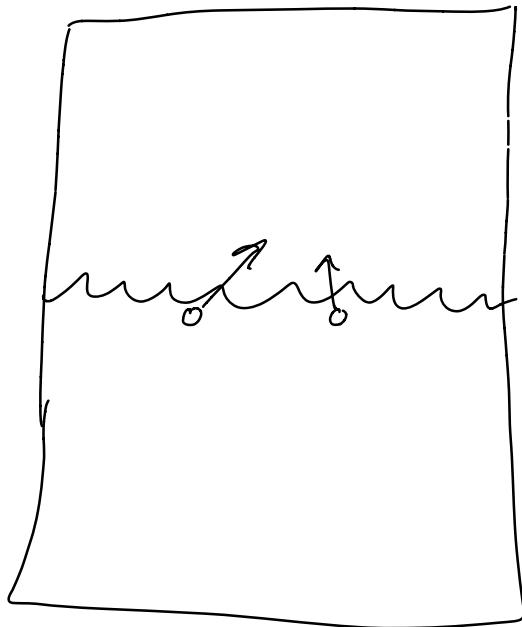
$$\ln(P) = -\frac{mL}{Nk} \frac{1}{T} + \text{const}$$



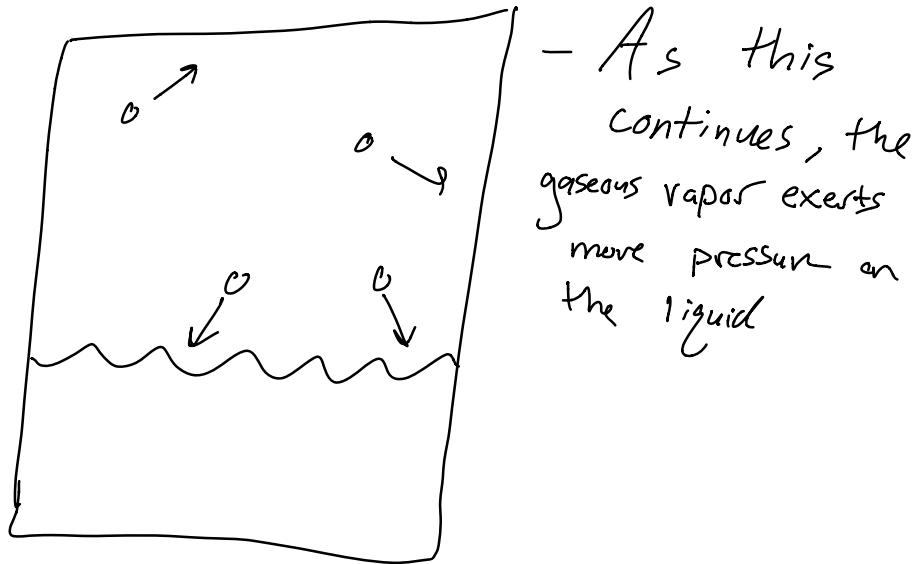
Triple point: all 3 phases exist in equilibrium

The "P" in the above is the vapor pressure: The pressure exerted by the vapor hovering above its condensed state in equilibrium

Ex:



- If I increase the temp, some liquid molecules @ the surface get enough energy to join the gas



- Some of these gas molecules will re-condense into the liquid

Every second, a certain number of liquid turns to gas, and a certain number of gas turns to liquid

Eventually, these rates will equal (equilibrium)

- Pressure of the vapor when this happens is the "vapor pressure"

(If you placed a cup of water in a sealed container, it will evaporate until it reaches this equilibrium)

- What matters is the pressure exerted by water vapor, not air or other molecules

In a mixture of many^{ideal} gases the total pressure is equal to the sum of the partial pressure of each species

$$P = P_A + P_B + P_C + \dots$$

Dalton's Law

- Liquid water only "feels" pressure from water vapor, not all of the air

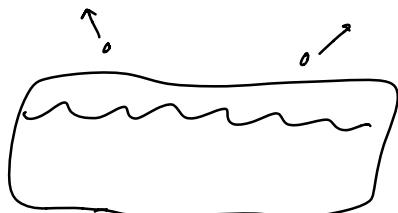
- Evaporation is normally spontaneous, even below 100°C , because the partial pressure of water vapor in the air is below equilibrium

- This is what humidity is: the ratio of current pressure of water vapor to its equilibrium vapor pressure

when $H = 100\%$, no more evaporation

Consider a pot of water on the stove
(no lid)

1) Don't turn stove on



- Pressure of water vapor is low
 - molecules toward the surface will leave + join the gas
 - This doesn't alter the pressure
 - water level slowly depletes into gas

2) Add heat to the water

- molecules leave the surface \oplus faster rate
- At high enough temp, the new vapor molecules exert upward pressure against the atmospheric air molecules
 - This reduces the pressure pushing down on the liquid
- At a high enough temp, the pressure of evaporated molecules is enough to cancel the atmospheric pressure
- Now, even water molecules at the bottom of the pan can become gaseous, forming bubbles which rise to the surface
 - This is called boiling

Boiling point: vapor pressure = exterior pressure

For water, $P(T) = 1 \text{ atm } \oplus 100^\circ\text{C}$

This is why it's easier to boil water \oplus higher altitudes

In the preceding chapters, we have strayed somewhat from microscopic physics

General formula:

$$\text{Find } \sigma_2, \sigma_2 \rightarrow S \quad \frac{\partial S}{\partial U} = \frac{1}{T} \text{ etc...}$$

$$\frac{\partial U}{\partial T} = C_v$$

Did this for

Einstein Solids

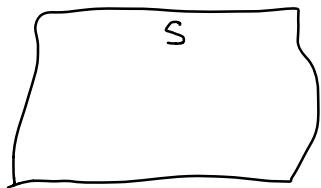
Ideal gas (monoatomic)

Paramagnet

Generally v. hard / impossible to explicitly find

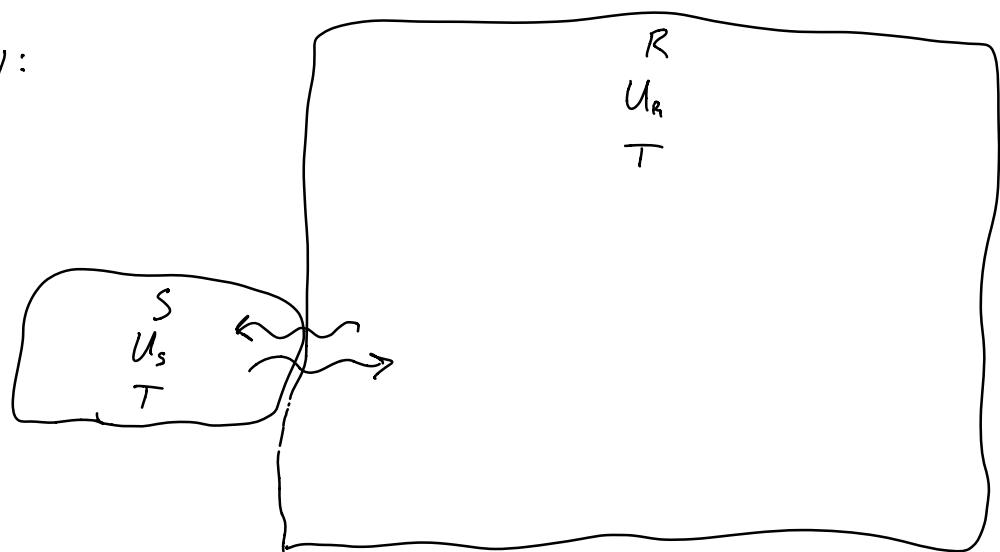
σ_2

Consider a system we are interested in
(ideal gas, E. solid, etc ... anything!)



- If the system is isolated: All microstates are equally likely, since U_s doesn't change
- Consider: If the system is allowed to exchange energy w/ a much larger environment
 - (Energy flows into + out of a glass of water)

Model:



- System in thermal contact with a large reservoir
 - ④ temp T

$$\text{Total energy} = U_s + U_r$$

microstates of combined system still equally likely

- We don't want to describe the reservoir
- Interested only in the system

Now, microstates of the system are not
equally likely!

- Microstates w/ different energies have different probabilities
- Microstates w/ same energy still equally likely

We want to know $P(U_{sys})$ vs U_{sys}

We suspect that higher energies will
be less likely

1) Total energy

$$U_{tot} = U_r + U_s \quad \left(\frac{U_s}{U_{tot}} \ll 1 \right)$$

2) Prob. that system is in state w/ energy U_s

$$p(U_s) \propto \mathcal{S}_s(U_s)$$

$$\mathcal{S}_+ = \mathcal{S}_s \mathcal{S}_r$$

$$p(U_s) \propto \mathcal{S}_r(U - U_s)$$

"Prob that system in state with energy U_s

prop to # of microstates in which
the reservoir has $U_r = U - U_s$ "

We write it this way because $U_s \ll U$, we can
Taylor expand!

$$\mathcal{S}(U - U_s) \approx \mathcal{S}(U) - \frac{\partial \mathcal{S}(U)}{\partial U} U_s + \mathcal{O}(U_s^2)$$

What is $\frac{\partial \underline{S}}{\partial u}$? (Looks like $\frac{\partial S}{\partial u}$)

$$\frac{\partial S}{\partial u} = K \frac{\partial \ln \underline{S}}{\partial u} = \frac{K}{\underline{S}} \frac{\partial \underline{S}}{\partial u}$$

$$\frac{\partial S}{\partial u} = \frac{1}{T}$$

$$\frac{\partial \underline{S}}{\partial u} \left(\frac{K}{\underline{S}} \right) = \frac{1}{T}$$

$$\frac{\partial \underline{S}}{\partial u} = \frac{\underline{S}(u)}{KT}$$

$$\underline{S}(u - u_s) \approx \underline{S}(u) - \underline{S}(u) \frac{u_s}{KT}$$

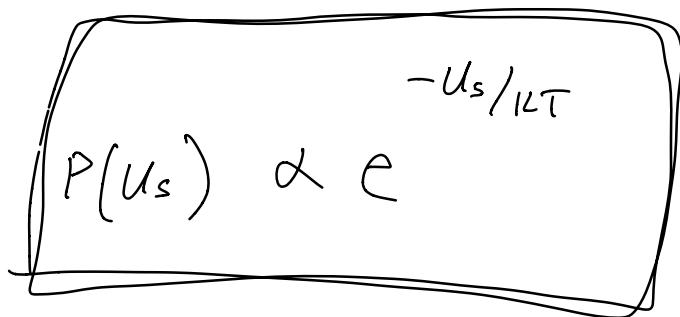
$$\frac{\underline{S}(u - u_s) - \underline{S}(u)}{u_s} = - \frac{\underline{S}(u)}{KT}$$

$$\frac{\partial \underline{S}}{\partial u_s} = - \frac{1}{KT} \underline{S}$$

$$\frac{d\ln \Omega}{\Omega} = -\frac{1}{kT} dU_s$$

$$\ln \Omega = -\frac{U_s}{kT} + \text{const}$$

$$\Omega(U-U_s) \propto e^{\frac{-U_s}{kT}}$$

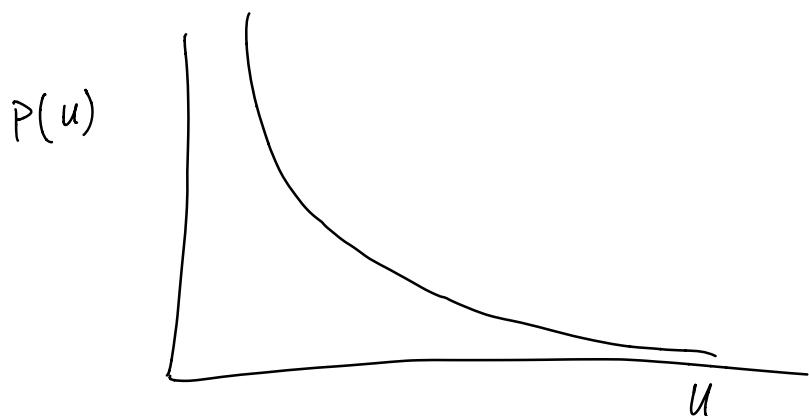


Boltzmann Factor

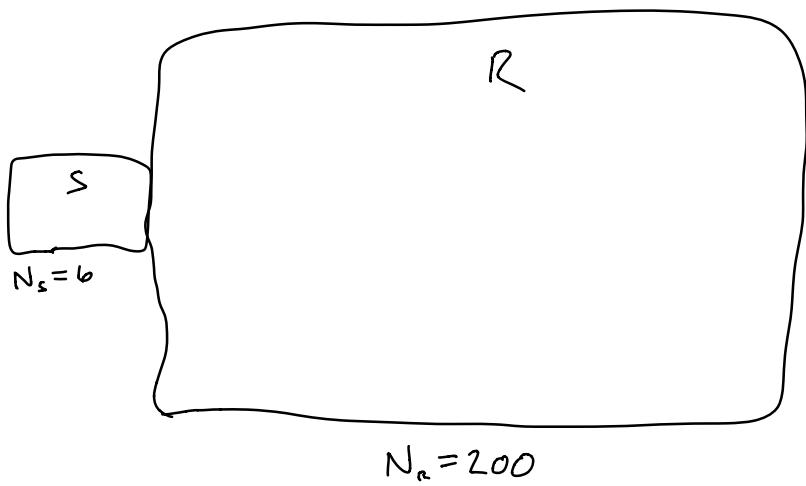
Gives the relative prob that

the system is in a microstate

w/ energy U_s



Ex: Two Einstein solids



$$q_{tot} = q_s + q_r = \text{const} = q = 500$$

$$\Omega_{tot} = \Omega_s \Omega_r$$

$$\Omega_{tot} = \frac{(q_s + N_s - 1)!}{q_s! (N_s - 1)!} \frac{(q - q_s + N_r - 1)!}{(q - q_s)! (N_r - 1)!}$$

We know the relative prob

$$P(u) \propto e^{-u/kT} \quad (\text{drop } S \text{ subscript})$$

The total probability

$$P \propto e^{-u/kT} \rightarrow P = a e^{-u/kT}$$

$$\sum_i a e^{-u_i/kT} = 1$$

$$a = \frac{1}{\sum_i e^{-u_i/kT}}$$

$$P(u=u_i) = \frac{e^{-u_i/kT}}{\sum_i e^{-u_i/kT}}$$

$$Z = \sum_i e^{-u_i/kT} \quad (\text{canonical partition function})$$

$$P(u=u_i) = \frac{1}{Z} e^{-u_i/kT}$$

Sum over all possible energies

$$Traditionally, \quad \beta = \frac{1}{kT}$$

Example : spin up/down elec (paramagnet)

$\circlearrowleft \uparrow \text{ or } \downarrow$

$B \uparrow$

$$H = -\mu B \quad (\mu = \pm 1)$$

$\overbrace{\quad}^{\text{Hamiltonian, not enthalpy}}$

$$Z = \sum_i e^{-\beta \mu_i} = e^{-\beta \mu B} + e^{\beta \mu B} \\ = 2 \cosh(\beta \mu B)$$

$$P(\mu = \mu B) = \frac{e^{-\beta \mu B}}{2 \cosh(\beta \mu B)}$$

Example: QM harmonic oscillator

(Like the Einstein Solid but only one)

In thermal contact with res @ temp T

Possible energies:

$$E_n = (n + \frac{1}{2})\hbar\omega$$

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta(n + \frac{1}{2})\hbar\omega}$$

$$Z = e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}$$

An aside: solving a geometric series

$$S = \sum a r^n = a + ar + ar^2 + \dots + ar^n$$
$$a = e^{-\frac{1}{2}\beta\hbar\omega}, \quad r = e^{-\beta\hbar\omega}$$



$$S = a + ar + ar^2 + \dots + ar^n$$

mult by r

$$rS = ar + ar^2 + ar^3 + \dots + ar^{n+1}$$

$$S - rS$$

$$S = a + ar + ar^2 + \dots + ar^n$$

mult by r

$$rS = ar + ar^2 + ar^3 + \dots + ar^{n+1}$$

$$S - rS = a - ar^{n+1}$$

$$S(1-r) = a(1-r^{n+1})$$

$$S = a \left(\frac{1-r^{n+1}}{1-r} \right) ; \quad r \neq 1$$

if $n \rightarrow \infty$ AND $|r| < 1$, then $r^{n+1} \rightarrow 0$

$$S = \frac{a}{1-r} ; \quad |r| < 1$$

$$S = \frac{a}{1 - r}$$

$$a = e^{-\frac{1}{2}\beta k\omega}, \quad r = e^{-\beta k\omega}$$

$$Z = S = \frac{e^{-\frac{1}{2}\beta k\omega}}{1 - e^{-\beta k\omega}}$$

mult top & bot by $e^{\frac{1}{2}\beta k\omega}$

$$= \frac{1}{e^{\frac{1}{2}\beta k\omega} - e^{-\frac{1}{2}\beta k\omega}}$$

$$Z = \frac{1}{2 \sinh(\frac{1}{2}\beta k\omega)}$$

$$P(n) = \frac{e^{-(n+\frac{1}{2})\beta k\omega}}{2 \sinh(\frac{1}{2}\beta k\omega)}$$

OK, so we know the probability distribution, big deal

Why is this useful?

We can use the probability distribution to obtain macroscopic (average) quantities

Ex: Say I have 5 atoms

Energies (above min) can be: 0, 4, 7 eV

Upon measurement

2 atoms have 0 eV

2 have 4 eV

1 has 7 eV

What is the average energy of all the atoms?

$$\bar{E} = \frac{(0 \text{ eV}) \cdot 2 + (4 \text{ eV}) \cdot 2 + (7 \text{ eV}) \cdot 1}{5}$$

$$\bar{E} = 3 \text{ eV}$$

Can write like this:

$$\bar{E} = (0 \text{ eV}) \cdot \frac{2}{5} + (4 \text{ eV}) \cdot \frac{2}{5} + (7 \text{ eV}) \cdot \frac{1}{5} = 3 \text{ eV}$$

$$\bar{E} = (E_{\text{state } 1})(P_{\text{state } 1}) + (E_{\text{state } 2})(P_{\text{state } 2}) + (E_{\text{state } 3})(P_{\text{state } 3})$$

$\text{Prob}(E)$ is the probability distribution

If we know the probability dist in advance,

we can calculate the expected value

Example: I put 10 dollar bills (of different values) in a bag. 2 are 20's, 3 are 10's 1 is a 5, 4 are 1's

Here's the game: you can randomly select 1 of the bills from the bag (no peeking!) but I charge you \$6.

Do you play?

How much should you expect to win if you play?

$$\text{Expected winnings} = \langle m \rangle$$

$$\langle m \rangle = \$20 \cdot P(\$20) + \$10 P(\$10) + \dots$$

$$\langle m \rangle = 20(0.2) + 10(0.3) + 5(0.1) + 1(0.4)$$

$$\langle m \rangle = \$7.90$$

it cost \$6 to play, but you should expect to win \$7.90

so you come out ahead, by \$1.90

- This is on average! If you played the game 1000 times, sometimes you draw \$20, sometimes \$1 (never \$7.90) but the average amount will be

$$\$7.90$$

$$\text{Expected outcome} = \sum_{\text{all outcomes}} (\text{outcome}_i) (P_{\text{outcome}_i})$$

$$\langle y \rangle = \sum_i y_i \cdot P(y_i)$$

$$\langle E \rangle = \sum_i E_i \cdot P(E_i)$$

$$= \sum_i E_i \frac{e^{-\beta E_i}}{Z}$$

$$\langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-\beta E_i}$$

Ex: The paramagnet

$$\begin{aligned} Z &= 2 \cosh(\beta \mu B) \\ \langle E \rangle &= \frac{1}{2 \cosh(\beta \mu B)} \left[\mu B e^{-\beta \mu B} + (-\mu B) e^{\beta \mu B} \right] \\ &= \frac{\mu B}{2 \cosh(\beta \mu B)} (-2 \sinh(\beta \mu B)) \end{aligned}$$

$$\langle E \rangle = -\mu B \tanh(\beta \mu B)$$

If there N many dipoles,
then we expect the total energy
to be simply $N \times$ the average

$$\langle E_{\text{tot}} \rangle = N \langle E \rangle$$

$\langle E_{\text{tot}} \rangle$ is just what we've been
calling " U "

$$U = N \langle E \rangle = \frac{N}{Z} \sum_i E_i e^{-\beta E_i}$$

$$U = -N \mu B \tanh\left(\frac{\mu B}{kT}\right), \text{ same as before}$$

$$\langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-\beta E_i}$$

$$E_i e^{-\beta E_i} = -\frac{\partial}{\partial \beta} e^{-\beta E_i}$$

$$\begin{aligned}\langle E \rangle &= -\frac{1}{Z} \sum_i \frac{\partial}{\partial \beta} e^{-\beta E_i} \\ &= -\frac{1}{Z} \frac{\partial}{\partial \beta} \left(\sum_i e^{-\beta E_i} \right) \\ &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta}\end{aligned}$$

$$\boxed{\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln(Z)}$$

$$Z = 2 \cosh(\beta \mu \beta)$$

$$\frac{\partial Z}{\partial \beta} = 2 \mu \beta \sinh(\beta \mu \beta)$$

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{1}{2 \cosh(\beta \mu \beta)} (2 \mu \beta \sinh(\beta \mu \beta))$$

$$\langle E \rangle = -\mu \beta \tanh(\beta \mu \beta) \quad \checkmark$$

We can also find $M = N(\mu)$

$$\langle \mu \rangle = \mu \frac{e^{\beta \mu \beta}}{Z} + (-\mu) \frac{e^{-\beta \mu \beta}}{Z}$$

$$= \frac{\mu}{Z} \left(e^{\beta \mu B} - e^{-\beta \mu B} \right)$$

$$= \frac{2 \mu \sinh(\beta \mu B)}{2 \cosh(\beta \mu B)} = \mu \tanh(\beta \mu B)$$

$M = N \mu \tanh(\beta \mu B)$