Why are Partition Functions products?

$$E_\ell^{tot} = E_1^a + E_2^b + E_1^c + E_0^d + \dots$$

total energy in system state labeled "ℓ"

energy of molecule "a" in state 1

energy of molecule "b" in state 2

energy of molecule "d" in state 0

$$\ell = \{1, 2, 1, 0, \dots\}$$

ℓ labels the ~~total~~ state of the system

So the system partition function is:

$$Q = \sum_\ell e^{-E_\ell^{tot}/k_BT}$$

ℓ ← visit all possible system states

$$= \underbrace{\sum_i}_{} \sum_j \sum_k \cdots e^{-(E_i^a + E_j^b + E_k^c \cdots)/k_BT}$$

visit all states for molecule b,

visit all states for molecule a

sum in exponent is product

$$Q = \sum_i \sum_j \sum_k \cdots e^{-E_i^a/k_BT} e^{-E_j^b/k_BT} e^{-E_k^c/k_BT} \cdots$$

sum of products is a product of sums

$$Q = \left(\sum_i e^{-E_i^a/k_BT}\right)\left(\sum_j e^{-E_j^b/k_BT}\right)\left(\sum_k e^{-E_k^c/k_BT}\right) \cdots$$

$$Q = \underbrace{q_a \times q_b \times q_c}_{} \cdots$$

product of single molecule partition functions

System Partition function

Explaining the magic of
sum of products = product of sums

Consider:

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

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

$$= x + xy + x^2 + x^2y$$

$$= x + x^2 + xy + x^2y$$

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

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

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

So:

$$Q(N,V,T) = [q(V,T)]^N$$ for identical distinguishable molecules

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For indistinguishable molecules, things are a bit more complicated.

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

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 system state.
If we count up molecular states, we will get:

$$Q = q^N$$ ← but this overcounts the identical states above

The amount we overcount is just the number of permutations of the molecules = $N!$

For <u>indistinguishable</u> molecules

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

q^N ← single molecule partition function

$N!$ ← correction for overcounting system states

Q: "system" partition function

A simple example: 2 identical molecules "a", "b" with 2 energy states

(indistinguishable)

a	b	
E_1	E_1	← (unique system state, but 2 possible permutations of a & b
E_1	E_2	identical system states that we over count by 2
E_2	E_1	
E_2	E_2	← (unique system state, but 2 possible permutations of a & b

$$Q = \frac{(q_1)^N}{N!} = \frac{\left(\sum_{i=1}^{2} e^{-E_i/k_BT}\right)^2}{2}$$

There are additional subtleties for QM particles (Fermions & Bosons) but we'll come back to this later.

Molecular Partition Functions

These can also be decomposed into factors:

$$\varepsilon_n^a = \varepsilon_i^{trans} + \varepsilon_j^{rot} + \varepsilon_k^{vib} + \varepsilon_\ell^{electronic}$$

ε_n^a total energy for molecule "a" in molecular state n

n describes the <u>entire</u> state

$n \rightarrow \{i, j, k, \ell\}$

$$q^a = \sum_n e^{-E_n^a/k_BT}$$

$$= \sum_n e^{-(\varepsilon_i^{trans} + \varepsilon_j^{rot} + \varepsilon_k^{vib} + \varepsilon_\ell^{elect})/k_BT}$$

$$= \sum_i \sum_j \sum_k \sum_\ell e^{-\beta\varepsilon_i^{trans}} e^{-\beta\varepsilon_j^{rot}} e^{-\beta\varepsilon_k^{vib}} e^{-\beta\varepsilon_\ell^{elect}}$$

$$= \left(\sum_i e^{-\beta\varepsilon_i^{trans}}\right)\left(\sum_j e^{-\beta\varepsilon_j^{rot}}\right)\left(\sum_k e^{-\beta\varepsilon_k^{vib}}\right)\left(\sum_\ell e^{-\beta\varepsilon_\ell^{elect}}\right)$$

$$q^a = q_{trans} \times q_{rot} \times q_{vib} \times q_{elect}$$

So for N <u>identical</u> <u>indistinguishable</u> molecules:

$$Q = \frac{q^N}{N!} = \frac{q_{trans}^N \, q_{rot}^N \, q_{vib}^N \, q_{elect}^N}{N!}$$

And we can also get avereage energies for particular kinds of motion:

$$\langle \varepsilon_{vib} \rangle = -\left(\frac{\partial \ln q_{vib}}{\partial \beta}\right)$$

average vibrational energy for 1 molecule

And so on.