Considering a system in which $0 < \beta < \infty$ and $0 < T < \infty$, then
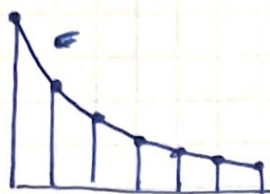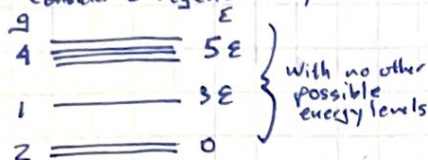

$$e^{-\frac{\varepsilon}{k_B T}}, \text{ if}$$
$$\varepsilon = k_B T, \quad e^{-1} = 0.37$$
$$\varepsilon = 2 k_B T, \quad e^{-2} = 0.13$$
$$\ldots$$

Consider a degenerate system:

$$\begin{array}{ll} g & \varepsilon \\ 4 \quad\equiv\equiv\equiv & 5\varepsilon \\ 1 \quad\underline{\quad\quad} & 3\varepsilon \\ 2 \quad\equiv\equiv & 0 \end{array} \left.\begin{array}{l} \\ \\ \end{array}\right\} \begin{array}{l} \text{with no other} \\ \text{possible} \\ \text{energy levels} \end{array}$$

Then the partition function may be represented as:

$$q = \sum_{states} e^{-\varepsilon_i \beta} \cdot g_i$$
$$q = 2 \cdot e^0 + 1 \cdot e^{-3\varepsilon\beta} + 4 e^{-5\varepsilon\beta}$$

$\rightarrow$ Maximum q, $\beta \to 0$, $T \to \infty = 7$
$\rightarrow$ Minimum q, $\beta \to \infty$, $T \to 0 = 2$

What about for a harmonic oscillator?

$$E_{HO}(n) = h\nu(n + \tfrac{1}{2}) \rightarrow \text{No limit on the number of energy levels possible}$$
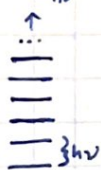
• For the zero point energy, $\varepsilon_{HO} = h\nu n$, and $q = 1 + e^{-h\nu\beta} + e^{-2h\nu\beta} + \ldots$
Let $e^{-h\nu\beta} = b$. Then, $q = 1 + b + b^2 + b^3 + \ldots + b^n \rightarrow$ a taylor approximation!

$$q = 1 + b + b^2 + b^3 + \ldots + b^n = \frac{1 - b^{n+1}}{1 - b}, \text{ Since } n \to \infty, \text{ the expression simplifies to } \frac{1}{1-b}.$$
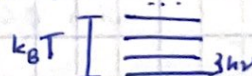
We find the partition function of the harmonic oscillator:

$$\boxed{q_{HO} = \frac{1}{1 - e^{-h\nu\beta}}}, \quad q_{T \to 0} = 1. \quad \text{If } h\nu \lll k_B T, \text{ then } e^{-h\nu\beta} \to e^{-x}, \text{ where } x$$
is a small number.

Recall that $e^x \approx 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots$ Then for $q = \frac{1}{1 - e^{-x}}$,

$$q = \frac{1}{1 - e^{-h\nu\beta}} \approx \frac{1}{1 - (1 - h\nu\beta)} = \frac{1}{h\nu\beta} = \frac{k_B T}{h\nu}$$ | Result tells us how many levels fall between the range of 0 to $k_B T$:

A Consideration of Entropy

Recall that for any reversible thermodynamic process,

$$\oint \frac{\delta q_{rev}}{T} = 0. \quad \text{Then entropy is defined } \Delta S = \int_{S_1}^{S_2} \frac{\delta q_{rev}}{T}, \text{ and } dS = \frac{\delta q_{rev}}{T}$$

Entropy is a measure of disorder. So what is disorder?
$\rightarrow$ More than 1 possibility: (1) All states are in one spin = no disorder. (2) All states can be in two different spins = disorder. Therefore, the more possible microstates, the more disorder.

S is an extensive function: $\boxed{S_A \, S_B}$, $S_{tot} = S_A + S_B$. Just as energies add and wave functions multiply, entropies add and the number of microstates, W, multiply.

what function does this? — Logarithm.

$$\begin{array}{l} \text{Statistical} \\ \text{Weight} \end{array} \left\{ \begin{array}{l} W_A = \text{number of microstates in } A \\ W_B = \text{number of microstates in } B \\ \text{then } W_A(W_B), \text{ assuming } W_A \text{ is} \\ \text{independent of } W_B. \end{array} \right\} \rightarrow S = f(N) = f(W_A) + f(W_B) = f(W_A \cdot W_B)$$

Therefore,

$$S = f(w) = f(w_A) + f(w_B) = f(w_A \cdot w_B) = \log(w), \text{ the relation } S = k_B \log(w) \text{ then holds.}$$

If there is just 1 state, then $W = 1$, $\log(1) = 0 = S \rightarrow$ <u>No entropy</u>

<u>Deriving a full relation of entropy to the partition function</u>

Recall that $\quad W = \dfrac{N!}{\prod a_i!}$, and $\ln N! = N \ln N - N$

$$(\text{since } \sum a_i = N)$$

Therefore $\quad \ln W = N \ln N - N - \sum_i (a_i \ln a_i - a_i) = \left(\sum a_i\right) \ln N - \sum a_i - \sum a_i \ln a_i + \sum a_i$

$$\ln W = -\sum a_i (\ln a_i - N)$$

$$= -\sum a_i \ln \left(\boxed{\dfrac{a_i}{N}}\right) \qquad \dfrac{e^{-\varepsilon_i \beta}}{q} \quad -\sum a_i \ln \left(\dfrac{e^{-\varepsilon_i \beta}}{q}\right) = \sum a_i \ln \left(e^{-\varepsilon_i \beta}\right) + \sum a_i \ln(q)$$

$$\sum a_i \ln \left(e^{-\varepsilon_i \beta}\right) + \sum a_i \ln(q) = \beta \underbrace{\sum_i a_i \varepsilon_i}_{E} + N \ln q$$

$$\ln W = \beta E + N \ln q, \qquad S = \cancel{k_B} \dfrac{1}{\cancel{k_B} T} E + k_B N \ln q, \qquad \boxed{S = \dfrac{E}{T} + k_B N \ln q}$$

Similarly, $\boxed{E = -N \dfrac{d}{d\beta} \ln q}$ Once q is known, both S and E may be known, and G, A may also be determined: q is very powerful

<u>On the relation of the partition function to Energy and Entropy.</u>

The partition function represents the number of thermally accessible states for a molecule. Suppose we had altered one partition function, A, such that one of its energy levels is higher in a new partition function, B:

When $T \rightarrow 0$, $q_A = q_B = 1$
When $T \rightarrow \infty$, $q_A = q_B = 5$ (since there are five energy levels)
When $0 < T < \infty$, $q_A > q_B$

How would entropy and energy be affected by an increase in the partition function by a factor of A? $q \rightarrow q \cdot A$, then:

$$S = \dfrac{E}{T} + k_B N \ln q$$

$$\ln(q \cdot A) = \ln(q) + \ln(A)$$

$$E = -N \dfrac{d}{d\beta} \ln q$$

$$S = \dfrac{E}{T} + N k_B (\ln q + \ln A)$$

$$\begin{cases} \text{If } A > 1, S \text{ inc.} \\ \text{If } A < 1, S \text{ dec} \end{cases}$$

$$E = -N \dfrac{d}{d\beta} (\ln q + \ln(A))$$

$$\quad\hookrightarrow \text{Constant,} \quad \dfrac{d}{d\beta} \ln(A) = 0$$

Energy is <u>not</u> imparted by a temperature independent factor.
Entropy <u>is</u> imparted by a change in the partition function.

So far we have observed $q = \sum e^{-\mathcal{E}_i \beta}$, where $\mathcal{E} = \underbrace{\mathcal{E}_{tr} + \mathcal{E}_{rot} + \mathcal{E}_{vib} + \mathcal{E}_{e^-} + \mathcal{E}_{spin} + \mathcal{E}_{nuc} + \dots}$

Each of these could change, but we assume they are all independent of each other.

If energies add, wave functions multiply. Similarly, if energies add, partition functions must multiply:
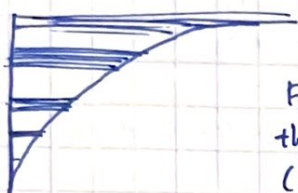
• Consider just $\mathcal{E}_{tr}$ and $\mathcal{E}_{rot}$:

$$\mathcal{E}_{tr} = \frac{h^2}{8ma^2}n^2, \qquad \mathcal{E}_{rot} = hcBJ(J+1), \quad \text{then} \quad q = \sum_{n,J} e^{-(\mathcal{E}_{tr}+\mathcal{E}_{rot})\beta} = \underbrace{\left[\sum_n e^{-\mathcal{E}_t(n)\beta}\right]}_{q_{tr}} \underbrace{\left[\sum_J e^{-\mathcal{E}(J)\beta}\right]}_{q_{rot}}$$

∴ $q_{tot} = q_{tr} \cdot q_{rot}$, and $q_{tot} = q_{tr} \cdot q_{rot} \cdot q_{vib} \cdot q_{e^-} \cdot q_{spin} \cdot q_{nuclear}$ in general.

We will take a look at how to find the partition functions for each of these quantities:

① q_{e^-}, electronic state

for a hydrogen atom, $E_n = -\frac{\hbar^2}{2mq_o^2}\frac{1}{n^2}$, and $\boxed{q_{e^-} = 1 = q_o}$ ← degeneracy of ground state.

From previous calculations, we know that $\Delta E \ggg k_B T$ for hydrogen. Therefore, only the first exponential of the partition function would contribute an appreciable amount. (We can ignore the other terms).

② q_{spin}, spin (and q_{nuc})

A spin ½ system contains 2 states:

$$\underline{\quad}\Big\} \Delta E \qquad s = I = \frac{1}{2}, \quad \boxed{q = 1 + e^{-\Delta\mathcal{E}\beta}} \qquad\qquad \text{And so on and so forth}$$

If $I = 1$, $\quad$ Where $\Delta E = g \hbar B_0$

$$2\Delta E \Big\{ \underline{\underline{\quad}}\Big\}3\Delta E \qquad s = I = 1, \quad q = 1 + e^{-\Delta\mathcal{E}\beta} + e^{-2\Delta\mathcal{E}\beta}$$

③ q_{vib}, harmonic oscillator

We have previously determined that $q_{HO} = \frac{1}{h\nu\beta} = \frac{1}{1 - e^{-h\nu\beta}}$, with equally spaced states.

$$\equiv \Big\}\frac{5}{2}h\nu$$
$$\equiv \Big\}\frac{3}{2}h\nu$$

$T \to 0$, $\frac{h\nu}{k_B T} \to \infty$, and $q_{HO} = 1$

$0 < T < \infty$, if $h\nu < k_B T$, $q_{HO} = \frac{1}{h\nu\beta} = \frac{k_B T}{h\nu}$

$T \to \infty$, $\frac{h\nu}{k_B T} \to 0$, and $q_{HO} \to \infty$

④ q_{rot}, rotational motion

Recall $\mathcal{E}_{rot} = hcBJ(J+1)$, where $J = 0, 1, 2, \dots$ Is a degenerate system:

9
5 $\equiv$ $J=2$ ⎫
$\qquad\qquad\qquad$ ⎬ Overall degeneracy
3 $\equiv$ $J=1$ ⎪ is $2J+1$
$\qquad\qquad\qquad$ ⎭
1 $\underline{\quad}$ $J=0$

$$q_{rot} = \sum_{J=0}^{\infty} \underbrace{(2J+1)}_{g_i} e^{-\overbrace{hcBJ(J+1)}^{\mathcal{E}_{rot}}\beta}$$

This function increases smoothly when J increases, since we can sway out for integration. →

$$\int_0^{\infty} (2J+1)e^{-hcB\beta J(J+1)}\,dJ$$

↳ let $u = J(J+1)$ then $du = (2J+1)\,dJ$

$$\int_0^{\infty} e^{-hcB\beta u}\,du = \boxed{\frac{1}{hcB\beta}} = \boxed{\frac{k_B T}{hcB}}$$

When $T \to 0$, $q = 1$
When $T \to \infty$, $q \to \infty$ (no limit on energy levels?)
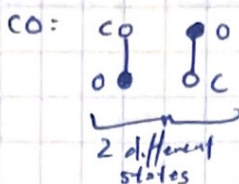When $0 < T < \infty$, $q_{rot} = \frac{hcB}{k_B T} \lll 1$

Note the similarity:
$q_{HO} = \frac{1}{h\nu\beta}$, $q_{rot} = \frac{1}{hcB\beta}$

Consider 2 molecules, N_2 and CO. Both of these molecules rotate, but what is the difference in rotation between each?

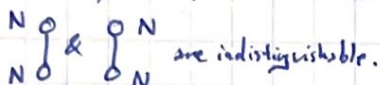→ $\mu_{N_2} \approx \mu_{CO}$, and $r_{N_2} \approx r_{CO}$, but the difference is in symmetry:

N_2: N O
                vs
         N O

(Indistinguishable)
→ Overcounts

CO: C O   O
      O   O C

2 different states
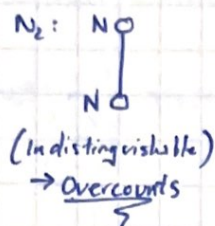
To accomodate for overcounting,

$$q_{rot} = \left(\frac{1}{hc\beta B}\right) / \sigma$$

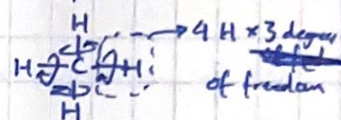A correction factor
"Symmetry factor"

The symmetry factor:

For N_2, $\sigma = 2$, since

N O & O N
N O   O N   are indistinguishable.

For NH_3, $\sigma = 3$, since

For CH_4, $\sigma = 12$

→ 4 H × 3 degrees of freedom
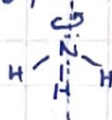
So far, both q_{rot} and q_{vib} resulted in terms with β in the denominator. Why is this significant?

$$q_{vib} = \frac{1}{h\nu\beta} \quad \text{and} \quad q_{rot} = \left(\frac{1}{hc\beta B}\right)/\sigma. \quad \text{In general, this can be represented as } q = \frac{1}{A\beta}.$$

In this case, $\ln q = -\ln A - \ln \beta$. Substituting for energy,

$$E = -N\frac{d}{d\beta}\left(-\ln A - \ln \beta\right) = -N\left(-\frac{1}{\beta}\right) = \boxed{Nk_B T} \quad (\text{Look familiar ?})$$

○ Rotation
○ Vibration

⑤ q_{trans}, translational motion.

→ Consider a 1-dimensional case, $E_{trans} = \frac{h^2}{8ma^2}n^2$, where $n = 1,2,3,\dots$ and a is the length of the box.

Recall that

$$\Delta E_{trans} = \frac{h^2}{8ma^2}(n^2-1), \quad \text{let } \frac{h^2}{8ma^2} = c, \quad \text{then } q_{tr} = \sum_{n=1}^{\infty} e^{-c(n^2-1)\beta}$$

We adjust the bounds of summation (to make the integral easier)

$$q_{tr} = \sum_{n=1}^{\infty}\left(e^{-c(n^2-1)\beta}\right) = e^{c\beta}\left(\sum_{n=1}^{\infty}e^{-cn^2\beta} + 1 - 1\right) = e^{c\beta}\sum_{n=0}^{\infty}e^{-cn^2\beta} - e^{c\beta}.$$

Since $c = \frac{h^2}{8ma^2} \lll k_B T$, the transition of the exponential between states changes smoothly. We may use integration in its place:

Let $n = x$

$$e^{c\beta}\int_0^{\infty}e^{-cx^2\beta}dx \not\approx e^{c\beta}$$

$$\int_0^{\infty}e^{-ax^2}dx = \frac{\sqrt{\pi}}{2}\frac{1}{\sqrt{a}}$$

Additionally, since $c\beta \lll 1$, we can simplify this further:

$$\longrightarrow 1\cdot\frac{\sqrt{\pi}}{2}\left(\frac{1}{\sqrt{c\beta}}\right) - 1 \approx \frac{\sqrt{\pi}}{2\sqrt{c\beta}} \cdot \quad q_{tr} = \frac{\sqrt{\pi}}{2\sqrt{c}}\left(\frac{1}{\sqrt{\beta}}\right)$$

↳ This term becomes very large

Constant, $= A$

This term also divides by β: what is its effect on E?

$$q = \frac{A}{\beta^{1/2}}, \quad \ln q = \ln A - \frac{1}{2}\ln\beta$$

$$E = -N\frac{d}{d\beta}\left(\ln A - \frac{1}{2}\ln\beta\right) = -N\left(-\frac{1}{2}\right)\left(\frac{1}{\beta}\right) = \boxed{\frac{1}{2}Nk_B T}$$

(look familiar?)

○ Translation

$$\boxed{q_{tr} = \frac{A}{\beta^{1/2}}}$$

How do we apply this to 3-D motion?

$$\frac{\sqrt{\pi}}{2\sqrt{c\beta}} = q \text{, where } c = \frac{h^2}{8ma^2}. \quad q = \left(\frac{\sqrt{\pi}}{\frac{h\beta}{\sqrt{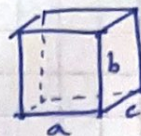8ma^2}}}\right) = \left(\frac{a}{h/\sqrt{2\pi mk_BT}}\right) \quad \begin{array}{l}\text{Recall that} \\ \rightarrow p = \sqrt{2mE} \text{ and } \lambda = \frac{h}{p}.\end{array}$$

$$\underbrace{\phantom{\frac{h}{\sqrt{8ma^2}}}}_{\text{Resembles } p}$$

$$q = \left(\frac{h}{p}\right)\left(\frac{1}{\sqrt{2\pi}}\right), \quad \text{then} \quad \Lambda = \frac{h}{\sqrt{2\pi mk_BT}}$$

$q_{tr} = \frac{a}{\Lambda} \rightarrow$ how many wavelengths feed into one box. For 3D motion,

$$q_{tr} = \left(\frac{a}{\Lambda}\right)\left(\frac{b}{\Lambda}\right)\left(\frac{c}{\Lambda}\right) = \boxed{\frac{V}{\Lambda^3}}, \text{ where } V \text{ is the volume of the box}$$

Comparing q_{vib}, q_{rot}, and q_{tr} at 300 K :

$$q_{vib} : \frac{h\nu}{k_BT} \approx 10 \qquad\qquad q_{rot} : \frac{1}{hc B\beta} \approx 110 \qquad\qquad q_{tr} : \frac{V}{\Lambda^3} :$$

For a gas, $22.4 \text{ L} = 22.4 \times 10^{-3} m^3 / mol$ at standard temp & pressure

$\Lambda \sim \frac{1}{\sqrt{m}}$, and for H, $\Lambda = 1 A = 10^{-10} m$

Why is q_{tr} so massive? Consider a box of volume V:

$q =$ how many small cubes we can place into the large box.

$\circ$ We have not considered the effect to which particles take up space on their own — if we put a particle in the box, it takes up space, and a second particle has less possible places to be placed.
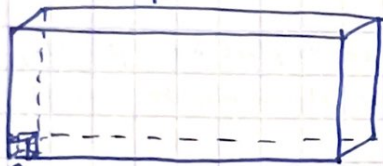
— Small cube, representing a particle

$$q_{tr} = \frac{22.4 \times 10^{-3} m^3}{(10^{-10})^3} \approx 2.2 \times 10^{28}$$

Massive number! There is something wrong with our calculation.

$E = \sum\limits_{\text{particles}} E_i \rightarrow$ Sum of all particle's energies.
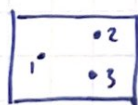
In principle, the partition functions of all particles may be multiplied since the particles are independent of e/o.

$$Q = q_1 \cdot q_2 \cdot q_3 \cdots = q^N \longrightarrow \text{Through the energy equation,}$$
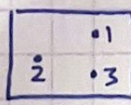
(of molecules)

q_t is $q_{molecule}^{vibra}$

$$-N\frac{d}{d\beta}\ln q^\circ = -\frac{d}{d\beta}\ln q^N = -\frac{d}{d\beta}\ln Q$$

Similarly, in $S = \frac{E}{T} + k_B N \ln q$, $\quad S = \frac{E}{T} + k_B \ln q^N = \frac{E}{T} + k_B \ln Q$

Particles by themselves are distinguishable (Not in the QM) sense. They have a fixed position in space.

Taken together, however, these two are indistinguishable, since they can move and swap positions.

If the particles are indistinguishable, a correction factor is needed:

$$N(N-1)(N-2)\ldots = N!$$

Available space for first particle

For second particle

For third ...

Therefore:

Distinguishable : $Q = q^N$

Indistinguishable: $Q = \frac{q^N}{N!}$

↳ Contribution by translational motion

So how are E and S affected by this approximation?

Effect of indistinguishable correction factor on E and S:

$$q^N \rightarrow \frac{q^N}{N!} = \left(\frac{q}{(N!)^{1/N}}\right)^N \quad \text{Applying sterling's approximation, } N! = \sqrt{2\pi}\, N^{N+1/2}\, e^{-N},$$

$$(N!)^{1/N} = (\sqrt{2\pi})^{1/N} N^{1+\frac{1}{2N}} e^{-1}, \quad N \text{ is large, so } (N!)^{1/N} \approx (\sqrt{2\pi})^{0} N^{1+\frac{1}{2N}} e^{-1} = \frac{N}{e}$$

Then $\left(\frac{q}{(N!)^{1/N}}\right)^N = \left(\frac{q}{N} e\right)^N \approx 10^5$

$$E = -\frac{d}{d\beta} \ln\left(\frac{Q}{N!}\right) \rightarrow \frac{d}{d\beta}\left(\ln(Q) - \ln(N!)\right)^{0} \rightarrow E \text{ doesn't care about this correction factor.}$$

$\rightarrow \frac{3}{2} k_B N$

$$S = \frac{E}{T} + k_B T \ln Q \quad , \quad S_{tr} \text{ for a monatomic gas: } \frac{3}{2} k_B N + k_B N \ln\left(\frac{q}{N} e\right), \quad q = \frac{V}{\Lambda^3}, \text{ so}$$

$$S_{tr} = \frac{3}{2} k_B N + k_B N \ln\left(\frac{Ve}{\Lambda^3 N}\right) \rightarrow S_{tr} = k_B N \ln\left(\frac{V e^{5/2}}{\Lambda^3 N}\right)$$

$\underbrace{}_{k_B N \ln e^{3/2}}$

$\downarrow$ How many particles there are.

$\downarrow$ How many small cubes are in the big cube

$\rightarrow$ At some point, $\ln\left(\boxed{\frac{V e^{5/2}}{\Lambda^3 N}}\right)^{1}$. In this case, there are no more spaces to place a new particle, and the entropy becomes 0. Since $E = U - U(T=0)$, all the other relations may be derived:

$$H = U + pV$$
$$A = U - TS$$
$$G = H - TS = A + pV$$

$\longrightarrow$ Recall maxwell relation $P = -\left(\frac{\partial A}{\partial V}\right)_T$

Then $^{1)}P = -\frac{d}{dV} A$

$$A = E - \left(\frac{E}{T} + k_B N \ln(Q)\right) T$$
$$^{2)}A = k_B T \ln Q \quad \downarrow S$$

$\downarrow \frac{d}{dV} \ln Q = \frac{1}{V}, \text{ since}$

$\frac{d}{dV} \ln Q = \frac{d}{dV}\left(\ln V + \underbrace{\ln e}_{} - (\ln \Lambda^3 + \ln N)\right) \quad = 0 \text{ after } \frac{d}{dV}$

With 1) and 2), we find
$$P = -\frac{d}{dV} A = k_B T \frac{1}{V} N$$
Rearranging, we get the ideal gas law, $\underline{PV = N k_B T}$

END