From 'Physical Biology of the Cell' by Phillips et al.

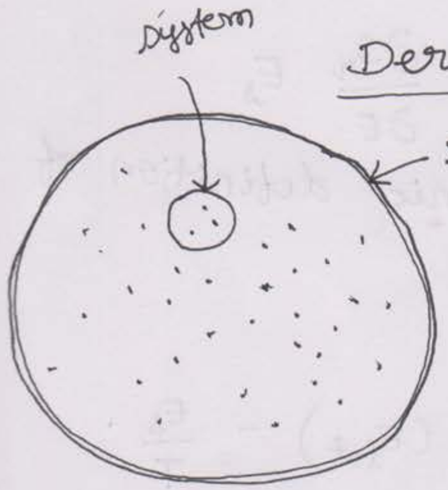
✻ Boltzmann's 'law' can be <u>derived</u> if we assume the following:

(i) Boltzmann equation: $\underset{\text{entropy}}{S} = k_B \ln \underset{\#\text{ of states}}{W}$

(ii) Thermodynamic identity: $\dfrac{\partial S}{\partial E} = \dfrac{1}{T}$.

Both of these are, or can be considered to be, definitions of entropy and temperature.

<u>Derivation</u>



$$E_{total} = E_{reservoir} + E_{system}$$

$$E_{tot} = E_r + E_s$$

The probability of finding a state of the system with energy E_s is proportional to the number of states available for the reservoir when the system is in that state. That is,

$$p(E_s) \propto W_r(E_r) = W_r(E_{tot} - E_s).$$

Then, for two states with energies E_{s_1} and E_{s_2},

$$\frac{p(E_{s_1})}{p(E_{s_2})} = \frac{W_r(E_{tot} - E_{s_1})}{W_r(E_{tot} - E_{s_2})}.$$

By using Boltzmann equation,

$$S = k_B \ln W$$

$$\Rightarrow \ln W = \frac{S}{k_B} \Rightarrow W = e^{S/k_B}$$

We can write,

$$\frac{W_r(E_{tot} - E_{s_1})}{W_r(E_{tot} - E_{s_2})} = \frac{e^{\frac{S_r(E_{tot} - E_{s_1})}{k_B}}}{e^{\frac{S_r(E_{tot} - E_{s_2})}{k_B}}}$$

Consider now the first-order approximation:

$$S_r(E_{tot} - E_s) \approx S_r(E_{tot}) - \frac{\partial S_r}{\partial E} E_s$$

Now, use the thermodynamic definition of temperature, $\frac{\partial S}{\partial E} = \frac{1}{T}$.

Then, $S_r(E_{tot} - E_s) \approx S_r(E_{tot}) - \frac{E_s}{T}$.

Now, we get

$$\frac{p(E_{s_1})}{p(E_{s_2})} = \frac{W_r(E_{tot} - E_{s_1})}{W_r(E_{tot} - E_{s_2})} = \frac{e^{\frac{S_r(E_{tot} - E_{s_1})}{k_B}}}{e^{\frac{S_r(E_{tot} - E_{s_2})}{k_B}}} = \frac{e^{-E_{s_1}/k_B T}}{e^{-E_{s_2}/k_B T}}$$

Thus, the probability of finding a state with energy $E_{s_i} = p(E_{s_i}) = \frac{1}{Z} e^{-E_{s_i}/k_B T}$

where Z = partition function $= \sum_i e^{-E_{s_i}/k_B T}$

summed over all states.