

Now that we know entropy is defined as:

$$S \equiv k \ln \Omega$$

We can find the probability of any system's microstate by using the Boltzmann factor. To derive it we need only a firm understanding of Combinatorics and large numbers.

The multiplicity of one macrostate is usually not equal to the multiplicity of a different macrostate:

$$\Omega(1) \neq \Omega(2)$$

If the total number of microstates is $\sum_{i=0}^n \Omega(i)$ then the probability of us finding the system in either of the two macrostates is:

$$P(1) = \frac{\Omega(1)}{\sum_{i=0}^n \Omega(i)}$$

$$P(2) = \frac{\Omega(2)}{\sum_{i=0}^n \Omega(i)}$$

Now, we want to know what the probability is of finding the system in macrostate 2 relative to macrostate 1:

$$\frac{P(2)}{P(1)} = \frac{\frac{\Omega(2)}{\sum_{i=0}^n \Omega(i)}}{\frac{\Omega(1)}{\sum_{i=0}^n \Omega(i)}} = \frac{\Omega(2) \sum_{i=0}^n \Omega(i)}{\Omega(1) \sum_{i=0}^n \Omega(i)} = \frac{\Omega(2)}{\Omega(1)}$$

$$\frac{P(2)}{P(1)} = \frac{\Omega(2)}{\Omega(1)}$$

Next we solve for Ω using the entropy equation:

$$S = k \ln \Omega$$

$$\frac{S}{k} = \ln \Omega$$

$$e^{S/k} = e^{\ln \Omega} \quad (e^{\ln x} = x)$$

$$e^{S/k} = \Omega \Rightarrow \Omega_1 = e^{S_1/k} + \Omega_2 = e^{S_2/k}$$

Putting it all together:

$$\frac{P(2)}{P(1)} = \frac{\Omega_2}{\Omega_1} = \frac{e^{S_2/k}}{e^{S_1/k}} = e^{\left(\frac{S_2}{k} - \frac{S_1}{k}\right)} = e^{(S_2 - S_1)/k}$$

This gives the probability as:

$$P(S) = e^{(S_2 - S_1)/K}$$

Thermodynamics has found a clear relationship between entropy, energy, Volume and the number of "parts" defined by the thermodynamic identity

$$dS = \frac{1}{T} (dU + PdV - \mu dN)$$

The "d" means this relationship holds microscopically. S is entropy, T is temperature, U is energy, P is pressure, V is Volume, μ is the chemical potential a.k.a. the energy in $1 N$ and N is the number of atoms.

If we let the energy U be our variable and make the Volume and N constant then:

$$dS = \frac{1}{T} dU$$

The derivative of a constant = 0
because constants do not "change"
 $dV=0 \Rightarrow PdV=0$
 $dN=0 \Rightarrow \mu dN=0$

Next we integrate and change " U " to the more familiar symbol " E " which denotes the total energy.

$$dS = \frac{1}{T} dU$$

$$S = \frac{E}{T} \Rightarrow S_1 = \frac{E_1}{T} + S_2 = \frac{E_2}{T}$$

Putting it together now:

$$P(S) = e^{(S_2 - S_1)/K} \Rightarrow P(S) = e^{(E_2 - E_1)/KT}$$

This is a relationship between entropy and energy based on the thermodynamic identity which describes a much larger system or "reservoir". What is gained by the reservoir is lost by our subsystem and vice versa. To account for this opposite we must include a minus sign "-".

$$P(S) = e^{-\frac{(E_2 - E_1)}{KT}}$$

This gives us:

$$P(S_2) = e^{-\frac{E_2}{KT}} + P(S_1) = e^{-\frac{E_1}{KT}}$$

Or more generally as:

$$P(S) = e^{-\frac{E(S)}{KT}}$$

$e^{-\frac{E(S)}{KT}}$ is known as the Boltzmann factor

The Boltzmann factor is very close to giving the correct probability but just like the quantum mechanical wavefunction there is a constant of proportionality we must find:

Quantum

$$\Psi(x,s) = A e^{-i(kx - \omega t)}$$

Thermo

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

Since both are probability densities \sum or \int over every possible superposition Ψ_i or macrostate S_i will give 1 because something must happen.

$$1 = A^2 \int_{-\infty}^{\infty} \Psi^* \Psi$$

$$1 = \frac{1}{Z} \sum_{i=0}^n e^{-E(S_i)/kT}$$

Notice
 $kx = \frac{2\pi}{\lambda}(x) = \frac{2\pi}{\text{meters}}(\text{meters}) = \text{Scalar}$
 $\omega t = 2\pi \nu(t) = \frac{2\pi}{\text{seconds}}(\text{seconds}) = \text{Scalar}$

Notice
 $\frac{E}{kT} = \frac{\text{Joules}}{\frac{\text{Joules}}{\text{Kelvin}} \text{Kelvin}} = \text{Scalar}$

If we were to redefine $\frac{1}{Z}$ as $\frac{1}{A}$ then hypothetically if the multiplicity were imaginary and squaring it made it real (inner product) then A would have to be squared too.

In other words we are doing this:

Roll a die then $1 = A(\square + \square + \square + \square + \square + \square)$ each of these 6 macrostates has a multiplicity of 1: $\Omega(1)=1, \Omega(2)=1, \Omega(3)=1, \Omega(4)=1, \Omega(5)=1, \Omega(6)=1$
 $\Omega(6)=1 \Rightarrow 1 = A(\Omega(1) + \Omega(2) + \Omega(3) + \Omega(4) + \Omega(5) + \Omega(6)) = A(1+1+1+1+1+1)$

Now solve for A a.k.a. normalize the wavefunction.

$$1 = A \cdot 6 \Rightarrow A = \frac{1}{6}$$

So the probability that we get one of the die values is $\frac{1}{6}$, one in six chance. What about the A^2 in quantum?

$$A^2(\Omega(1)^2 + \dots + \Omega(n)^2) = A(\Omega(1) + \dots + \Omega(n)) \text{ only if we ignore the cross terms from factoring a.k.a. the Hilbert space inner product}$$

If $\Psi = \Psi_i + \Psi_j + \Psi_k$ then Ψ^2 gives:

$$\begin{aligned} (\Psi_i + \Psi_j + \Psi_k)^2 &= (\Psi_i + \Psi_j + \Psi_k)(\Psi_i + \Psi_j + \Psi_k) \\ &= \langle \Psi_i | \Psi_i \rangle + \langle \Psi_i | \Psi_j \rangle + \langle \Psi_i | \Psi_k \rangle + \langle \Psi_j | \Psi_i \rangle + \langle \Psi_j | \Psi_j \rangle + \langle \Psi_j | \Psi_k \rangle + \langle \Psi_k | \Psi_i \rangle + \langle \Psi_k | \Psi_j \rangle + \langle \Psi_k | \Psi_k \rangle \end{aligned}$$

Remember $\langle \Psi_n | \Psi_m \rangle = \delta_{nm}$
 if $n=m$ then $\langle \Psi_n | \Psi_m \rangle = 1$
 if $n \neq m$ then $\langle \Psi_n | \Psi_m \rangle = 0$

$$= \Psi_i^2 + \Psi_j^2 + \Psi_k^2 = \Psi^2$$

The equation: $P(s) = \frac{1}{Z} e^{-\frac{E(s)}{KT}}$

is called the Boltzmann distribution or the canonical distribution.

$$1 = \sum_{i=0}^n P(s_i) = \sum_{i=0}^n \frac{1}{Z} e^{-\frac{E(s_i)}{KT}} = \frac{1}{Z} \sum_{i=0}^n e^{-\frac{E(s_i)}{KT}}$$

$$1 = \frac{1}{Z} \sum_{i=0}^n e^{-E(s_i)/KT}$$

$$Z = \sum_{i=0}^n e^{-\frac{E(s_i)}{KT}} \quad \left(Z \text{ is called the Partition function} \right)$$

The Boltzmann distribution was used by Planck to explain blackbody radiation. Planck's solution to the blackbody radiation problem is considered to be the birth of quantum mechanics. To solve the problem we use the Rayleigh-Jeans formula which is the number of degrees of freedom for a frequency ν , multiplied by the average energy per degree of freedom:

$$\frac{8\pi\nu^2}{c^3}, \quad \bar{E} = \frac{\int_0^{\infty} E e^{-E/KT} dE}{\int_0^{\infty} e^{-E/KT} dE} \quad (\bar{E} \equiv \text{Average energy})$$

Both integrals can be solved using integration by parts and the result is:

$$\bar{E} = KT$$

The Rayleigh-Jeans formula gives the energy density as:

$$P(\nu, T) = \frac{8\pi\nu^2}{c^3} KT$$

When the frequency is small the equation works but for larger frequencies the ν^2 in the numerator creates an energy density that is many times larger than what is observed in experiment. The mismatch between theoretical prediction and experimental results was called the ultraviolet (high frequency) catastrophe.

Planck's solution was to make the average energy discrete:

$$E = nh\nu \quad (n=0, 1, 2, 3) \quad + h = \text{Planck's constant}$$

As a result of his discrete "assumption" the resulting series converge providing theoretical predictions that match experimental results:

$$\bar{E} = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/KT}}{\sum_{n=0}^{\infty} e^{-nh\nu/KT}} \Rightarrow \frac{h\nu}{e^{(h\nu/KT)} - 1}$$

$$P(\nu, T) = \frac{8\pi h \nu^3}{c^3 e^{h\nu/KT} - 1}$$

Conclusion:

Combinatorics is discrete mathematics, from it we get the multiplicity, $\Omega(N) = \binom{N}{n}$. Ω may be a large number but it is built from discrete parts. Taking the logarithm of Ω gives the entropy S , $S = k \ln \Omega$, and entropy is related to energy by the thermodynamic identity $S = \frac{E}{T}$ (assuming V & N are constant).

The multiplicities in classical physics are so large that for all intents and purposes we can assume E, S, Ω are continuous. However, on the quantum scale E, S, Ω are much smaller and the continuous assumption of integrating no longer works. Planck did not assume it was discrete, instead classical physicists assumed E, S, Ω were continuous.

There is one remaining classical continuous assumption and that is the frequency ν .

$$\Omega \Rightarrow S \Rightarrow E = n h \nu \quad (n = 0, 1, 2, \dots)$$

How is it possible to derive Ω from discrete mathematics but then still include a continuous variable ν ?

The idea that the frequency is continuous came from classical E+M as well as the $\Psi(x,t) = e^{-i\epsilon(kx - \omega t)}$. Making ν discrete resolves this discrete/continuous crisis and it still provides all the correct theoretical predictions. ν , the frequency, is the inverse of the period and has units of Hertz (Hz) also written as $\frac{1}{\text{seconds}}$ this suggests time is discrete.

Next Einstein would show through the photoelectric effect that photons were discrete. From Planck's results, $E = h\nu$, Einstein was able to find the momentum of the photons.

$$\begin{aligned} \text{Photons} \quad \lambda \nu &= v \\ &\downarrow \\ &\text{velocity of the photon} \end{aligned} \quad \begin{aligned} E^2 &= m^2 c^4 + c^2 p^2 \quad (\text{relativistic energy}) \\ E^2 &= (0)^2 c^4 + c^2 p^2 \quad (\text{Photons have zero rest mass}) \\ E^2 &= c^2 p^2 \Rightarrow \boxed{E = c p} \end{aligned}$$

$$\begin{aligned} \text{From Planck: } E = h\nu & \quad \left. \begin{array}{l} E = h\nu \\ E = c p \end{array} \right\} \Rightarrow \frac{h\nu}{c} = p \quad \left. \begin{array}{l} \frac{h\nu}{c} = p \\ \lambda \nu = c \end{array} \right\} \Rightarrow \frac{h\nu}{\lambda \nu} = p \Rightarrow p = \frac{h}{\lambda} \end{aligned}$$

Quantum mechanics is a discrete theory built from the equations:

$$E = h\nu \quad + \quad p = \frac{h}{\lambda}$$

Both men created discrete equations and theories but still they cling to classical ideas of continuity. As the above derivation suggests if time (ν) is discrete then space (λ) must be discrete too.

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