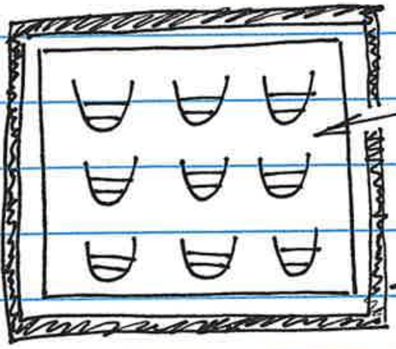


A thermal reservoir (constant T) can exchange energy between members of the ensemble

thermal insulation (no energy in or out)

An ensemble of oscillators make up our system

Energies $E_i = (n_i + \frac{1}{2})\hbar\omega$

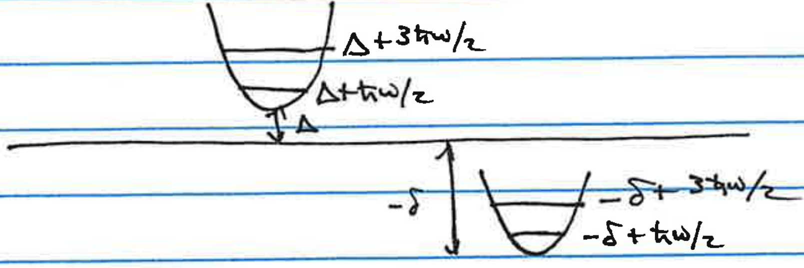
a_i = # of members of ensemble with energy E_i

$$\frac{a_2}{a_1} = f(E_1, E_2)$$

relative populations of states depends on energies of states

this function is like $\rho(\vec{q}, \vec{p})$ classically

Energy is always measured relative to some fixed arbitrary value :



If we move the zero bar up or down, the relative fraction, $\frac{a_1}{a_0}$ should <u>not</u> change

$$\therefore \quad \frac{a_2}{a_1} = f(E_1, E_2) = f(E_1 - E_2)$$

The important thing about energies is in the <u>difference</u> between two states.

Let's consider 3 states:

$$\frac{a_3}{a_2} = f(E_2 - E_3) \qquad \frac{a_2}{a_1} = f(E_1 - E_2)$$

$$\frac{a_3}{a_1} = \frac{a_3}{a_2} \cdot \frac{a_2}{a_1} = \boxed{f(E_1 - E_3) = f(E_2 - E_3)\, f(E_1 - E_2)}$$

says something about our probability function f

$$f(x+y) = f(x)\, f(y)$$

one of your homework problems is to prove something about f. We'll assume it here:

$$\text{If} \quad f(x) = e^{\beta x} \quad \text{and} \quad f(y) = e^{\beta y}$$

$$e^{\beta(x+y)} = e^{\beta x} e^{\beta y} \quad ✓$$

← That's what we need!

There fore: $f(E) = e^{\beta E}$

Returning to our 3 states:

$$e^{\beta(E_1 - E_3)} = e^{\beta(E_1 - E_2)}\, e^{\beta(E_2 - E_3)} \quad ✓$$

$$\frac{a_2}{a_1} = e^{\beta(E_1 - E_2)}$$

likelihood of a state is proportional to an exponential factor of the energy of that state

So:

$$a_n = C e^{-\beta E_n}$$

Suppose we have a fixed number of states and we want probability information:

$$P_n = \frac{a_n}{\sum_i^{\text{all states}} a_i} = \frac{c\, e^{-\beta E_n}}{\sum_{i=1}^{\text{all states}} c\, e^{-\beta E_i}}$$

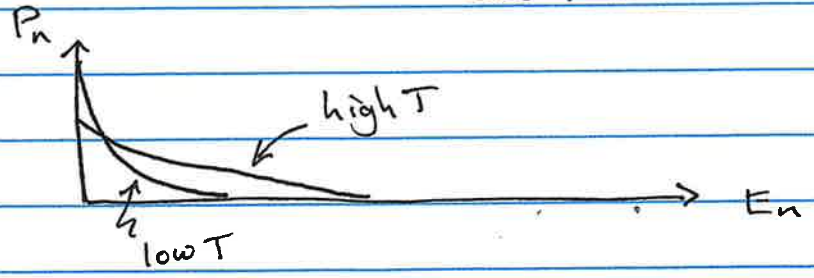
$$= \frac{e^{-\beta E_n}}{\sum_i e^{-\beta E_i}}$$ ← This denominator is something special called the partition function

$$Q(N, V, \beta) = \sum_i e^{-\beta E_i}$$

β can be derived, but for now: $\beta = \frac{1}{k_B T}$

$$Q(N, V, T) = \sum_i e^{-E_i/k_B T}$$

$$P_n(N, V, T) = \frac{e^{-E_n/k_B T}}{Q(N, V, T)}$$



What can we do with Q?

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

Partition Function Tricks

energy of that state

temperature of the ensemble

$$Q = \sum_i e^{-\beta E_i} = \underbrace{\sum_i}_{\text{sum over all states}} \underbrace{e^{-E_i/k_B T}}_{\text{Boltzmann factor: How probable is that State}}$$

Consider:

$$\frac{\partial \ln Q}{\partial \beta} = \frac{1}{Q}\frac{\partial Q}{\partial \beta}$$

$$= \frac{1}{Q}\sum_i \frac{\partial}{\partial \beta}\left(e^{-\beta E_i}\right)$$

$$= \frac{1}{Q}\sum_i -E_i e^{-\beta E_i}$$

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

$$= -\sum_i E_i P_i = -\langle E \rangle$$

If we'd prefer to use T, there's a chain rule

$$\beta = \frac{1}{k_B T}$$

$$\frac{\partial f}{\partial T} = \frac{\partial f}{\partial \beta}\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial f}{\partial \beta} \Rightarrow \frac{\partial f}{\partial \beta} = -k_B T^2 \frac{\partial f}{\partial T}$$

$$\boxed{\langle E \rangle = +k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}}$$

What is Q?

The partition function is a way of expressing the likelihood of a state in an ensemble of

N identical particles in volume V. Once we have the likelihood of all microscopic states, we can predict macroscopic properties (like $\langle E \rangle$)

If we have identical, indistinguishable particles

$$Q(N,V,T) = \frac{q(V,T)^N}{N!}$$

$q(V,T)$ is the single particle partition function for states available to that particle

$Q(N,V,T)$ is the partition function for states available to all particles.

What is $q(V,T)$ for an ideal gas?

$$T = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right) \leftarrow \text{one particle} \qquad V = 0$$

$$\mathcal{H}(q,p) = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

$$q(T,V) = \sum_{\text{all states}} e^{-\beta E_{state}} = \iint e^{-\beta \mathcal{H}(q,p)}\, d\vec{q}\, d\vec{p}$$

$$= \underbrace{\int dx \int dy \int dz}_{L_x L_y L_z} \int dp_x \int dp_y \int dp_z\, e^{-\frac{\beta}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)}$$

$$\underbrace{L_x L_y L_z}_{V} \left(\int dp\, e^{-\beta p^2/2m}\right)^3 \leftarrow \text{gaussian integral}$$

$$V \left(\sqrt{\frac{2\pi m}{\beta}}\right)^3$$

$$q(T,V) = V\left(2\pi m k_B T\right)^{3/2}$$

Last time:

$$Q = \sum_{i=1}^{\text{all states}} e^{-\beta E_i} \qquad \beta = \frac{1}{k_B T}$$

E_i = energy of <u>system</u> state i

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right) = +k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

A short interlude on sums-of-products & products-of-sums

Consider:

$$S = \sum_{i=1}^{2} \sum_{j=0}^{1} x^i y^j \quad = \text{sum-of-products}$$

$$= x(1+y) + x^2(1+y)$$

$$= (x+x^2)(1+y)$$

$$= \left(\sum_{i=1}^{2} x^i\right)\left(\sum_{j=0}^{1} y^j\right) \quad = \text{product-of-sums}$$

What if our <u>system</u> consists of N <u>identical</u>, <u>distinguishable</u> particles:

$$E_i^{tot} = E_1^a + E_0^b + E_1^c + E_2^d + \cdots$$

↑ total energy in system state i

↑ energy of molecule "a" in state 1

↑ energy of molecule "d" in state 2

$$i = \{\underset{\text{"a"}}{1}, 0, 1, \underset{\text{"d"}}{2}, \ldots\}$$

i describes the total state of the system

$$Q = \sum_i e^{-\beta E_i^{tot}}$$

Suppose we visit every molecular state instead

$$Q = \underbrace{\sum_i}_{\text{all system states =}} e^{-\beta E_i^{tot}} = \underbrace{\sum_j \sum_k \sum_l \cdots}_{\text{all states of all molecules}} e^{-\beta(E_j^a + E_k^b + E_l^c + \cdots)}$$

sum in the exponent is a product

$$Q = \sum_j \sum_k \sum_l \cdots e^{-\beta E_j^a} e^{-\beta E_k^b} e^{-\beta E_l^c} \cdots$$

sum-of-products
‖
product-of-sums

$$= \underbrace{\sum_j e^{-\beta E_j^a}} \underbrace{\sum_k e^{-\beta E_k^b}} \underbrace{\sum_l e^{-\beta E_l^c}} \cdots$$

product of single molecule partition functions

$$= q_a * q_b * q_c * \cdots$$

If we have N distinguishable, but identical molecules:

$$Q = q^N$$

For indistinguishable molecules things are a bit more complicated:

$$E_{tot} = \overset{a}{E_1} + \overset{b}{E_2} + \overset{c}{E_1} + \overset{d}{E_0}$$

But, we can't tell which molecule is which, so we also have this possibility:

$$E_{tot} = E_0 + E_1 + E_1 + E_2$$

These are considered the same state from a system-wide point of view.

If we were to compute Q the same as before we would overcount the system states!

In fact, we overcount by the number of permutations of those N molecules $= N!$

$\therefore$ for indistinguishable molecules,

$$Q(N,V,T) = \frac{\underbrace{q(V,T)}_{\leftarrow\ \text{single molecule P.F.}}{}^{\overset{\text{N molecules}}{N}}}{\underset{\uparrow\ \text{correction for overcounting system states.}}{N!}}$$

A 2 molecule example: (each molecule has 2 levels)

a	b	
E_1	E_1	← unique state but 2 permutations of (A,B)
E_1	E_2	identical system states that we overcount by 2
E_2	E_1	
E_2	E_2	← unique state, but 2 permutations of (A,B)

There are some subtleties for quantum particles (Fermions & Bosons) particularly at low T, but we'll revisit this later.

Back to the ideal gas: N non-interacting indistinguishable particles in volume V.

Total Potential $V(\vec{q}) = 0$

Kinetic Energy $T(\vec{p}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$

$$\mathcal{H}(\vec{q},\vec{p}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} = \frac{1}{2m}\overbrace{\left(p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + \dots\right.}^{3N \text{ terms}}$$

For 1 particle,

$$h(\vec{q},\vec{p}) = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

$$q(V,T) = \sum_{\text{states}} e^{-\beta E_{\text{state}}}$$

10-4

$$q(V,T) = \underbrace{\int_0^{L_x} dq_x \int_0^{L_y} dq_y \int_0^{L_z} dq_z}_{V} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \, e^{-\frac{\beta}{2m}(p_x^2+p_y^2+p_z^2)}$$

$$V \cdot \left(\int_{-\infty}^{\infty} dp \; \underbrace{e^{-\beta p^2/2m}}_{\text{Gaussian w/ } \sigma^2 = m k_B T} \right)^3$$

$$q(V,T) = V \left(\sqrt{2\pi\sigma^2} \right)^3 = V \left(2\pi m k_B T \right)^{3/2}$$

One problem $q(V,T)$ is a <u>normalization factor</u> and must be unitless, so we add a "patch" which is a factor of <u>h</u> for <u>each</u> (q,p) pair

$$q(V,T) = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} = V \left(\frac{2\pi m}{\beta h^2} \right)^{3/2}$$

The <u>total</u> system P.F. :

$$Q(N,V,T) = \frac{q(V,T)^N}{N!}$$

$$\boxed{Q(N,V,T) = \frac{\left(\frac{2\pi m}{h^2 \beta} \right)^{3N/2} V^N}{N!}}$$

What can we do with this?

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} \qquad C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N,V}$$

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} \qquad \mu = -k_B T \left(\frac{\partial \ln Q}{\partial N} \right)_{V,T}$$

Consider what we've learned so far about the Partition Function:

- $$Q = \sum_{\text{states}} e^{-\beta E_{\text{state}}}$$ ← contains Boltzmann-weighted information about every <u>system</u> state

- Many physical (e.g. thermodynamic) properties are <u>derivatives</u> of the partition function:

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right) \Rightarrow C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V$$

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)$$

$$\mu = k_B T \left(\frac{\partial \ln Q}{\partial N}\right)$$

- System Partition functions for <u>identical</u>, <u>indistinguishable</u> particles can be derived from <u>single</u> particle partition functions

$$Q(N,V,T) = \frac{q(V,T)^N}{N!}$$

- For a classical system of non-interacting particles

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{\underbrace{h^2}}\right)^{3N/2} V^N$$

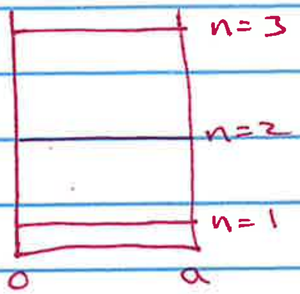
← a classical fudge factor to make Q unitless!

Now, let's consider non-interacting Quantum particles!

$$q(V,T) \text{ came from } \sum_{\text{states}} e^{-\beta E_{\text{state}}} \longrightarrow \iint_{\substack{\text{phase}\\\text{space}}} e^{-\beta \mathcal{H}(q,p)}\, dq\, dp$$

Integral over phase space was <u>identical</u> to sum over states

Consider a particle in a 1-D box:



$$\varepsilon_n = \frac{n^2h^2}{8ma^2} \qquad n = 1, 2, \ldots$$

Or in a 2-D square box:

$$\varepsilon_{n_x n_y} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2\right)$$

Or in a 3-D cube:

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

These energy expressions describe translational energy levels for a particle of mass m in a box of length a on a side.

- What happens when we make the box very large?
- Do the levels get closer in energy or further apart

Road map:

Translational energy states in small box → q → large box limit

$$q_{trans} = \sum_{states} e^{-\beta\varepsilon_{state}} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} e^{-\frac{\beta h^2}{8ma^2}\left(n_x^2+n_y^2+n_z^2\right)}$$

Last time we also convinced ourselves that

sum-of-products == product-of-sums

So:

$$q_{trans} = \left(\sum_{n_x=1}^{\infty} e^{-\frac{\beta h^2}{8ma^2} n_x^2}\right)\left(\sum_{n_y=1}^{\infty} e^{-\frac{\beta h^2}{8ma^2} n_y^2}\right)\left(\sum_{n_z=1}^{\infty} e^{-\frac{\beta h^2}{8ma^2} n_z^2}\right)$$

All 3 of these factors are identical

$$q_{trans} = \left(\sum_{n=1}^{\infty} e^{-\frac{\beta h^2 n^2}{8ma^2}}\right)^3$$

So how do we do this sum?

$$\sum_{n=1}^{\infty} e^{-\frac{\beta h^2 n^2}{8ma^2}} \approx \int_1^{\infty} e^{-\beta h^2 n^2/8ma^2}\, dn \approx \int_0^{\infty} e^{-\frac{\beta h^2 n^2}{8ma^2}}\, dn$$

Treating n as continuous is only a bit dodgy

OK if $\frac{\beta h^2}{8ma^2}$ is small

- Remember as the box gets larger, the levels get closer and energy of $n=1$ level gets close to zero!

$$\int_0^{\infty} e^{-\frac{\beta h^2}{8ma^2} n^2} = \int_0^{\infty} e^{-\alpha n^2}\, dn = \sqrt{\frac{\pi}{4\alpha}}$$

So:

$$\int_0^{\infty} e^{-\beta h^2/8ma^2\, n^2} = \sqrt{\frac{\pi\, 8ma^2}{4\beta h^2}} = \sqrt{\frac{2\pi m k_B T}{h^2}}\; a$$

side of box

$$\therefore \quad q_{trans} = \left(\sum_{n=1}^{\infty} e^{-\frac{\beta h^2 n^2}{8ma^2}}\right)^3 \approx \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} a^3$$

volume of the box

$$\therefore \quad q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

$$Q(N,V,T) = \frac{q_{trans}^{N}}{N!} = \frac{\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} V^{N}}{N!}$$

Same as classical result, this time with no fudge factor.

Last time, we derived $\langle E \rangle = \left(\frac{\partial \ln Q}{\partial T}\right) k_B T^2$

$$= \frac{3}{2} N k_B T$$

$$C_V = \frac{3}{2} N k_B = \frac{3R}{2}$$

Today:

$$P = k_B T\left(\frac{\partial \ln Q}{\partial V}\right)$$

$$\ln Q = \frac{3N}{2} \ln\left(\frac{2\pi m k_B T}{h^2}\right) + N \ln V - \ln N!$$

$$\frac{\partial \ln Q}{\partial V} = N \cdot \left(\frac{1}{V}\right)$$

$$P = k_B T\left(\frac{\partial \ln Q}{\partial V}\right) = \frac{k_B T N}{V}$$

$\therefore \quad PV = N k_B T$ ← ideal gas law!

Back to atoms momentarily:

$$\mathcal{E} = \mathcal{E}_{trans} + \mathcal{E}_{electronic}$$

Electronic states are organized into levels:

For Hydrogenic atoms: $n=1 \Rightarrow 1s$

$n=2 \Rightarrow 2s, 2p$

$n=3 \Rightarrow 3s, 3p, 3d$ ← all have the same energy

$$E_n = \frac{-m_e Z^2 e^4}{8\varepsilon_0^2 h^2 n^2}$$

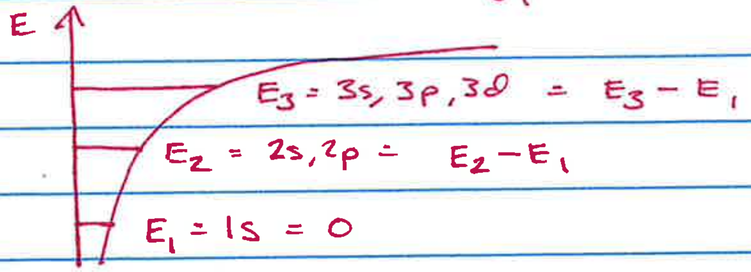
It is most convenient to leave the partition function in level form:

$$q_{elect} = \sum_{states} e^{-\beta E_{state}} = \sum_{levels} g_{level}\, e^{-\beta E_{level}}$$

$\mathcal{E}_{level}$ = energy of that level

g_{level} = degeneracy of that level

If we set the zero of energy to the ground state:



then:

$$q_{elect} = g_{e_1} e^{-\beta(0)} + g_{e_2} e^{-\beta(E_2 - E_1)} + g_{e_3} e^{-\beta(E_3 - E_1)} \dots$$

$$\underbrace{q_{elect}}_{\text{normalization}} = \underbrace{g_{e_1}}_{\text{Boltzmann factor for } n=1} + g_{e_2} e^{-\beta(E_2 - E_1)} + \dots$$

12-2

Where does g come from?

This is a topic for Quantum Mechanics, but g is related to the # of ways of arranging unpaired electrons in particular excited states:

		Term Symbol	g
H:	$(1s)^1$:	$^2S_{1/2}$	2
He:	$(1s^2)$:	$^1S_0$	1
	$(1s^1 2p^1)$	$^3S_1$	3

We can ask about how populated an electronic state will be:

$$f_2(T) = \frac{g_{e_2} e^{-\beta(E_2-E_1)}}{q_{elect}}$$

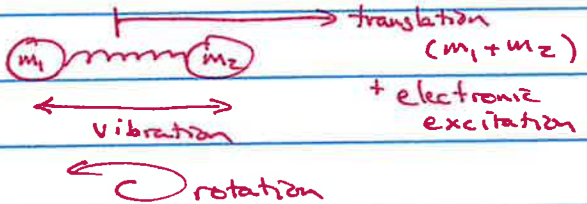
For Fluorine:

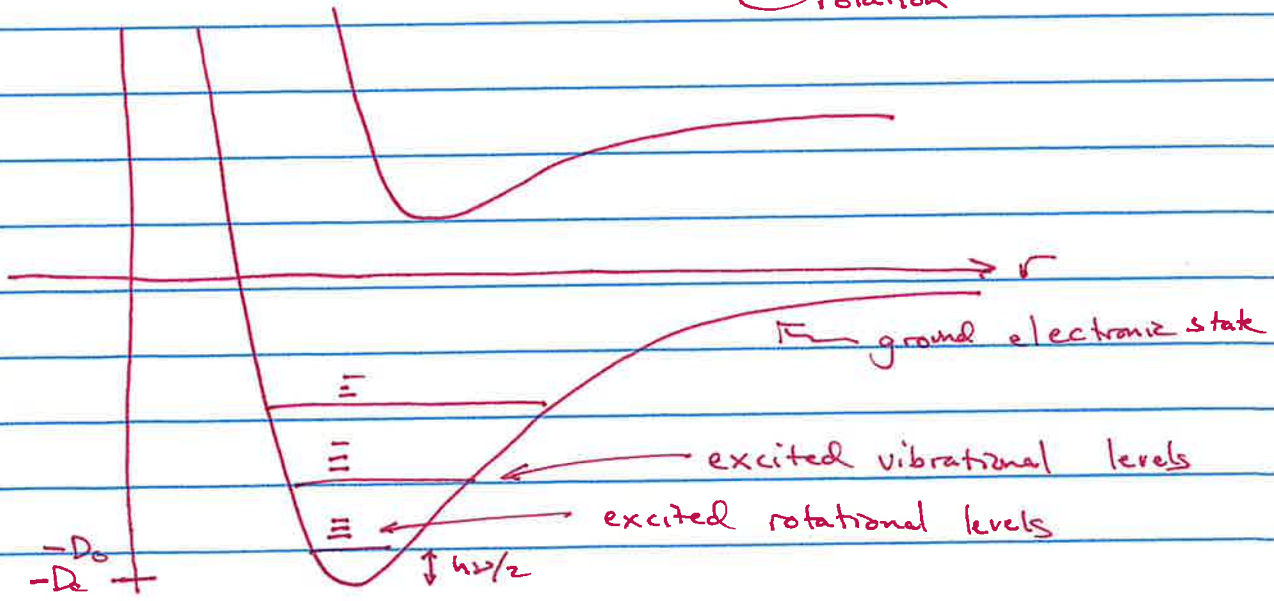
$f_2(300) = 0.0672$ ← excited states are usually not significantly populated at room temperature

$f_2(1000) = 0.219$

$f_2(2000) = 0.272$

Back to Diatomics





total mass of diatomic

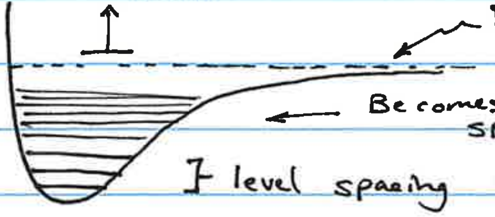
$$q_{trans} = \left(\frac{2\pi (m_1+m_2) k_B T}{h^2}\right)^{3/2} V$$

$$q_{elect} = g_{e_1} e^{\beta D_e} + g_{e_2} e^{-\beta \varepsilon_{e2}}$$

zero of energy is **above** D_e

we usually stop here

Vibrational Motion



"continuum" unbound states

Dissociation Threshold

Becomes more closely spaces with increasing E

level spacing is pretty uniform here

$$E_v \cong (v+\tfrac{1}{2})h\nu - h\nu x_e (v+\tfrac{1}{2})^2$$

levels of morse oscillator

The Harmonic Model:

$$E_v = (v+\tfrac{1}{2})h\nu$$

↑ no maximum level

level spacing is always $h\nu$

$$v = 0, 1, 2, \ldots \infty$$

$$q_{vib} = \sum_{v=0}^{\infty} \underbrace{e^{-\beta h\nu(v+\frac{1}{2})}}$$

Boltzmann factor for that state

sum over states

$$= \sum_{v=0}^{\infty} e^{-\beta h\nu/2} e^{-\beta h\nu v}$$

first factor does not depend on v

$$= e^{-\beta h\nu/2} \sum_{v=0}^{\infty} e^{-\beta h\nu v}$$

Let $X = e^{-\beta h\nu}$

$$= \sqrt{X} \sum_{v=0}^{\infty} X^v$$

this is a geometric series!

$$q_{vib} = \sqrt{X} \frac{1}{1-X}$$

12-4

$$q_{vib} = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} = \frac{e^{-h\nu/2k_BT}}{1 - e^{-h\nu/k_BT}}$$

$\frac{h\nu}{k_B}$ has units of <u>temperature</u>

$$\Theta_{vib} = \frac{\overset{\leftarrow \text{ constant}}{h}\nu \leftarrow \text{property of molecule}}{\underset{\uparrow \text{ constant}}{k_B}}$$

$$q_{vib} = \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}}$$

← functional form is independent of molecular species!

Let's do it <u>classically</u> also: $\mathcal{H}(q,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2$

$$q_{vib} = \sum_{\text{states}} e^{-\beta E_{\text{state}}}$$

note the $\frac{1}{h}$ for units!

$$= \frac{1}{h}\int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dq \; e^{-\beta\left(\frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}\right)}$$

$$= \frac{1}{h}\int_{-\infty}^{\infty} e^{-\beta p^2/2m}\,dp \int_{-\infty}^{\infty} e^{-\beta m\omega^2 q^2/2}\,dq$$

$$= \frac{1}{h}\int_{-\infty}^{\infty} e^{-\alpha p^2}\,dp \int_{-\infty}^{\infty} e^{-\alpha' q^2}\,dq$$

$$\alpha = \frac{\beta}{2m} \qquad \alpha' = \frac{\beta m\omega^2}{2}$$

$$q_{vib} = \frac{1}{h}\sqrt{\frac{\pi}{\alpha}}\sqrt{\frac{\pi}{\alpha'}}$$

$$= \frac{1}{h}\sqrt{\frac{\pi 2m}{\beta}}\sqrt{\frac{\pi 2}{\beta m\omega^2}} = \frac{2\pi}{h}\frac{1}{\beta\omega}$$

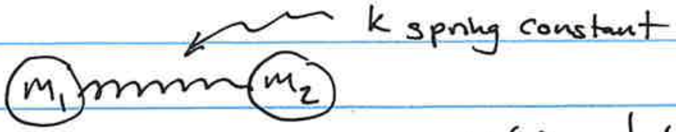
12-5

$$q_{vib} = \frac{2\pi}{h} \frac{1}{\omega} \frac{1}{\beta}$$

$$= \frac{1}{\hbar\omega} k_B T$$

$$= \frac{k_B}{h\nu} \cdot T$$

$$q_{vib}^{cl} = \frac{T}{\Theta_{vib}} \qquad q_{vib}^{QM} = \frac{e^{-\Theta_{vib}/2T}}{1-e^{-\Theta_{vib}/T}}$$



$$V(r) = \frac{1}{2}k(r-r_e)^2$$

$$\varepsilon = \varepsilon_{trans} + \varepsilon_{elect} + \varepsilon_{vib} + \varepsilon_{rot}$$

$$q(V,T) = q_{trans}(V,T) * q_{elect}(T)\, q_{vib}(T)\, q_{rot}(T)$$

$$q_{trans}(V,T) = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \qquad M = m_1 + m_2$$

$$q_{elect}(T) = g_{e_1} e^{\beta D_e} + g_{e_2} e^{-\beta \varepsilon_{e_2}} + \ldots .$$

$$q_{vib}(T) = \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} \qquad \Theta_{vib} = \frac{h\nu}{k_B} = \frac{\hbar\omega}{k_B} = \frac{\hbar\sqrt{\frac{k}{\mu}}}{k_B}$$

$\mu =$ <u>reduced mass</u> $= \frac{m_1 m_2}{m_1 + m_2}$

<u>What about rotations?</u>

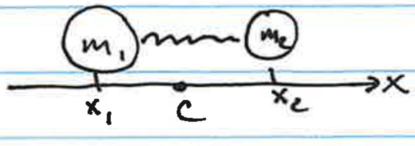
<u>Quantum Mechanically</u> : $\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \qquad J = 0, 1, 2, \ldots$

$g_J = 2J+1$ ← degeneracy of rotational <u>levels</u>

I is a moment of inertia

For diatomics: $I = m_1 d_1^2 + m_2 d_2^2$

↑ distance from center of mass



$$c = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

$$\underbrace{d_1 = x_1 - c \qquad d_2 = x_2 - c}$$

$$\Downarrow$$

a bit of algebra →

$$I = \mu r_e^2 \quad (\text{for a diatomic})$$

Partition function:

$$q_{rot} = \sum_{states} e^{-\beta E_{state}} = \sum_{levels} g_{level}\, e^{-\beta \epsilon_{level}}$$

$$= \sum_{J=0}^{\infty} g_J\, e^{-\beta E_J} = \sum_{J=0}^{\infty} (2J+1)\, e^{-\frac{\beta \hbar^2}{2I} J(J+1)}$$

$\frac{\hbar^2}{2Ik_B}$ has units of temperature, so let's define

$$\boxed{\Theta_{rot} = \frac{\hbar^2}{2Ik_B}} \longleftarrow$$

contains only constants and fixed properties of the molecule

$\therefore$

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1)\, e^{-J(J+1)\Theta_{rot}/T}$$

If $T \gg \Theta_{rot}$ the rotational levels are nearly continuous, so:

$$q_{rot} \approx \int_0^{\infty} (2J+1)\, e^{-J(J+1)\Theta_{rot}/T}\, dJ$$

let $X = J(J+1) = J^2 + J$

$dX = (2J+1)\, dJ$

$$\therefore \quad q_{rot} = \int_0^{\infty} e^{-\Theta_{rot} X/T}\, dX$$

$$= \frac{-T}{\Theta_{rot}} \left[e^{-\Theta_{rot} X/T} \right]_0^{\infty}$$

$$q_{rot} = \frac{T}{\Theta_{rot}}$$

$$\boxed{q_{rot}(T) = \frac{2Ik_BT}{\hbar^2} = \frac{8\pi I k_B T}{h^2} = \frac{T}{\Theta_{rot}}}$$

Level Populations

How likely are we to see vibrational level 2 at temperature T?

$$f_2^{vib}(T) = \frac{\text{Boltzmann weight for } v=2}{\text{Sum over all Boltzmann weights}} = \frac{e^{-\beta h\nu\frac{5}{2}}}{q_{vib}}$$

$$= \frac{e^{-5h\nu/2k_BT}}{q_{vib}} = \frac{e^{-5\Theta_{vib}/2T}\left(1-e^{-\Theta_{vib}/T}\right)}{e^{-\Theta_{vib}/2T}}$$

$$f_2^{vib}(T) = \underset{\substack{\uparrow \\ \text{makes } f_2=0 \\ \text{at } T=0}}{e^{-2\Theta_{vib}/T}} \underbrace{\left(1-e^{-\Theta_{vib}/T}\right)}_{\substack{\uparrow \text{ makes } f_2=0 \\ \text{as } T\to\infty}}$$

We can do this for v = 0 also:

$$f_0^{vib}(T) = \frac{e^{-\beta h\nu/2}}{q_{vib}} = e^{-\Theta_{vib}/2T}\frac{\left(1-e^{-\Theta_{vib}/T}\right)}{e^{-\Theta_{vib}/2T}}$$

$$= \left(1-e^{-\Theta_{vib}/T}\right) \longleftarrow \text{exponentially dies off as } T\to\infty$$

Rotational Populations

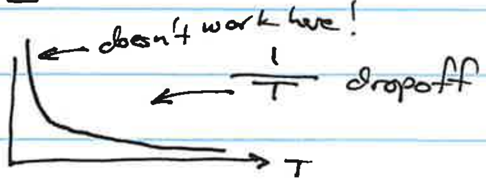
fraction of molecules in J = 2

$$f_J^{rot} = \frac{(2J+1)\,e^{-\Theta_{rot}J(J+1)/T}}{q_{rot}}$$

$q_{rot} \longleftarrow \frac{T}{\Theta_{rot}}$ when $T \gg \Theta_{rot}$

$$f_J^{rot}(T) = (2J+1)\frac{\Theta_{rot}}{T}\,e^{-\Theta_{rot}J(J+1)/T}$$

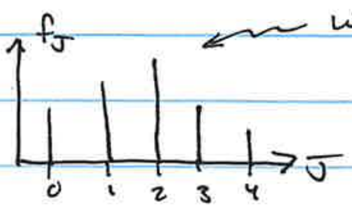
$$f_0^{rot}(T) = \frac{\Theta_{rot}}{T} =$$



$$f_2^{rot}(T) = 5\frac{\theta_{rot}}{T}\,\underbrace{e^{-6\theta_{rot}/T}}_{\approx 1 \text{ at high } T}$$

So the $J=2$ level is more populated at some temperatures than the lower energy $J=0$ level.

Degeneracy causes this.

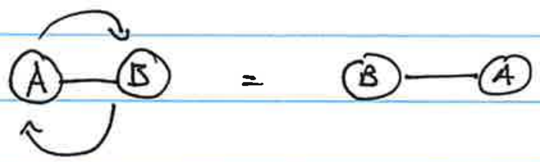


← where is this peak?

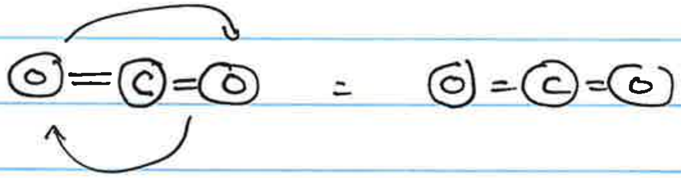
$$\frac{df_J}{dJ} = 0 \quad \text{says where } J_{max} \text{ is!}$$

$$J_{max} = \sqrt{\frac{T}{2\theta_{rot}}} - \frac{1}{2} \qquad \leftarrow \text{ increases with } \sqrt{T}$$

Symmetry



← still distinguishable from original configuration



← indistinguishable from original

for CO_2, twice per rotation, we end up in an indistinguishable configuration, so we need to adjust the rotational partition function to account for this:

$$q_{rot} = \frac{T}{\sigma\,\theta_{rot}}$$

σ ↖ symmetry number = number of indistinguishable orientations of the rotation

N_2 : $\sigma = 2$

HCl : $\sigma = 1$

14-1

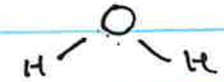
Polyatomics

$$O=C=O$$

3 atoms = 9 degrees of freedom

$$\begin{array}{l} 3 \text{ translations} \\ \underline{2 \text{ rotations}} \\ 4 \text{ vibrational modes} \end{array}$$

linear molecules → 2 rotations



3 atoms = 9 degrees of freedom

$$\begin{array}{l} 3 \text{ translations} \\ \underline{3 \text{ rotations}} \\ 3 \text{ vibrational modes} \end{array}$$

nonlinear molecules → 3 rotations

$$q = q_{trans}\, q_{elect}\, q_{vib}\, q_{rot}$$

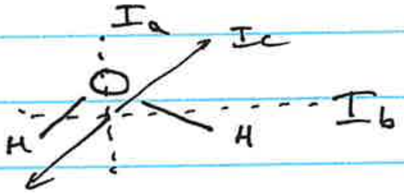
$$= \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \left(g_1 e^{\beta D_e} + g_2 e^{\beta(E_2-E_1)} + \cdots\right)\left(\prod_{j=1}^{N_{vib}} q^j_{vib}(T)\right)\left(\, ? \,\right)$$

q_{rot} for linear molecules is easy:

$$\underline{I} = \sum_i m_i d_i^2 \qquad \varepsilon_J = \frac{\hbar^2}{2I} J\cdot(J+1)$$

$$q_{rot} = \frac{T}{\sigma\, \Theta_{rot}} \quad \text{with} \quad \Theta_{rot} = \frac{h^2}{8\pi^2 I k_B}$$

for water



$$I_a \neq I_b \neq I_c$$

$\overleftrightarrow{I}$ is the moment of inertia tensor

$$I_{xx} = \sum_i m_i \left((y_i - y_{cm})^2 + (z_i - z_{cm})^2\right)$$

$$I_{yy} = \sum_i m_i \left((x_i - x_{cm})^2 + (z_i - z_{cm})^2\right)$$

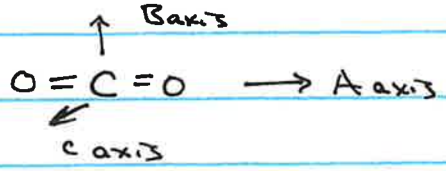
$$I_{zz} = \sum_i m_i \left((x_i - x_{cm})^2 + (y_i - y_{cm})^2\right)$$

off-diagonals: $I_{xy} = I_{yx} = \sum_i m_i (x_i - x_{cm})(y_i - y_{cm})$

$\overleftrightarrow{I}$ can be <u>diagonalized</u>

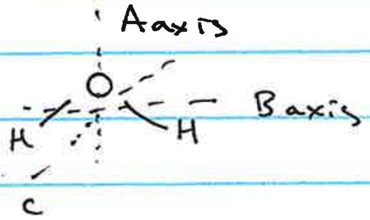
$$\overleftrightarrow{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \xrightarrow[\text{diagonalization}]{} \begin{pmatrix} I_A & 0 & 0 \\ 0 & I_B & 0 \\ 0 & 0 & I_C \end{pmatrix}$$

All rigid objects have 3 <u>principal axes of rotation</u> each with its own <u>moment of inertia</u>. They can sometimes be hard to identify, or can be <u>degenerate</u>:



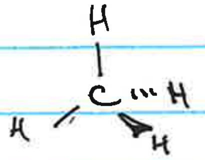
$$\left. \begin{matrix} I_A = 0 \\ I_B = I_C \end{matrix} \right\}$$ linear rotors have one moment = 0

All diatomics



$I_A \neq I_B \neq I_C$

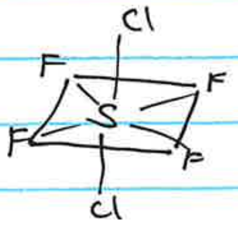
This is called an asymmetric top



$I_A = I_B = I_C$

This is called a spherical top

(e.g. CH_4, SF_6)



$I_A \neq I_B = I_C$

this is called a symmetric rotor

NH_3, C_6H_6 ("oblate"), CH_2Cl_2

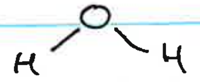
Spherical Tops : $$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{T}{\Theta_{rot}}\right)^{3/2}$$

Symmetric Tops : $$q_{rot} = \sqrt{\frac{\pi}{\sigma}}\left(\frac{T}{\Theta_{rot,A}}\right)\left(\frac{T}{\Theta_{rot,B}}\right)^{1/2}$$

Asymmetric Tops : $$q_{rot} = \sqrt{\frac{\pi}{\sigma}}\left(\frac{T^3}{\Theta_{rot,A}\,\Theta_{rot,B}\,\Theta_{rot,C}}\right)^{1/2}$$

Linear Rotor : $$q_{rot} = \frac{T}{\sigma\,\Theta_{rot}}$$

Multiple Vibrational Modes :



$$\varepsilon_{vib} = \varepsilon_{\substack{symm.\\stretch}} + \varepsilon_{\substack{asymm\\stretch}} + \varepsilon_{bend}$$

$$= \left(v_{ss}+\tfrac{1}{2}\right)h\nu_{ss} + \left(v_{as}+\tfrac{1}{2}\right)h\nu_{as} + \left(v_b+\tfrac{1}{2}\right)h\nu_b$$

$$q_{vib} = \sum_{states} e^{-\beta\varepsilon_{state}}$$

$$= \sum_{v_{ss}=0}^{\infty}\sum_{v_{as}=0}^{\infty}\sum_{v_b=0}^{\infty} e^{-\beta\left[h\nu_{ss}(v_{ss}+\frac{1}{2}) + h\nu_{as}(v_{as}+\frac{1}{2}) + h\nu_b(v_b+\frac{1}{2})\right]}$$

$$= \left(\sum_{v_{ss}=0}^{\infty} e^{-\beta h\nu_{ss}(v_{ss}+\frac{1}{2})}\right)\left(\sum_{v_{as}=0}^{\infty} e^{-\beta h\nu_{as}(v_{as}+\frac{1}{2})}\right)\left(\sum_{v_b=0}^{\infty} e^{-\beta h\nu_b(v_b+\frac{1}{2})}\right)$$

$$= q_{vib}^{ss} \times q_{vib}^{as} \times q_{vib}^{bend}$$

$$q_{vib} = \prod_{j=1}^{N_{vib}} \frac{e^{-\Theta_{vib,j}/2T}}{1-e^{-\Theta_{vib,j}/T}} \qquad \Theta_{vib,j} = \frac{h\nu_j}{k_B}$$

$\leftarrow$ q is product of modes

Equipartition

$$q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

$$\langle E_{trans}\rangle = k_B T^2 \left(\frac{\partial \ln q_{trans}}{\partial T}\right) = \frac{k_B T^2 \, V \left(\frac{3}{2}\right)\left(\frac{2\pi m k T}{h^2}\right)^{1/2} \cdot \left(\frac{2\pi m k}{h^2}\right.}{q_{trans}}$$

$$= \frac{3}{2} k_B T$$

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{T^3}{\Theta^A_{rot}\,\Theta^B_{rot}\,\Theta^C_{rot}}\right)^{1/2}$$

$$\langle E_{rot}\rangle = kT^2\left(\frac{\partial \ln q_{rot}}{\partial T}\right) = \frac{kT^2}{q_{rot}}\sqrt{\frac{\pi}{\sigma}}\,\frac{1}{2}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{-1/2}\frac{3T^2}{\Theta_A\Theta_B\Theta_C}$$

$$= \frac{3}{2} k_B T^2$$

$$q_{vib} = \frac{e^{-\Theta_{vib}/2T}}{1-e^{-\Theta_{vib}/T}} \longleftarrow \text{for each mode}$$

$$\langle \varepsilon_{vib}\rangle = k_B\left(\frac{\Theta_{vib}}{2} + \Theta_{vib}\frac{e^{-\Theta_{vib}/2T}}{1-e^{-\Theta_{vib}/T}}\right)$$

$$\lim_{T\to\infty}\langle \varepsilon_{vib}\rangle \approx k_B T \quad \text{for each vibrational mode}$$

$$\langle \varepsilon_{tot}\rangle = \underset{\underline{\text{trans}}}{\frac{3}{2}k_B T} + \underset{\underline{\text{rot}}}{\frac{3}{2}k_B T} + \underset{\underline{\text{vib}}}{N_{vib}\,k_B T}$$

A simple theorem that explains this:

$$\langle \varepsilon \rangle = \frac{\sum_{\text{all states}} \varepsilon_n e^{-\beta\varepsilon_n}}{\sum_{\text{all states}} e^{-\beta\varepsilon_n}} \approx \frac{\int_0^\infty \varepsilon(n)\, e^{-\beta\varepsilon(n)}\, dn}{\int_0^\infty e^{-\beta\varepsilon(n)}\, dn}$$

If $\varepsilon(n) \sim cn^2$ where $c > 0$
(that is if the energy rises parabolically)

$$\langle \varepsilon \rangle = \frac{\int_0^\infty cn^2 e^{-\beta cn^2}\, dn}{\int_0^\infty e^{-\beta cn^2}\, dn} = \frac{\frac{c}{4\beta c}\sqrt{\frac{\pi}{\beta c}}}{\sqrt{\frac{\pi}{4\beta c}}}$$

$$= \frac{k_B T}{2}$$

∴ for each degree of freedom which has energy rising like n^2, the average energy should be approximately $\frac{k_B T}{2}$

$$\varepsilon_{trans} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \quad \text{or} \quad \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

3 d.o.f. in both QM and classical treatments

$$\varepsilon_{rot} = \frac{h^2}{2I} J(J+1) \sim cJ^2$$

Harmonic oscillator has $\underline{\underline{2}}$: $E = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 q^2$

= 2 quadratic terms!