State Variables
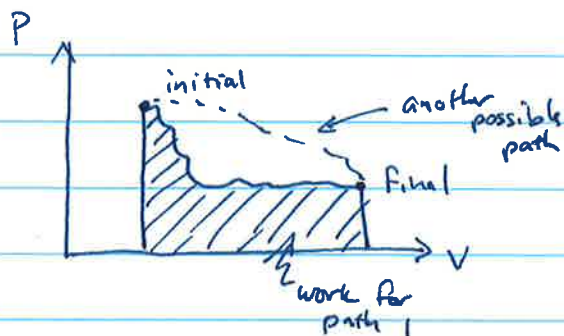
$Q(N,V,T)$

P, V, T, μ ~~chemical potential~~ or any 2 of them.

Pressure is a force per area

$$\frac{f}{A} = P$$

$$f = PA$$

area A

$$W = \int_i^f P \, dV$$

$$work = f \cdot \Delta L$$

$$f = P \cdot A$$

$$work = PA \Delta L$$

$$W = P\Delta V$$

So __work__ will depend on the path we take from initial to final states.

If there is a function that does not depend on path: i.e.

$$\int_i^f dU = U_f - U_i = \Delta U$$

U is then called a __state__ function and it's value depends only on current state of the system (P, V, T) and not on the path we took to get there

__State Funcs__

U = total energy
S = total entropy
H = enthalpy
G = gibbs free energy
A = Helmholtz free energy
PV

__Non-state funcs__

work (ω)
heat (q)

Ties between what we've done so far:

$$\rho(\vec{q}, \vec{p}) = \text{density of our ensemble near point } \vec{q}, \vec{p} \text{ in phase space}$$

$$S \equiv -k_B \iint \rho(\vec{q},\vec{p}) \ln\left[\rho\frac{(\vec{q},\vec{p})}{h^{3N}} \right] d\vec{q}\, d\vec{p}$$
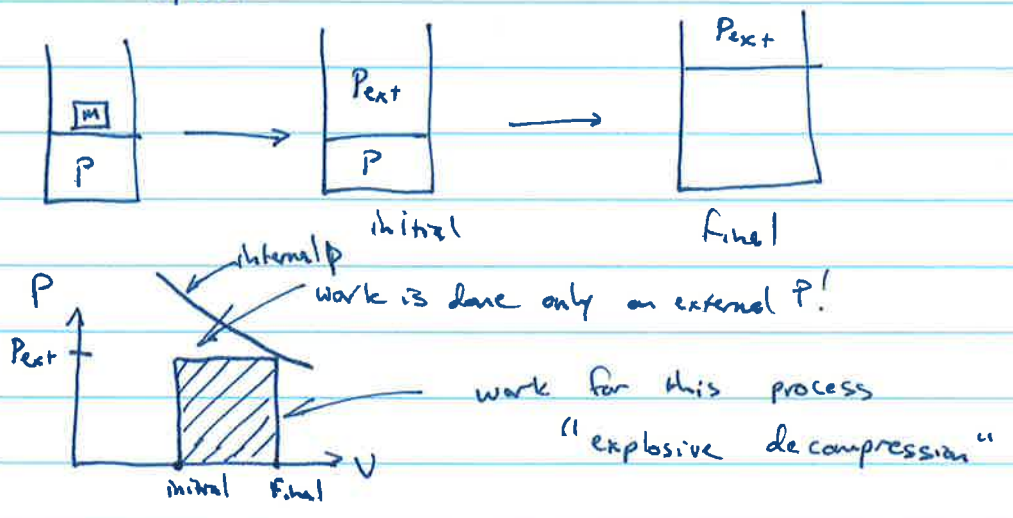
↳ definition of the entropy of an ensemble

$$U = \langle E \rangle = \cancel{} -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

$$A = -$$

Reversible processes:

We must have $\quad P_{ext} > P \quad$ to compress a gas

or $\quad P_{ext} < P \quad$ to expand a gas

Consider this expansion:

initial   final

internal p
work is done only on external P!

work for this process
"explosive decompression"

initial final

Another way to do the same expansion

remove
1 grain of sand at a time
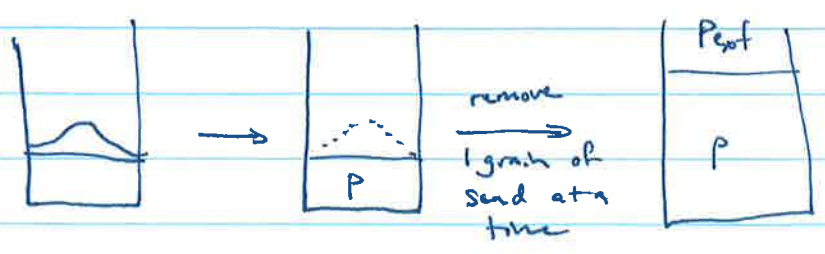
Here, P_{ext} is kept just barely above P for the entire expansion

work for "reversible expansion"

work for explosive expansion
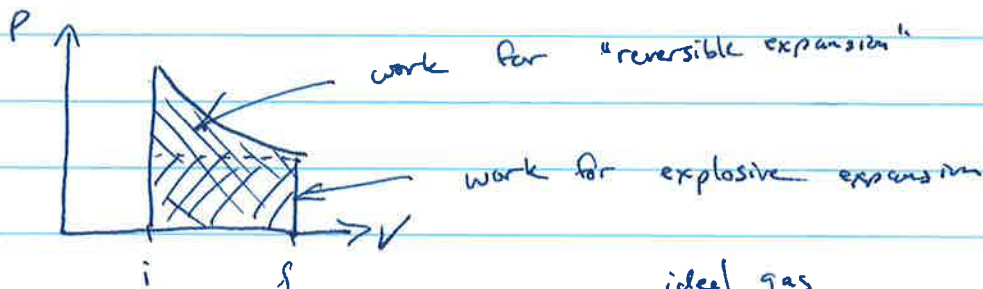
$$W_{rev} = -\int_{init}^{final} P_{internal} \, dV = -\int_{init}^{fin} \frac{nRT}{V} \, dV$$

ideal gas

$$= -nRT \int_i^f \frac{dV}{V} = -nRT \left[\ln V \right]_{V_i}^{V_f}$$

$$\boxed{W_{rev} = -nRT \ln \frac{V_f}{V_i}}$$

If $V_f > V_i$, $-W_{rev} \leq 0$, so the system has done work ($\oplus \longrightarrow$ surroundings do work)

If $V_f < V_i$, $W_{rev} > 0$, so the surroundings did work on the system

---

Energy is a state function

$$\int_1^2 \delta w = w \quad \longleftarrow \text{inexact differential} \quad \longleftarrow \text{path funct}$$

$$\int_1^2 \delta q = q \quad \longleftarrow \text{heat \& work are both path functs}$$

$$\int_1^2 dU = U_2 - U_1 = \Delta U \quad \longleftarrow \text{exact differential}$$

Both heat & work are forms of energy, so if we lose energy going from 1 state to another, it goes in to heat or work or a combination of the 2:

$$dU = \delta q + \delta w$$
$$\Delta U = q + w$$

} forms of the 1st law

1st thing to notice:

δq & δw are path dependent, but their sum dU is <u>not</u>

2nd thing to notice: this is a conservation law

If we make a complicated path

ΔU for this must be 0!
1) total work theat is conserved
2) total energy is conserved.

Energy laws tend to favor <u>Stable</u> equilibria

$$S \equiv k_B \ln W$$

$\hat{} $ entropy

← degeneracy or multiplicity of microscopic states that make up macroscopic state

<u>Maximizing</u> entropy also maximizes W

Connecting W to <u>state</u> probabilities:

$$W = \frac{N!}{n_1! \, n_2! \, \cdots \, n_t!}$$

← N trials with t possible outcomes

$n_i = $ # of outcomes in state i

<u>Stirling's approximation</u>

$$\ln n! \cong n \ln(n) - n$$

$$\approx n \ln(n) - n \ln(e)$$

$$= n \ln\left(\frac{n}{e}\right)$$

$$\ln n! = \ln\left(\left(\frac{n}{e}\right)^n\right)$$

$$n! \approx \left(\frac{n}{e}\right)^n$$

$\therefore$

$$W = \frac{(N/e)^N}{\left(\frac{n_1}{e}\right)^{n_1} \left(\frac{n_2}{e}\right)^{n_2} \cdots \left(\frac{n_t}{e}\right)^{n_t}}$$

Since $n_1 + n_2 \cdots + n_t = N$ there are the same number of e's on top and bottom, so:

$$W = \frac{N^N}{n_1^{n_1} \, n_2^{n_2} \cdots \, n_t^{n_t}}$$

<u>And</u>, since $\qquad P_1 = \frac{n_1}{N} \qquad , \qquad P_2 = \frac{n_2}{N}$

$$P_1^{n_1} = \frac{n_1^{n_1}}{N^{n_1}} \qquad , \qquad P_2^{n_2} = \frac{n_2^{n_2}}{N^{n_2}}$$

We have:

$$W = \frac{N^N}{n_1^{n_1} \, n_2^{n_2} \cdots n_t^{n_t}} = \frac{N^{n_1} * N^{n_2} \cdots N^{n_t}}{n_1^{n_1} * n_2^{n_2} \cdots n_t^{n_t}}$$

$$= \frac{1}{p_1^{n_1} \, p_2^{n_2} \cdots p_t^{n_t}}$$

Entropy is in terms of $\ln W$, so:

$$\ln W = \ln 1 - n_1 \ln p_1 - n_2 \ln p_2 \cdots - n_t \ln p_t$$

$$\ln W = - \sum_{i=1}^{t} n_i \ln p_i$$

$$\frac{1}{N} \ln W = - \sum_{i=1}^{t} \frac{n_i}{N} \ln p_i = - \sum_{i=1}^{t} p_i \ln p_i$$

$$\frac{S}{N k_B} = - \sum_{i=1}^{t} p_i \ln p_i \qquad \longleftarrow \text{probability of outcome } i$$
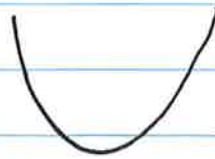
Entropy is a function of the <u>distribution</u> of state probabilities!

What distribution of p_i values will maximize the entropy?
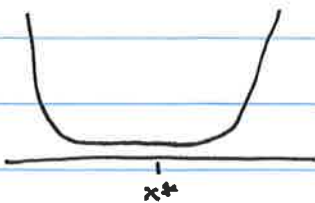
Extremum Principles

Stable: $f(x)$

$f(x) - f(x^*) > 0$
$\forall x \neq x^*$

$\left(\dfrac{\partial f}{\partial x}\right)_{x^*} = 0$

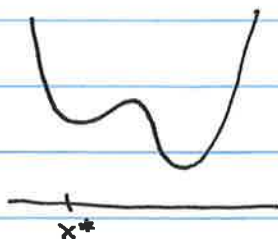$\left(\dfrac{\partial^2 f}{\partial x^2}\right)_{x^*} > 0$

Neutral:

$\left(\dfrac{\partial f}{\partial x}\right)_{x^*} = 0$

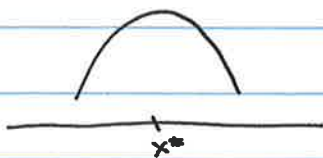and $\left(\dfrac{\partial^2 f}{\partial x}\right)_{x^*} = 0$

Metastable:

$\left(\dfrac{\partial f}{\partial x}\right)_{x^*} = 0$

$\left(\dfrac{\partial^2 f}{\partial x^2}\right)_{x^*} > 0$

$f(x) - f(x^*) > 0$
for small $|x - x^*|$
but **not** for **all** x

Unstable:
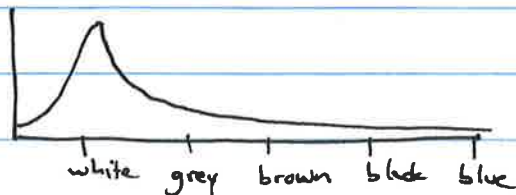
$\left(\dfrac{\partial f}{\partial x}\right)_{x^*} = 0$

$\left(\dfrac{\partial^2 f}{\partial x^2}\right)_{x^*} < 0$

Maximizing Entropy

$P(\text{socks})$

low-entropy
distribution

white   grey   brown   black   blue

high-entropy
distribution $\longrightarrow$

what distribution will give us the maximum entropy?

$\dfrac{dS}{dp_i} = 0$ for all p_i and $\dfrac{d^2 S}{dp_i^2} < 0$

There is a constraint, however:

$$\sum_{i=1}^{t} P_i = 1 \qquad \longleftarrow \quad \text{total probability must be conserved}$$

Method of Lagrange Multipliers applied to Maximizing Entropy

$$S = -k \sum_i P_i \ln P_i$$

$$\delta S = -k \sum_i (\ln P_i + 1) dP_i \qquad \longleftarrow \quad \text{won't preserve constraint}$$

$$F = -k \sum_i P_i \ln P_i + \alpha P_i$$

$$\delta F = -k \sum_i \underbrace{(\ln P_i + 1 + \alpha)}_{\overset{\|}{0}} dP_i \qquad \longleftarrow \quad \text{will preserve constraint}$$

$\longleftarrow$ if all of these are zero, the sum over i will also be zero

$\longleftarrow$ Probability of state i that maximizes entropy

$$-k\left(\ln P_i^* + 1 + \alpha\right) = 0$$

$$\ln P_i^* = -1 - \alpha$$

$$P_i^* = e^{-1-\alpha} \qquad \longleftarrow \quad \text{no dependence on the state } i$$

Conservation

$$\sum_{i=1}^{t} P_i^* = t\left(e^{-\alpha-1}\right) = 1$$

$$\text{So} \quad e^{-\alpha-1} = \frac{1}{t} \qquad \longleftarrow \quad \begin{array}{l}\text{solves Lagrange} \\ \text{multiplier } \alpha \\ \text{in terms of} \\ \text{number of states} \\ t.\end{array}$$

And individual state probabilities:

$$\frac{P_i^*}{\sum_i P_i^*} = \frac{e^{-1-\alpha}}{t\left(e^{-\alpha-1}\right)} = \frac{1}{t}$$

Maximum entropy = Equal a priori probabilities = Probability independent of state

There's one more constraint

$$U = \langle E \rangle = \frac{E}{N} = \sum_{i=1}^{t} P_i \, \varepsilon_i$$

Moving probability around must conserve total energy as well as total probability

$\therefore \quad \delta F = 0 \quad$ where

second Lagrange multiplier

$$F = -k \sum_{i=1}^{t} \left[P_i \ln P_i + \alpha P_i + \beta \varepsilon_i P_i \right]$$

$$\delta F = -k \sum_{i=1}^{t} \left[\ln P_i^* + 1 + \alpha + \beta \varepsilon_i \right] dP_i = 0$$

$$\parallel$$
$$0 \quad \longleftarrow \quad$$ same logic. Total sum will be zero when **each** contribution is zero

$$\ln P_i^* + 1 + \alpha + \beta \varepsilon_i = 0$$

$$\ln P_i^* = -1 - \alpha - \beta \varepsilon_i$$

$$P_i^* = e^{-1-\alpha} e^{-\beta \varepsilon_i}$$

Now we need to apply the constraints:

$$\sum_{i=1}^{t} P_i^* = 1 = \sum_{i=1}^{t} e^{-1-\alpha} e^{-\beta \varepsilon_i} = e^{-1-\alpha} \sum_{i=1}^{t} e^{-\beta \varepsilon_i} = 1$$

Conservation of probability

$$\sum_{i=1}^{t} e^{-\beta \varepsilon_i} = e^{1+\alpha} \quad \longrightarrow \quad$$ let's call this total $= q$

Now the energy constraint:

$$\langle E \rangle = \sum_{i=1}^{t} \varepsilon_i P_i = \sum_{i=1}^{t} e^{-1-\alpha} e^{-\beta \varepsilon_i} \varepsilon_i = \sum_{i=1}^{t} \frac{1}{q} e^{-\beta \varepsilon_i} \varepsilon_i$$

$$\langle E \rangle = \frac{1}{q} \sum_{i=1}^{t} \varepsilon_i e^{-\beta \varepsilon_i}$$

this second Lagrange multiplier is why we use
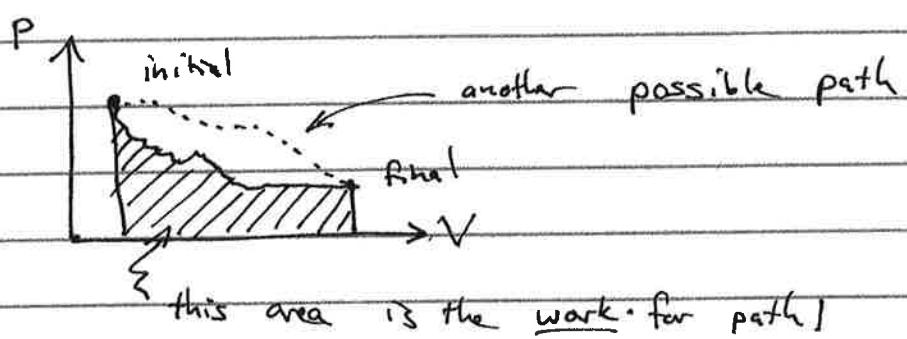
$$\beta = \frac{1}{k_B T}$$

State variables

$$P_1, V_1, T_1 \xrightarrow{\text{add heat}} \begin{array}{c} q \\ \text{under various} \\ \text{conditions} \end{array} \xrightarrow{\text{calculate } \omega} P_2, V_2, T_2, \Delta U \text{ and } \Delta S$$

If we change the state variables, we can do work:

this area is the work for path 1

Work depends on the path we take from initial to final states

$$\delta w = -\int_i^f P dV$$

1st law of thermodynamics:

$$\boxed{dU = \delta w + \delta q}$$

state function   path dependents

A state function doesn't depend on the path we take, just on the initial & final states:

$$\int_i^f dU = U_f - U_i = \Delta U$$

$\delta q > 0$ when heat flows into a system

$\delta w > 0$ when work is performed on a system

Examples of State Functions

U = internal energy

S = entropy

H = enthalpy

G = gibbs free energy

A = Helmholtz free energy
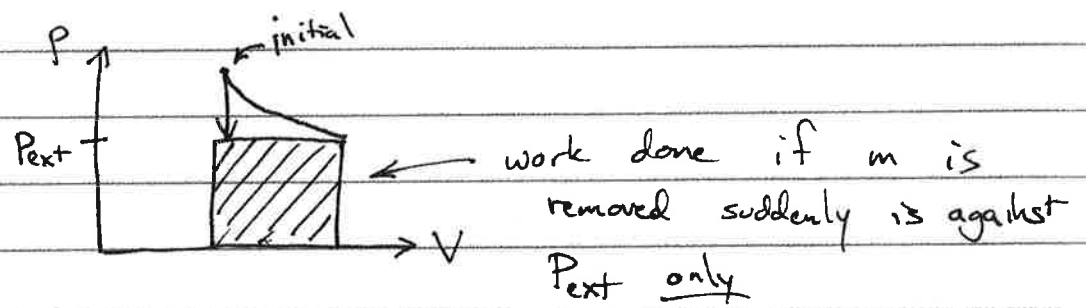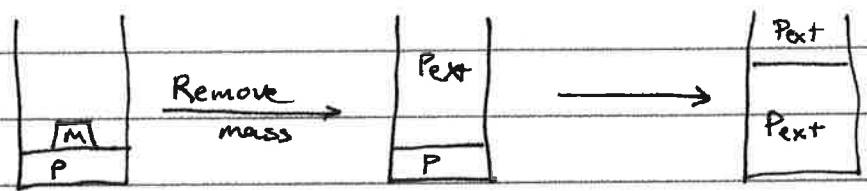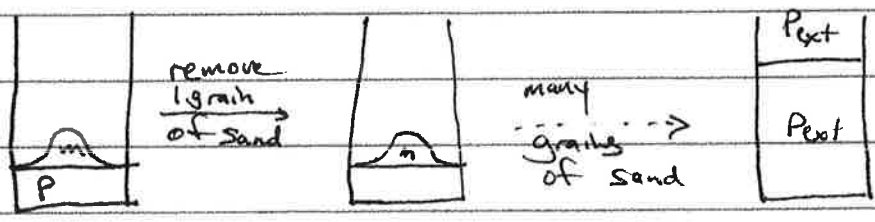
Pressure - Volume work : $\delta w = -P_{ext} dV$

valid only if the expansion or compression occurs very slowly in a quasistatic process

Note: $\delta w > 0$ if $dV < 0$ work done on system

Consider this expansion:

work done if m is removed suddenly is against P_{ext} only

Another way to do the same expansion

In this gradual expansion, the external pressure is kept just above P for the entire expansion

work for reversible expansion
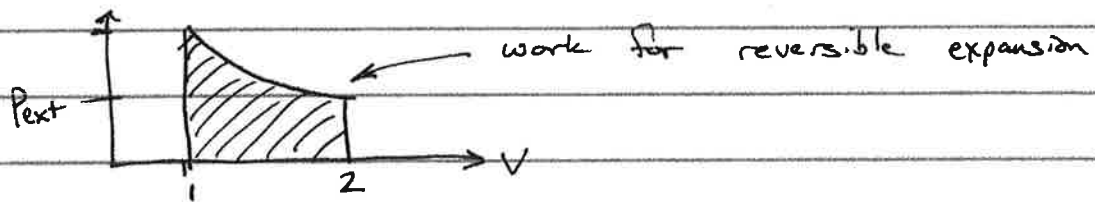
$$W_{rev} = -\int_1^2 P_{internal} \, dV$$

If the gas is an ideal gas, $P = \dfrac{nRT}{V}$

$$W_{rev} = -\int_1^2 \frac{nRT}{V} \, dV = -nRT \int_1^2 \frac{1}{V} \, dV$$

$$= -nRT \left[\ln V\right]_1^2 = -nRT \ln \frac{V_2}{V_1}$$

- If $V_2 > V_1$ $W_{rev} \leq 0$ so the system has done work (remember, $\oplus \rightarrow$ surroundings do work)

- If $V_2 < V_1$ $W_{rev} > 0$, so the surroundings did work on the gas.

∴ Reversible (isothermal) expansions & compressions make W_{rev} as close as possible to zero!

Heat

- Heat describes energy transfer via thermal exchange
- Heat capacity is heat uptake per unit temperature change:

$$C_V = \left(\frac{\delta q}{\delta T}\right)_V = \left(\frac{\partial u}{\partial T}\right)$$

since V is <u>fixed</u>

$$\delta w = 0$$

<u>Energy</u> is a <u>state</u> function:

inexact differential

$$\int_1^2 \delta w = w \longleftarrow \text{path function}$$

$$\int_1^2 \delta q = q \longleftarrow \text{heat \& work are generally path functions}$$

exact differential

$$\int_1^2 du = u_2 - u_1 = \Delta u$$

If V is <u>fixed</u>:

$$\Delta u = \int_{T_1}^{T_2} C_V(T)\, dT = C_V(T_2 - T_1)$$

only if C_V is <u>constant</u> over temperature range $T_1 \rightarrow T_2$

<u>In general</u>, $C_V(T)$ must be measured experimentally or <u>derived</u> from statistical mechanics. Thermodynamics alone cannot deduce it.

Let's explore ideal gases for a bit:

$$U = U(T, V) \longleftarrow \text{internal energy, } \langle E \rangle \text{ depends only on these because } Q(N,V,T)$$

$$U = \frac{\langle E \rangle}{N}$$

So:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

↗ exact
differential

↗ all the stuff U
can depend on.

We know:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{for an ideal gas}$$

(they don't interact, so their energy
can't depend on density changes.)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT$$

We've derived $C_V = \frac{3}{2} R$ for an ideal gas,

$$\underline{\Delta U = C_V (T_2 - T_1)}$$

Reversible processes

Consider 3 possibilities

1) work ⟶ work

2) work ⟶ heat

3) heat ⟶ work

1) In principle, work ⟶ work can be done
with 100% efficiency (if friction can be eliminated)
typical electric motors convert electricity
to mechanical work with 95% efficiency

2) Work ⟶ heat can be done with 100% efficiency
(sandpaper, stirring water)

3) heat $\rightarrow$ work is only possible with efficiencies $< 30\% - 50\%$

Why?

- Interconverting work $\overset{\text{with maximal efficiency}}{\wedge}$ just requires slow conversion (quasistatic)
- Heat $\rightarrow$ work with maximal efficiency requires reversible processes.

A reversible process is one in which returning the system to its initial state also returns the surroundings to their initial conditions

$$dS = \frac{\delta q_{rev}}{T} \quad \text{for a reversible process}$$

$$\delta q_{rev} = dU = C_V dT$$

$$\Delta S = \int_{T_A}^{T_B} \frac{C_V}{T} dT = C_V \ln\left(\frac{T_B}{T_A}\right)$$

$\underset{\text{any reversible process}}{\zeta} \qquad \underset{\substack{\text{only if } C_V \text{ is constant} \\ \text{like an ideal gas.}}}{\zeta}$

Next time we'll go into the 4 basic kinds of transformation we can do to an ideal gas.

<u>A review</u>:

$$S \equiv k_B \ln W$$

Stirling's approximation (and countable states) gave us

$$S = -k_B \sum_i p_i \ln p_i$$

The <u>Second Law</u> of thermodynamics tells us to maximize S subject to constraints: $\sum_i p_i = 1$ & $\langle \varepsilon \rangle = \sum_i p_i \varepsilon_i$

$$F = -k_B \left[\sum_i p_i \ln p_i + \alpha \left(\sum_i p_i - 1 \right) + \beta \left(\sum_i \varepsilon_i p_i - \langle \varepsilon \rangle \right) \right]$$

$$\left(\frac{\partial F}{\partial p_i} \right)_{p_i^*} = 0 = -k_B \left[(\ln p_i + 1) + \alpha + \beta \varepsilon_i \right] = 0$$

$$\longrightarrow \quad \ln p_i^* + 1 = -\alpha - \beta \varepsilon_i$$

$$p_i^* = e^{-1-\alpha} e^{-\beta \varepsilon_i}$$

Now apply constraints:

$$\sum_i p_i^* = e^{-1-\alpha} \underbrace{\sum_i e^{-\beta \varepsilon_i}}_{Q} = 1$$

$$\therefore \quad e^{-1-\alpha} = \frac{1}{Q}$$

$$\therefore \quad p_i^* = \frac{1}{Q} e^{-\beta \varepsilon_i}$$

$$U = \langle \varepsilon \rangle = \sum_i p_i^* \varepsilon_i = \frac{1}{Q} \sum_i \varepsilon_i e^{-\beta \varepsilon_i}$$

This is now on firm footing from $S = k_B \ln W$ and 2nd Law

Also:
$$p_i^* = \frac{1}{Q} e^{-\beta \varepsilon_i}$$

$$\ln p_i^* = -\beta \varepsilon_i - \ln Q$$

$$p_i^* \ln p_i^* = -\beta \varepsilon_i p_i^* - \ln Q \, p_i^*$$

$$= -\beta \varepsilon_i \left(\frac{1}{Q} e^{-\beta \varepsilon_i} \right) - \ln Q \left(\frac{1}{Q} e^{-\beta \varepsilon_i} \right)$$

$\therefore$

$$S = -k_B \left[\frac{-\beta}{Q} \sum_i \varepsilon_i e^{-\beta \varepsilon_i} - \frac{\ln Q}{Q} \sum_i e^{-\beta \varepsilon_i} \right]$$

$$= -k_B \left[-\frac{1}{k_B T} \langle E \rangle - \ln Q \right]$$

$$S = \frac{U}{T} + k_B \ln Q$$

$$\boxed{S = k_B \ln W \qquad\qquad S = \frac{U}{T} + k_B \ln Q \qquad\qquad dS = \frac{\delta q_{rev}}{T}}$$

All are equivalent expressions for the entropy!

We can now connect one of the <u>free energies</u> to Q

Helmholtz free energy: $\qquad A = U - TS$

$$A = U - T \left(\frac{U}{T} + k_B \ln Q \right)$$

$$= U - U - k_B T \ln Q$$

$$\boxed{A = -k_B T \ln Q} \qquad \longleftarrow \qquad \text{Helmholtz free energy is } \underline{\text{directly}} \text{ related to canonical (NVT) ensemble!}$$

Some more revelations:

We know Q is a function of N, V, T (or N, V, β):

and energy (total) depends on N and V $\underset{\text{why?}}{\longleftarrow}$

$$\sum_{\text{molecules}} E$$

$\therefore$ the state probability:

$$P_j = \frac{e^{-\beta E_j (N,V)}}{Q(N,V,\beta)} = P_j (N, V, \beta)$$

Let's write out an expression for energy (thermodynamic)

$$U = \langle E \rangle = \sum_j P_j E_j = \sum_j P_j (N, V, \beta) E_j (N, V)$$

To make a total differential,

$$dU = \sum_j P_j \, dE_j + \sum_j E_j \, dP_j$$

And we know

$$dE_j = \left(\frac{\partial E_j}{\partial N} \right) dN + \left(\frac{\partial E_j}{\partial V} \right) dV$$

$$\underset{\text{due to translational states}}{\longleftarrow}$$

If we keep N fixed, like in a closed box,

$$dE_j = \left(\frac{\partial E_j}{\partial V} \right) dV$$

$$dU = \sum_j P_j \left(\frac{\partial E_j}{\partial V} \right) dV + \sum_j E_j \, dP_j$$

Compare this to the thermodynamic definition

$$dU = \delta w_{rev} + \delta q_{rev}$$

$$= -P \, dV + \delta q_{rev}$$

Therefore

pressure $\quad P = -\sum_j P_j (N, V, \beta) \left(\frac{\partial E_j}{\partial V}\right)_N$

$$= -\left\langle \left(\frac{\partial E}{\partial V}\right)_N \right\rangle$$

And more importantly,

$$\delta q_{rev} = \sum_j E_j P_j$$

From thermodynamic definition of S,

$$dS = \frac{\delta q_{rev}}{T}$$

We now have

$$T dS = \sum_j E_j P_j$$

(This was a missing piece in our Lagrange multipliers.)

Consider a reaction

$$AB + CD \longrightarrow AC + BD$$

$$Q_{reactant} = \frac{q_{AB}^{N_{AB}} \; q_{CD}^{N_{CD}}}{N_{AB}! \; N_{CD}!} \qquad\qquad Q_{product} = \frac{q_{AC}^{N_{AC}} \; q_{BD}^{N_{BD}}}{N_{AC}! \; N_{BD}!}$$

$$\Delta A = A_{prod} - A_{react}$$

$$= -k_B T \ln Q_{product} - (-k_B T \ln Q_{reactant})$$

$$\Delta A = -k_B T \ln \frac{Q_{product}}{Q_{reactant}}$$

↯ Free energy change in a reaction is derivable
from <u>ratios</u> of partition functions

Chemical Equilibria

$$aA + bB \rightleftharpoons cC + dD$$

Could also be written

$$0 = cC + dD - aA - bB$$

$$= \nu_c C + \nu_d D + \nu_a A + \nu_b B$$

ν_i = stoichiometric coefficient in one sided reaction!

We'll also need to consider what happens if
the <u>number</u> of molecules changes in the
reaction. To do that we'll need the
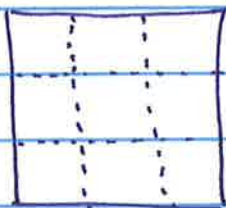Grand Canonical Ensemble!

Grand Canonical Ensemble

To get this ensemble, we allow the number of particles to fluctuate, but constrain the average number of particles $\langle N \rangle$. This is like allowing the energy to fluctuate, but constraining the average energy $\langle E \rangle$

We need to maximize S, with 3 constraints

$$\sum_i P_i = 1 \qquad \sum_i \varepsilon_i P_i = \langle E \rangle \qquad + \text{ one for particles!}$$

Consider

← each member of the ensemble has fixed $V \& T$, but they can exchange particles!

$a_{N,j}$ = # of systems in ensemble with N molecules <u>and</u> in state j

$$\sum_N \sum_j a_{N,j} = \mathcal{M} = \text{total \# of systems in ensemble}$$

$$\sum_N \sum_j E_{N,j} \, a_{N,j} = \mathcal{E} = \underline{\text{total}} \text{ energy of ensemble}$$

$$\sum_N \sum_j N a_{N,j} = \mathcal{N} = \text{total \# of molecules in ensemble}$$

$$P_{N,j} = \frac{a_{N,j}}{\mathcal{M}} = \text{probability of 1 system having } N \text{ particles \& found in state } j$$

We need to maximize <u>entropy</u>:

$$S = -k_B \sum_N \sum_j P_{N,j} \ln P_{N,j}$$

But we need to write our constraints first.

Total probability: $\sum_N \sum_j P_{N,j} = 1$

Energy : $\sum_N \sum_j E_{N,j} P_{N,j} = \langle E \rangle = \mathcal{E}/\mathcal{M}$

Avg. Particle number: $\sum_N \sum_j N P_{N,j} = \langle N \rangle = \eta/\mathcal{M}$

Our New objective function to $\overset{\text{maximize}}{\cancel{\text{minimize}}}$:

$$F = -k_B \sum_N \sum_j P_{N,j} \ln P_{N,j} + \alpha \left(P_{N,j}\right) + \beta E_{N,j} P_{N,j} + \gamma N P_{N,j}]$$

Lagrange Multipliers

Remember: we set $\left(\dfrac{\partial F}{\partial P_{N,j}}\right) = 0$, then apply constraints.

$$\left(\frac{\partial F}{\partial P_{N,j}}\right) = -k_B \left[\ln P_{N,j} +1 + \alpha + \beta E_{N,j} + \gamma N \right] = 0$$

Solve for $P_{N,j}^* \longleftarrow$ probabilities that maximize entropy

$$P_{N,j}^* = e^{-1-\alpha} \; e^{-\beta E_{N,j}} \; e^{-\gamma N}$$

Now, we need to apply the constraints:

Conservation of probability: $1 = \sum_N \sum_j e^{-1-\alpha} \; e^{-\beta E_{N,j}} \; e^{-\gamma N}$

So:

$$e^{1+\alpha} = \sum_N \sum_j e^{-\beta E_{N,j}} \; e^{-\gamma N} \equiv \Xi = \text{Grand Canonical Partition Function!}$$

By comparing to some known thermodynamic quantities, we can identify the other Lagrange multipliers:

$$\beta = \frac{1}{k_B T} \qquad \gamma = \frac{-\mu}{k_B T} \quad \leftarrow \text{chemical potential}$$

$$\Xi(V, T, \mu) = \sum_N \sum_j e^{-E_{N,j}(V)/k_B T} e^{\mu N/k_B T}$$

$$= \sum_N Q(N, V, T) e^{\mu N/k_B T}$$

Let's connect this partition function to thermodynamics like we did for Q:

$$S = -k_B \sum_N \sum_j P_{N,j} \ln P_{N,j}$$

but we know

$$P_{N,j} = \frac{e^{-\beta E_{N,j}} e^{\beta \mu N}}{\Xi}$$

So:

$$\ln P_{N,j} = -\beta E_{N,j} + \beta \mu N - \ln \Xi$$

$$P_{N,j} \ln P_{N,j} = -\beta E_{N,j} P_{N,j} + \beta \mu N P_{N,j} - \ln \Xi \, P_{N,j}$$

$$S = -k_B \sum_N \sum_j P_{N,j} \ln P_{N,j} = -k_B \sum_N \sum_j \left(-\beta E_{N,j} P_{N,j} + \beta \mu N P_{N,j} - \ln \Xi \, P_{N,j} \right)$$

$$= -k_B \left(-\beta \langle E \rangle + \beta \mu \langle N \rangle - \ln \Xi \right)$$

$$S = \frac{\langle E \rangle}{T} - \frac{\mu \langle N \rangle}{N} + k_B \ln \Xi$$

Multiply everyone by T:

$$TS = U - \underbrace{\mu N}_{} + k_B T \ln \Xi$$

chemical potential is just $\mu = \dfrac{G}{N}$

$$\therefore \quad G = U - TS + k_B T \ln \Xi$$

(but we know)

$$G = U - TS + PV$$

$$\therefore \quad \boxed{PV = k_B T \ln \Xi(V, T, \mu)}$$

Table 3-1. **A summary of formulas for several types of ensemble**

microcanonical ensemble, $\Omega(N, V, E)$

$$S = k \ln \Omega$$

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN$$

$$\frac{1}{kT} = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N, V} \tag{3-25}$$

$$\frac{p}{kT} = \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N, E} \tag{3-26}$$

$$\frac{\mu}{kT} = -\left(\frac{\partial \ln \Omega}{\partial N}\right)_{V, E} \tag{3-27}$$

canonical ensemble, $Q(N, V, T)$

$$A = -kT \ln Q$$

$$dA = -S\, dT - p\, dV + \mu\, dN$$

$$S = k \ln Q + kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N, V} \tag{3-28}$$

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N, T} \tag{3-29}$$

$$\mu = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{V, T} \tag{3-30}$$

$$E = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N, V} \tag{3-31}$$

grand canonical ensemble, $\Xi(V, T, \mu)$

$$pV = kT \ln \Xi$$

$$d(pV) = S\, dT + N\, d\mu + p\, dV$$

$$S = k \ln \Xi + kT\left(\frac{\partial \ln \Xi}{\partial T}\right)_{V, \mu} \tag{3-32}$$

$$N = kT\left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{V, T} \tag{3-33}$$

$$p = kT\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\mu, T} = kT\frac{\ln \Xi}{V} \tag{3-34}$$

isothermal-isobaric ensemble, $\Delta(N, T, p)$

$$G = -kT \ln \Delta$$

$$dG = -S\, dT + V\, dp + \mu\, dN$$

$$S = k \ln \Delta + kT\left(\frac{\partial \ln \Delta}{\partial T}\right)_{N, p} \tag{3-35}$$

$$V = -kT\left(\frac{\partial \ln \Delta}{\partial p}\right)_{N, T} \tag{3-36}$$

$$\mu = -kT\left(\frac{\partial \ln \Delta}{\partial N}\right)_{T, p} \tag{3-37}$$

Quantum particles

Ideal systems & non-interacting subsystems

$$E = E_1 + E_2$$

$$Q = \sum_{\substack{States1 \\ States2}} e^{-\beta(E_1+E_2)}$$

$$= \sum_{\substack{States1 \\ States2}} e^{-\beta E_1} e^{-\beta E_2}$$

$$= \left(\sum_{States1} e^{-\beta E_1}\right)\left(\sum_{States2} e^{-\beta E_2}\right) = Q_1 Q_2$$

$$Q = q^N \qquad \longleftarrow \quad \text{distinguishable particles}$$

$$= \frac{q^N}{N!} \qquad \longleftarrow \quad \text{indistinguishable particles}$$

Other Stats:

Bose-Einstein: Any # of particles in same Quantum State

Fermi-Dirac: No 2 particles in same quantum state

$$n_i = \text{# of atoms in quantum state labeled by } i$$

$$n_i = \begin{cases} 0 \\ 1 \end{cases} \quad F-D \qquad \text{no restriction for B-E}$$

$$E_j = \text{energy of } \underline{\text{system}} = \sum_k \varepsilon_k n_k$$

$\longleftarrow$ energy of quantum state k

$\longleftarrow$ # of particles in state k

$$N = \text{total # of particles} = \sum_k n_k$$

$$Q = \sum_j e^{-\beta E_j} = \sum_{n_0, n_1, n_2 \cdots}^{*} e^{-\beta \sum_k \varepsilon_k n_k}$$

$\longleftarrow$ restricted sum

not a free sum

internal restriction on #'s in states

If we try to use Q, $\displaystyle\sum_{n_0, n_1, \dots}^{*}$

the indices must sum to N

Consider 3 particles:

For Fermi-Dirac:

n_0	n_1	n_2	
1	1	1	✓
2	1	0	✗ not allowed

For Bose-Einstein:

n_0	n_1	n_2	
3	0	0	✓
2	1	0	✓
2	0	1	✓
2	2	0	✗ not allowed

So rather than try to use a <u>restricted</u> sum, we'll use the Grand canonical Partition function instead:

$$\boxed{\Xi} = \sum_{N=0}^{\infty} e^{\beta \mu N} \, Q(N, V, T) \quad \leftarrow \text{let's call } e^{\beta \mu} = \lambda$$

$$= \sum_{N=0}^{\infty} \lambda^N \sum_{n_0, n_1, n_2 \dots}^{*} e^{-\beta \sum_k \varepsilon_k n_k} \quad \leftarrow \text{But } N = n_1 + n_2 + \dots = \sum_k n_k$$

$$= \sum_{N=0}^{\infty} \sum_{n_0, n_1, \dots}^{*} \lambda^{\sum_k n_k} e^{-\beta \sum_k \varepsilon_k n_k} \quad \leftarrow \begin{array}{l}\text{combine the two} \\ \text{sums in an exponent} \\ \text{to get a } \underline{\text{product}}\end{array}$$

$$= \sum_{N=0}^{\infty} \underbrace{\sum_{n_0, n_1, \dots}^{*} \prod_k \left(\lambda e^{-\beta \varepsilon_k} \right)^{n_k}}$$

allowing n_0, n_1, n_2 to range over <u>all</u> possible values (unrestricted) will actually <u>get</u> the variable particle number!

$$= \sum_{n_0=0}^{n_{max}} \sum_{n_1=0}^{n_{max}} \cdots \prod_k \left(\lambda e^{-\beta \varepsilon_k} \right)^{n_k}$$

<u>sum</u> of <u>products</u>
<u>product</u> of <u>sums</u>

$$= \sum_{n_0=0}^{n_{max}} \left(\lambda e^{-\beta \varepsilon_0} \right)^{n_0} \sum_{n_1=0}^{n_{max}} \left(\lambda e^{-\beta \varepsilon_1} \right)^{n_1} \cdots$$

$$\boxed{\Xi = \prod_k \sum_{n_k=0}^{n_{max}} \left(\lambda e^{-\beta \varepsilon_k} \right)^{n_k}}$$

In the case of Fermi-Dirac statistics

$$n_k = \begin{cases} 0 & \text{unoccupied} \\ 1 & \text{occupied} \end{cases}$$

$$\left(\lambda e^{-\beta \varepsilon_k}\right)^0 + \left(\lambda e^{-\beta \varepsilon_k}\right)^1$$

$\therefore$

$$\boxed{\Xi_{FD} = \prod_k \left(1 + \lambda e^{-\beta \varepsilon_k}\right)}$$

For Bose-Einstein statistics: $n_k = 0, 1, \ldots, \infty$

$$\Xi_{BE} = \prod_k \sum_{n_k = 0}^{\infty} x^{n_k} \qquad \text{with} \qquad x = \lambda e^{-\beta \varepsilon_k}$$

$$\boxed{\Xi_{BE} = \prod_k \left(\frac{1}{1 - \lambda e^{-\beta \varepsilon_k}}\right)}$$

These can be combined in a compact notation:

$$\Xi_{\substack{FD \\ BE}} = \prod_k \left(1 \pm \lambda e^{-\beta \varepsilon_k}\right)^{\pm 1}$$

One odd side effect: $\langle n_k \rangle = \frac{1}{\Xi} \prod_{k=0}^{k-1} \left(\lambda e^{-\beta \varepsilon_k}\right) n_k \prod_{k=k+1} \left(\lambda e^{-\beta \varepsilon_k}\right)$

$$\langle n_k \rangle = \frac{\partial \ln \Xi}{\partial (-\beta \varepsilon_k)} \qquad \longleftarrow \quad \text{average occupancy of state } k$$

Let's do it for $\Xi_{BE} = \prod_{k'} \left(1 - \lambda e^{-\beta \varepsilon_{k'}}\right)^{-1}$

$$\ln \Xi = \sum_{k'} -\ln\left(1 - \lambda e^{-\beta \varepsilon_{k'}}\right)$$

$$\langle n_k \rangle = \frac{\partial \ln \Xi}{\partial (-\beta \varepsilon_k)} = -\frac{1}{1 - \lambda e^{-\beta \varepsilon_k}} = \frac{1}{e^{\beta(\mu - \varepsilon_k)} - 1}$$

What happens when $\mu = \varepsilon_k$?   Bose-Einstein condensate!

Now, for Fermi-Dirac:

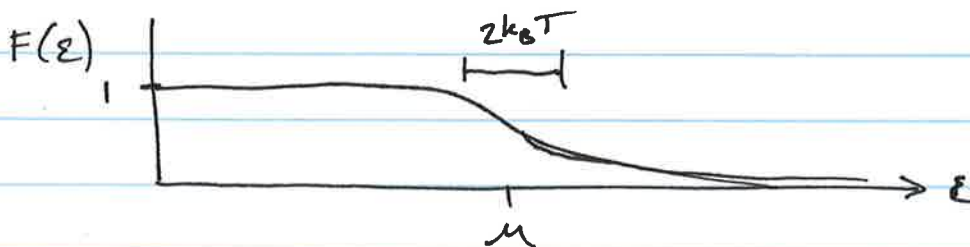$$\langle n_k \rangle_{FD} = \frac{\partial \ln \Xi}{\partial(-\beta \varepsilon_k)}$$

$$\Xi_{FD} = \prod_{k'} \left(1 + \lambda e^{-\beta \varepsilon_{k'}}\right)$$

$$\ln \Xi_{FD} = \sum_{k'} \ln \left(1 + \lambda e^{-\beta \varepsilon_{k'}}\right)$$

$$\frac{\partial \ln \Xi_{FD}}{\partial(-\beta \varepsilon_k)} = \frac{1}{1 + \lambda e^{-\beta \varepsilon_k}} \left(\lambda e^{-\beta \varepsilon_k}\right) = \frac{1}{\frac{1}{\lambda} e^{+\beta \varepsilon_k} + 1}$$

$$\langle n_k \rangle_{FD} = \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1}$$

$$F(\varepsilon) = \text{Fermi function} = \frac{1}{e^{(\varepsilon - \mu)/kT} + 1}$$

$$\langle n_k \rangle_{\substack{FD \\ BE}} = \frac{1}{e^{\beta(\varepsilon_k - \mu)} \pm 1} = \frac{e^{-\beta(\varepsilon_k - \mu)}}{1 \pm e^{-\beta(\varepsilon_k - \mu)}}$$

$$\lim_{T \to \infty} \langle n_k \rangle_{\substack{FD \\ BE}} = e^{-\beta \varepsilon_k}$$

Boltzmann statistics are high T limit of

Last time, we talked about quantum statistics:

Fermions: $\qquad n_k = \begin{cases} 0 & \text{unoccupied} \\ 1 & \text{occupied} \end{cases}$

n_k = occupation of kth quantum level

Bosons: $\qquad n_k = 0, \ldots, \infty$

We derived the grand canonical partition functions:

$$\Xi_{\substack{FD \\ BE}} = \prod_k \left(1 \pm e^{\beta \mu} e^{-\beta \varepsilon_k} \right)^{\pm 1}$$

Today, I want to think a bit about the <u>definition</u> of Ξ:

$$\Xi = \sum_{N=0}^{\infty} e^{\beta \mu N} Q(N,V,T) = \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_j e^{-\beta E_{j,N}}$$

Remember that Ξ is the normalization factor when our ensemble has lots of possible numbers of particles and lots of different possible energy states j.

What is:

$$\frac{\partial \ln \Xi}{\partial (\beta \mu)} = \frac{1}{\Xi} \frac{\partial}{\partial (\beta \mu)} \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_j e^{-\beta E_{N,j}}$$

$$= \frac{1}{\Xi} \sum_{N=0}^{\infty} N e^{\beta \mu N} \underbrace{\sum_j e^{-\beta E_{N,j}}}_{P(N)}$$

$\underset{\text{Normalization}}{\swarrow}$

$$\frac{\partial \ln \Xi}{\partial (\beta \mu)} = \langle N \rangle$$

$\therefore$

$$\boxed{ \langle N \rangle = \left(\frac{\partial \ln \Xi}{\partial (\beta \mu)} \right)_{V,T} = k_B T \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T} }$$

Now, say we want the average population in level k'

To get $\langle n_{k'} \rangle$ we can't use $\partial(\beta\mu)$ to do this, so we need to go back one level:

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{n_0, n_1, n_2 \ldots}^{*} e^{-\beta \sum_k \varepsilon_k n_k}$$

↳ remember this was a restricted sum so $n_0 + n_1 + \ldots = N$

We need a derivative that will pull down $n_{k'}$ into the sum and out of the exponent:

$$-\frac{\partial \ln \Xi}{\partial(\beta\varepsilon_{k'})} = \frac{-1}{\Xi} \cdot \frac{\partial}{\partial(\beta\varepsilon_{k'})} \sum_{N=0}^{\infty} e^{\beta\mu N} \sum^{*} e^{-\sum_k \beta\varepsilon_k n_k}$$

↗ acts in here

$$= \frac{-1}{\Xi} \sum_{N=0}^{\infty} e^{\beta\mu N} \sum^{*} -n_{k'} \cdot e^{-\sum_k \beta\varepsilon_k n_k}$$

$$-\frac{\partial \ln \Xi}{\partial(\beta\varepsilon_{k'})} = \langle n_{k'} \rangle \quad \longleftarrow \quad \text{so that's the appropriate derivative}$$

Let's apply it:

$$\Xi_{\substack{FD \\ BE}} = \prod_k \left(1 \pm e^{\beta\mu} e^{-\beta\varepsilon_k} \right)^{\pm 1}$$

$$\ln \Xi_{\substack{FD \\ BE}} = \sum_k \pm \ln \left(1 \pm e^{\beta\mu} e^{-\beta\varepsilon_k} \right)$$

$$-\frac{\partial \ln \Xi_{\substack{FD \\ BE}}}{\partial(\beta\varepsilon_{k'})} = \frac{1}{\pm \left(1 \pm e^{\beta\mu} e^{-\beta\varepsilon_{k'}} \right)} \cdot - \left(\pm e^{\beta\mu} e^{-\beta\varepsilon_{k'}} \right)$$

$$\langle n_{k'} \rangle_{\substack{FD \\ BE}} = \frac{e^{\beta\mu} e^{-\beta\varepsilon_{k'}}}{1 \pm e^{\beta\mu} e^{-\beta\varepsilon_{k'}}} = \frac{e^{-\beta(\varepsilon_{k'}-\mu)}}{1 \pm e^{-\beta(\varepsilon_{k'}-\mu)}}$$

The High temperature limit $(\beta \to 0)$ is fascinating when μ is small

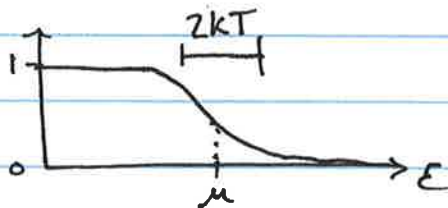$$\lim_{T \to \infty} \langle n_{k'} \rangle_{\substack{FD \\ BE}} = e^{-\beta(\varepsilon_{k'}-\mu)} \approx e^{-\beta\varepsilon_{k'}}$$

↳ Boltzmann!

So we recover Boltzmann statistics at high temperatures.
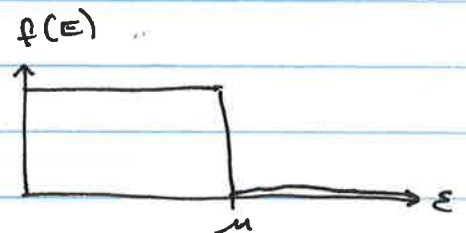

Fermions: $\quad \langle n_{k'} \rangle = \dfrac{e^{-\beta(\varepsilon_{k'} - \mu)}}{1 + e^{-\beta(\varepsilon_{k'} - \mu)}} = \dfrac{1}{1 + e^{\beta(\varepsilon_{k'} - \mu)}}$

If the energies of the quantum states are nearly continuous, we can turn this into the Fermi function:

$$f(\varepsilon) = \frac{1}{1 + e^{\beta(\varepsilon - \mu)}}$$

For a metal $\quad \mu_0 = \dfrac{h^2}{2m} \left(\dfrac{3}{8\pi}\right)^{2/3} \left(\dfrac{N}{V}\right)^{2/3}$

$\qquad\qquad N = \text{\# of valence electrons}$

$\qquad\qquad V = \text{per volume}$

μ_0 is usually in the $1-5eV$ range

At room temperature, $\beta\mu_0 \sim 100$, so we're close to the $T = 0$ limit of the fermi function!
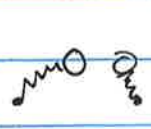
Bosons: $\quad \langle n_{k'} \rangle = \dfrac{1}{e^{\beta(\mu - \varepsilon_{k'})} - 1}$

For these particles, when $\mu = \varepsilon_{k'}$, we get a divergence in $\langle n_{k'} \rangle$ and <u>all</u> particles occupy the same QM state. This is a Bose-Einstein condensate

We had a problem in the last problem set on solids (i.e. Einstein's model):

 ← each atom is pinned to a lattice site with springs

This is equivalent to $3N$ independent harmonic oscillators each with frequency ω:

$$q_{HO} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$

← partition function for one oscillator

$$Q(N,V,T) = \left(\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}\right)^{3N}$$

← no factorial because the lattice sites are distinguishable

Helmholtz free energy:

$$A(T,N) = -k_B T \ln Q = -3Nk_B T\left[-\frac{\beta\hbar\omega}{2} - \ln\left[1-e^{-\beta\hbar\omega}\right]\right]$$

$$= \frac{3N}{2}\hbar\omega + 3Nk_B T \ln\left(1-e^{-\beta\hbar\omega}\right)$$

$$\langle E\rangle = -\frac{\partial \ln Q}{\partial \beta} = 3N\left[\frac{-\partial}{\partial\beta}\left(-\frac{\beta\hbar\omega}{2} - \ln\left(1-e^{-\beta\hbar\omega}\right)\right)\right]$$

$$= 3N\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)$$

$$C_V = \frac{\partial \langle E\rangle}{\partial T} = 3Nk_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{-\hbar\omega/kT}}{\left(1-e^{-\hbar\omega/kT}\right)^2} = 3Nk\left(\frac{\theta_v}{T}\right)^2 \frac{e^{-\theta_v/T}}{\left(1-e^{-\theta_v/T}\right)^2}$$
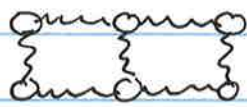
This works well as $T\to\infty$ ($C_V \to 3R$), but at low T

$$C_V \approx 3Nk\left(\frac{\theta_v}{T}\right)^2 e^{-\theta_v/T}$$

← This falls much more rapidly than the experimentally observed T^3

The Debye model:

include couplings between oscillators

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{P_i^2}{2m} + \sum_{j,i} A_{ij}\, q_i \cdot q_j$$

$\hookleftarrow$ includes q_i^2 terms!

If we change variables to new coordinates (Q_k, P_k) Such that matrix $\underset{=}{A}$ is diagonal, $\underset{=}{U}$ is a unitary transform:

mass weighted force constant matrix.

$$\underset{=}{\omega^2} = \left(\underset{=}{U^T} \underset{=}{A} \underset{=}{U}\right) \qquad \underset{=}{U^T} \underset{=}{U} = \underset{=}{I}$$

$\nwarrow$ identity matrix

$\hookleftarrow$ frequency matrix

Then:

$$\mathcal{H}(\vec{Q}, \vec{P}) = \sum_k \frac{P_k^2}{2m} + \sum_k \frac{m\omega_k^2}{2} Q_k^2$$

$\nearrow$ ω is not the same for each oscillator

$\hookleftarrow$ style sum

P_k & Q_k describe **phonons** or the normal modes of an extended solid.

Each ω_k is different, but the overall form of the Hamiltonian is preserved:

$$\mathcal{H} = \sum_k \left(\frac{P_k^2}{2m} + \frac{m\omega_k^2}{2} Q_k^2\right) \qquad \longleftarrow \text{classical}$$

$$\hat{\mathcal{H}} = \sum_k \hbar\omega_k \left(\hat{n}_k + \frac{1}{2}\right) \qquad \longleftarrow \begin{array}{l}\text{each oscillator has}\\ \text{a quantum number}\end{array}$$

$$E = E_{mode1} + E_{mode2} + E_{mode3} + \cdots$$

$$= \hbar\omega_1 \left(n_1 + \frac{1}{2}\right) + \hbar\omega_2 \left(n_2 + \frac{1}{2}\right) + \hbar\omega_3 \left(n_3 + \frac{1}{2}\right) + \cdots$$

$$E = \sum_k (\hbar\omega_k)(n_k + \tfrac{1}{2})$$

$$Q_N = \sum_{states} e^{-\beta E_{state}} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots e^{-\beta \sum_{k=1}^{3N} \hbar\omega_k (n_k + \frac{1}{2})}$$
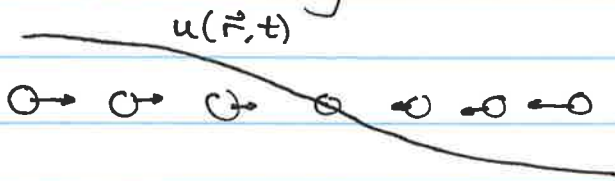
this can't move out front this time!

$$A(T,V,N) = \frac{\hbar}{2} \sum_{k=1}^{3N} \omega_k + k_BT \sum_{k=1}^{3N} \ln\left[1 - e^{-\beta\hbar\omega_k}\right]$$

If we have many modes, with closely-spaced frequencies:

$$= \frac{\hbar}{2} \int_0^\infty g(\omega)\, d\omega + k_BT \int_0^\infty g(\omega) \ln\left[1 - e^{-\beta\hbar\omega}\right] d\omega$$
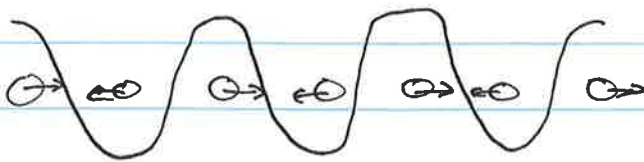
$g(\omega)\, d\omega$ = the number of modes with frequency between ω & $\omega + d\omega$, or the degeneracy of phonons with frequency ω. What does $g(\omega)$ look like?

Phonons are really waves moving through a crystal:

$u(\vec{r}, t)$

← low frequency

$u(\vec{r}, t)$ measures the displacement of atom at $\vec{r}$ at time t due to this phonon.

← high frequency

$$u(\vec{r}, t) = A e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

← wave with amplitude A travelling in $\vec{k}$ direction with frequency $\omega = 2\pi\nu$

$$|\vec{k}| = \frac{2\pi}{\lambda} \leftarrow \text{wavelength}$$

Useful relations:

$$\vec{|k|} = \frac{2\pi}{\lambda} \qquad \lambda = \frac{v_p}{\nu} \qquad \nu = \frac{v_p}{\lambda}$$
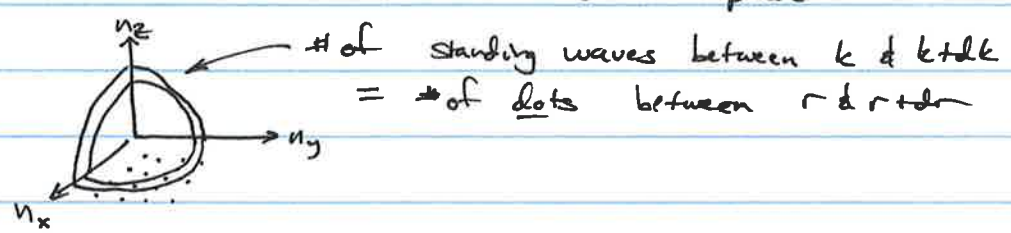
$$\omega = 2\pi\nu$$

A standing wave:

$$u(\vec{r}, t) = 2A\, e^{i\vec{k}\cdot\vec{r}} \cos \omega t$$

Since the wave must vanish at the edges of the crystal, we really have particle-in-a-box boundary conditions:

$$\vec{k} = \frac{\pi}{L}\vec{n} \longleftarrow \text{vector of } \underset{\text{positive}}{\wedge} \text{ integers } \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix}$$

$$\vec{|k|}^2 = \left(\frac{\pi^2}{L^2}\right)\left(n_x^2 + n_y^2 + n_z^2\right)$$

$\vec{|k|}^2$ is like the radius^2 of a sphere

→ # of standing waves between k & $k+dk$
= # of dots between r & $r+dr$

Volume of the sphere: $V = \frac{4}{3}\pi r^3 \cdot \frac{1}{8} = \frac{\pi}{6} r^3$

$\nwarrow$ one octant only

$$r = \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{|k| L}{\pi} \implies r^3 = \frac{k^3 L^3}{\pi^3} = \left(\frac{kL}{\pi}\right)^3$$

So:

$$\Phi(k) = \frac{\pi}{6}\left(\frac{Lk}{\pi}\right)^3 = \frac{L^3 k^3}{6\pi^3} = \frac{V\, k^3}{6\pi^3}$$

← volume

$\nwarrow$ number of dots contained within sphere defined by $|k|$

<u>But</u> # between k & $k+dk$ = surface area of shell $*dk$

$$g(k)\,dk = \frac{d\Phi(k)}{dk} * dk$$

$$g(k)\,dk = \frac{Vk^2}{2\pi^2}\,dk$$

But we want $g(\omega)$ or $g(\nu)$: $\nu = \frac{V_p}{\lambda} = \frac{V_p\,k}{2\pi}$ ← speed of propagation

So: $$g(\nu)\,d\nu = \frac{4\pi\,V\,\nu^2}{V_p^3}\,d\nu$$

There are 2 kinds of <u>transverse</u> waves
There is 1 kind of <u>longitudinal</u> wave

$$g(\nu)\,d\nu = \left(\frac{2}{V_T^3} + \frac{1}{V_\ell^3}\right) 4\pi\,V\nu^2\,d\nu$$

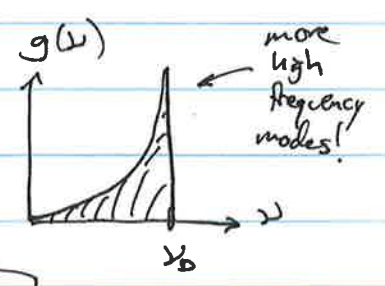These waves have an average velocity: $\dfrac{3}{V_0^3} \simeq \dfrac{2}{V_t^3} + \dfrac{1}{V_\ell^3}$

$$\therefore \quad g(\nu)\,d\nu = \frac{12\pi\,V}{V_0^3}\,\nu^2\,d\nu \qquad \begin{array}{l}\omega = 2\pi\nu \\ d\omega = 2\pi\,d\nu\end{array}$$

$$\therefore \quad g(\omega)\,d\omega = \frac{6V}{4\pi^2 V_0^3}\,\omega^2\,d\omega$$

Normalization: Total # of frequencies = $3N$

$$\int_0^{\nu_0} g(\nu)\,d\nu = 3N$$

$g(\nu)$ — more high frequency modes!

$$\nu_D = \left(\frac{3N}{4\pi V}\right)^{1/3} V_0$$

$$\boxed{g(\nu)\,d\nu = \begin{cases} \dfrac{9N}{\nu_D^3}\,\nu^2\,d\nu & \nu \le \nu_D \\[2mm] 0 & \nu > \nu_0 \end{cases}}$$

$$C_V = 9Nk \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \, dx$$

$$\theta_D = \frac{h\nu_0}{k_B} \qquad x = \frac{h\nu}{k_B T}$$

The Debye model gives almost perfect agreement with experiments!
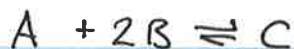
$$C_V(T \to \infty) = 3R$$

$$C_V(T \to 0) = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta_D}\right)^3$$

Chemical Equilibrium

Review of the basics:

$$A + 2B \rightleftharpoons C$$

$$K_{eq} = \frac{[C]}{[A][B]^2} \longleftarrow$$

K_{eq} is related to ΔG, one of the thermodynamic free energies.

$G(T, P, N_A, N_B, N_C)$ = Gibbs free energy (fixed T & P)

$A(T, V, N_A, N_B, N_C)$ = Helmholtz free energy (fixed T & V)

$$dA = \left(\frac{\partial A}{\partial T}\right)dT + \left(\frac{\partial A}{\partial V}\right)dV + \left(\frac{\partial A}{\partial N_A}\right)dN_A + \left(\frac{\partial A}{\partial N_B}\right)dN_B + \left(\frac{\partial A}{\partial N_C}\right)dN_C$$

$\underbrace{\qquad}_{exact\ differential}$ all the things A can depend on

$$dA = -SdT - PdV + \mu_A dN_A + \mu_B dN_B + \mu_C dN_C$$

If we hold the reaction volume & temperature fixed

$dV = 0$ & $dT = 0$, so

$$dA = \mu_A dN_A + \mu_B dN_B + \mu_C dN_C$$

But the numbers of particles are tied together by Stoichiometry:

$$dN_A = -dN_C \longleftarrow \text{every time we lose an A we gain a C}$$

$$dN_B = -2dN_C \longleftarrow \text{every time we lose 2 B's we gain a C}$$

$\therefore$
$$dA = \mu_A dN_A + \mu_B dN_B + \mu_C dN_C$$
$$= (-\mu_A + 2\mu_B + \mu_C) dN_C$$

At equilibrium the free energy is _minimized_ with respect to changes in N_c, so $\left(\frac{\partial A}{\partial N_c}\right) = 0$

∴ $\mu_A + 2\mu_B = \mu_c$

(A similar treatment works with G if we fix T & P)

What this tells us is that the thermodynamic property that predicts chemical equilibrium is the _chemical potential_
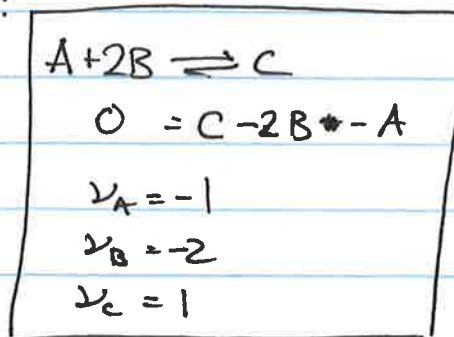
A more general reaction:

$$a A + b B \rightleftharpoons c C + d D$$

or

$$0 = c C + d D - a A - b B$$

$$0 = \sum_i \nu_i M_i$$

↖ symbol for compound i

stoichiometric coefficient for compound i

example:

$$A + 2B \rightleftharpoons C$$
$$0 = C - 2B - A$$
$$\nu_A = -1$$
$$\nu_B = -2$$
$$\nu_C = 1$$

We also define: $dN_i = \nu_i \, d\lambda$

→ _extent of reaction_

So we can write:

$$dA = \sum_c \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}} dN_i$$

$$= \sum_i \mu_i \, dN_i$$

$$dA = \sum_i \mu_i \nu_i \, d\lambda \quad = \left(\sum_i \mu_i \nu_i\right) d\lambda$$

Generally at equilibrium A is minimized with respect to the extent of the reaction, $\left(\frac{\partial A}{\partial \lambda}\right) = 0$

So we have:

$$\boxed{\sum_i \nu_i \mu_i = 0}$$

Now on to statistical mechanics:

For a mixture of $A + B + C + D$

$$Q = Q_A \, Q_B \, Q_C \, Q_D \quad \longleftarrow \quad \text{partition functions for separate components}$$

$$Q = \frac{q_A^{N_A}}{N_A!} \frac{q_B^{N_B}}{N_B!} \frac{q_C^{N_C}}{N_C!} \frac{q_D^{N_D}}{N_D!}$$

Also: $\quad A = -k_B T \ln Q$

And: $\quad \mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{V,T}$

So: $\quad \mu_A = \left(\frac{\partial A}{\partial N_A}\right)_{V,T} = -k_B T \left(\frac{\partial \ln Q}{\partial N_A}\right)_{V,T} = -k_B T \frac{\partial}{\partial N_A}\left[N_A \ln q_A - \ln N_A!\right]$

all other terms have <u>no</u> N_A

Remember that $\quad \ln N_A! \cong N_A \ln N_A - N_A$

Now, let's divide each of these factors by a volume:

$$\frac{\left(\frac{q_C}{V}\right)^c \left(\frac{q_D}{V}\right)^d}{\left(\frac{q_A}{V}\right)^a \left(\frac{q_B}{V}\right)^b} = \frac{\left(\frac{N_C}{V}\right)^c \left(\frac{N_D}{V}\right)^d}{\left(\frac{N_A}{V}\right)^a \left(\frac{N_B}{V}\right)^b} \longleftarrow \frac{N_A}{V} = [A]$$

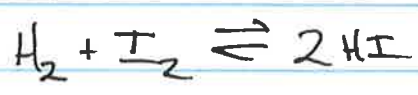$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_{eq}$$

$$K_c = \frac{\left(\frac{q_C}{V}\right)^c \left(\frac{q_D}{V}\right)^d}{\left(\frac{q_A}{V}\right)^a \left(\frac{q_B}{V}\right)^b} \longleftarrow$$ equilibrium constant is derivable from partition functions of reactants & products!

For gases:

$$K_p(T) = (k_B T)^{c+d-a-b} \, K_c(T)$$

An example: $H_2 + I_2 \rightleftharpoons 2HI$

$$K_c(T) = \frac{(q_{HI}/V)^2}{(q_{H_2}/V)(q_{I_2}/V)} = \frac{q_{HI}^2}{q_{H_2} \, q_{I_2}}$$

$$q = q_{trans} \, q_{vib} \, q_{rot} \, q_{elect} = \left(\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \frac{T}{\sigma \Theta_{rot}} \frac{e^{-\Theta_{vib}/2T}}{1-e^{-\Theta_{vib}/T}} g_{el} \, e^{D_e/kT}\right)$$

M = total mass of diatomic

for HI: $$q_{HI} = \left(\left(\frac{2\pi M_{HI} kT}{h^2}\right)^{3/2} V \frac{T}{\Theta_{HI}^{rot}} \frac{e^{-\Theta_{vib}^{HI}/2T}}{1-e^{-\Theta_{vib}^{HI}/T}} \, e^{D_o^{HI}/kT}\right)$$

for H_2: $$q_{H_2} = \left(\left(\frac{2\pi m_{H_2} kT}{h^2}\right)^{3/2} V \frac{T}{2\Theta_{rot}^{H_2}} \frac{e^{-\Theta_{vib}^{H_2}/2T}}{1-e^{-\Theta_{vib}^{H_2}/T}} \, e^{D_o^{H_2}/kT}\right)$$

$$\therefore \quad \mu_A = -k_B T \frac{\partial}{\partial N_A} \left[N_A \ln q_A - N_A \ln N_A + N_A \right]$$

$$= -k_B T \left[\ln q_A - \ln N_A - \frac{N_A}{N_A} + 1 \right]$$

$$= -k_B T \left[\ln q_A - \ln N_A \right]$$

$$\mu_A = -k_B T \ln \frac{q_A}{N_A}$$

Now, using our equilibrium condition: $\sum_i \mu_i \nu_i = 0$

$$\nu_C \ln \left(\frac{q_C}{N_C} \right) + \nu_D \ln \left(\frac{q_D}{N_D} \right) + \nu_A \ln \left(\frac{q_A}{N_A} \right) + \nu_B \ln \left(\frac{q_B}{N_B} \right) = 0$$

these two are positive
because C & D are
products

these two are negative because
A & B are reactants

Heres a neat trick:

$$\nu_C \ln \left(\frac{q_C}{N_C} \right) = \nu_C \ln q_C - \nu_C \ln N_C = \ln q_C^{\nu_C} - \ln N_C^{\nu_C}$$

Apply this to the equation above and we get

$$\ln q_C^{\nu_C} + \ln q_D^{\nu_D} + \ln q_A^{\nu_A} + \ln q_B^{\nu_B} = \ln N_C^{\nu_C} + \ln N_D^{\nu_D} + \ln N_A^{\nu_A} + \ln N_B^{\nu_B}$$

$$\ln \left[q_C^{\nu_C} q_D^{\nu_D} q_A^{\nu_A} q_B^{\nu_B} \right] = \ln \left[N_C^{\nu_C} N_D^{\nu_D} N_A^{\nu_A} N_B^{\nu_B} \right]$$

$$q_C^{\nu_C} q_D^{\nu_D} q_A^{\nu_A} q_B^{\nu_B} = N_C^{\nu_C} N_D^{\nu_D} N_A^{\nu_A} N_B^{\nu_B}$$

Remember $\quad \nu_A = -a \quad \nu_B = -b \quad \nu_C = c \quad \nu_D = d$

$$\frac{q_C^c \, q_D^d}{q_A^a \, q_B^b} = \frac{N_C^c \, N_D^d}{N_A^a \, N_B^b}$$

$$K_c(T) = \left(\frac{m_{HI}^2}{m_{H_2} m_{I_2}}\right)^{3/2} \left(\frac{4\,\Theta_{rot}^{H_2}\,\Theta_{rot}^{I_2}}{\left(\Theta_{rot}^{HI}\right)^2}\right) \frac{\left(1 - e^{-\frac{\Theta_{vib}^{H_2}}{T}}\right)\left(1 - e^{-\Theta_{vib}^{I_2}/T}\right)}{\left(1 - e^{-\Theta_{vib}^{HI}/T}\right)^2}$$

$$\times\; \frac{\left(e^{-\Theta_{vib}^{HI}/2T}\right)^2}{\left(e^{-\Theta_{vib}^{H_2}/2T}\right)\left(e^{-\Theta_{vib}^{I_2}/2T}\right)} \;\times\; e^{2D_o^{HI} - D_o^{H_2} - D_o^{I_2}/kT}$$

What do we need to know to predict K_{eq}?

$$\underbrace{m,\;\;M,}_{easy}\;\;\underbrace{r_o,\;\;k,\;\;D_o}_{\substack{come\ from\\ Spectroscopy!}}$$