

$$\sum_{n_{\uparrow}=0}^N \Omega(N, n_{\uparrow}) = \sum_{n_{\uparrow}} \frac{N!}{n_{\uparrow}!(N-n_{\uparrow})!} = 2^N = \Omega(N)$$

$\Omega(N)$ = total number of microstates.

$\Omega(N, n_{\uparrow})$ = total number of macrostates for a given microstate.

Boltzmann's law:

$$S = k_B \ln \Omega(N)$$

For large N , $\Omega(N, n) \approx$ Gaussian. Thus, fractional size of fluctuations from "mean"

$$\propto \frac{1}{\sqrt{N}}$$

Stirling's Approximation:

$$\ln(n!) = n \ln n - n + O(\ln n)$$

as $n \rightarrow \infty$

$$\text{Now: } S = k_B \ln \Omega(N) = k_B \ln \sum_n \Omega(N, n)$$

And the sum can be approximated by the biggest term in the series, i.e: $\Omega(N, N/2)$

Thus:

$$\ln \Omega(N) = \ln \Omega(N, N/2)$$

Statistical definitions:

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E} \right)_{V, N} \quad \frac{p}{T} \equiv \left(\frac{\partial S}{\partial V} \right)_{E, N} \quad -\frac{\mathbf{m}}{T} \equiv \left(\frac{\partial S}{\partial \mathbf{N}} \right)_{E, V}$$

Boltzmann distribution:

Now:

$$S = k_B \ln \Omega = k_B \ln \Omega(E_0 - \mathbf{e}_i)$$

For a system with E_0 total energy, in a state with energy \mathbf{e}_i . Thus, can rearrange to:

$$\Omega(E_0 - \mathbf{e}_i) = e^{\frac{1}{k_B} S(E_0 - \mathbf{e}_i)}$$

Now, Taylor expanding the function in the exponential for $E_0 \gg \mathbf{e}_i$:

$$S(E_0 - \mathbf{e}_i) = S(E_0) - \mathbf{e}_i \left(\frac{\partial S}{\partial E} \right)_{V,N} \Big|_{E_0} + \frac{1}{2!} \mathbf{e}_i^2 \left(\frac{\partial^2 S}{\partial E^2} \right)_{V,N} \Big|_{E_0} + \dots$$

Now:

$$\begin{aligned} \frac{1}{T} &\equiv \left(\frac{\partial S}{\partial E} \right)_{V,N} \\ \therefore \left(\frac{\partial^2 S}{\partial E^2} \right)_{V,N} &= \left(\frac{\partial}{\partial E} \left(\frac{1}{T} \right) \right)_{V,N} = -\frac{1}{T^2} \left(\frac{\partial T}{\partial E} \right)_{V,N} \\ &= -\frac{1}{T^2 c_V} \end{aligned}$$

Thus:

$$S(E_0 - \mathbf{e}_i) = S(E_0) - \frac{\mathbf{e}_i}{T} - \frac{\mathbf{e}_i^2}{2T^2 c_V}$$

Or, if $c_V T \gg \mathbf{e}_i$:

$$S(E_0 - \mathbf{e}_i) = S(E_0) - \frac{\mathbf{e}_i}{T}$$

Now, going back to an original idea:

$$p_i(\mathbf{e}_i) = \frac{\Omega(E_0 - \mathbf{e}_i)}{\Omega(E_0)} \Rightarrow p_i \propto \Omega(E_0 - \mathbf{e}_i)$$

Thus:

$$p_i = \text{const.} e^{\frac{1}{k_B} \left(S(E_0) - \frac{\mathbf{e}_i}{T} \right)} = \text{const.} e^{-\frac{\mathbf{e}_i}{k_B T}}$$

Let this constant be:

$$\frac{1}{Z} \quad \text{which will be a normalisation constant}$$

Thus:

$$p_i = \frac{1}{Z} e^{-\frac{\mathbf{e}_i}{k_B T}} \quad Z \equiv \sum_i e^{-\frac{\mathbf{e}_i}{k_B T}}$$

Where p_i is the probability to find the system in a state with energy \mathbf{e}_i . Z is basically a normalisation constant, but is known as the “partition function”.

More accurately, if there is degeneracy $g(\mathbf{e}_i)$ of a particular energy state \mathbf{e}_i , then:

$$Z = \sum_i g(\mathbf{e}_i) e^{-\frac{\mathbf{e}_i}{k_B T}}$$

More usual to write, and is more convenient:

$$p_i = \frac{1}{Z} e^{-\mathbf{e}_i b} \quad Z = \sum_i g(\mathbf{e}_i) e^{-\mathbf{e}_i b} \quad b \equiv \frac{1}{k_B T}$$

Now, the expectation value of the energy is:

$$\begin{aligned} \langle E \rangle &= \sum_i p_i \mathbf{e}_i = -\frac{1}{Z} \left(\frac{\partial Z}{\partial \mathbf{b}} \right)_{N,V} \\ &= k_B T \left(\frac{\partial \ln Z}{\partial T} \right)_{N,V} \end{aligned}$$

And that for the heat capacity:

$$\langle c_V \rangle \equiv \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N,V} = k_B b^2 \left(\frac{\partial^2 \ln Z}{\partial b^2} \right)_{N,V}$$

It will be useful to know the hyperbolic relations:

$$\sinh x = \frac{1}{2}(e^x - e^{-x}) \quad \cosh x = \frac{1}{2}(e^x + e^{-x})$$

$$\tanh x = \frac{\sinh x}{\cosh x} = \frac{1 - e^{-2x}}{1 + e^{-2x}}$$

$$\cosh^2 x - \sinh^2 x = 1$$