Getting the probability that a system at temperature $\boldsymbol{T}$ has energy $\boldsymbol{E}$ by maximizing the number of distributions

By now you are probably wondering that in the derivation of probability so far, we have not maximized anything to get the probability. We now do that.

- For this consider a collection of N similar systems in thermal contact with the reservoir at temperature T. *You can alternatively think of one system in contact with the reservoir and divided into N subsystems*.

- Let the average energy of these be $\bar{E}$. Then their total energy is $N\bar{E}$.

- Any of these systems can have any energy. When in equilibrium, the average energy of the systems remains unchanged. In that situation let n_1 systems have energy E_1, n_2 have energy E_2, ……………. n_i systems have energy E_i. Then $\sum_i n_i = N$ and $\sum_i n_i E_i = N\bar{E}$.

Maximization condition for Number of distributions

Distribution of N systems with n_1 having energy E_1 , n_2 having energy E_2, and so on…. can be done in $\Omega(n_1!\, n_2! \ldots \ldots n_i! \ldots ..) = \frac{N!}{n_1! n_2! \ldots\ldots n_i! \ldots..}$ ways.

Then equilibrium corresponds to that distribution $\{n_1!\, n_2! \ldots \ldots n_i! \ldots ..\}$ for which $\Omega(n_1!\, n_2! \ldots \ldots n_i! \ldots ..)$ is maximum.

At such distribution, if each n_i is change by δn_i, the corresponding change $\delta\Omega = 0$ since Ω is varying about its maximum value.

The changes δn_i are such that $\sum_i \delta n_i = 0$ and $\sum_i \delta n_i E_i = 0$.

Mathematics is much easier if we maximize $\ln \Omega$ instead of Ω for reasons discussed in the class.

$$\ln \Omega = \ln N! - \sum_i \ln n_i!$$

- Now we use Stirling's approximation which is $\ln n! = n \ln n - n$.
- Then $\ln \Omega = N \ln N - \sum_i n_i \ln n_i$ using $\sum_i n_i = N$.
- Therefore $\delta \ln \Omega = -\sum_i \delta n_i \ln n_i$ using $\sum_i \delta n_i = 0$.
- If all δn_i were completely arbitrary then for $\delta\Omega = 0$ we would have $\ln n_i = 0$.
- But δn_i are such that $\sum_i \delta n_i = 0$ and $\sum_i \delta n_i E_i = 0$.
- The for $\delta\Omega = 0$, we need not have $\ln n_i = 0$ but a more relaxed condition $\ln n_i = -\alpha - \beta E_i$.
- The condition above gives $n_i = Ce^{-\beta E_i}$ where $C = e^{-\alpha}$ is a constant.
- So the probability of a system having energy E_i is proportional to $e^{-\beta E_i}$.

Identifying β with $1/k_B T$

- With $n_i = Ce^{-\beta E_i}$, we have

  $$\ln\Omega = N\ln N - \sum_i n_i \ln n_i = N\ln N + \beta\sum_i n_i E_i - C\sum_i n_i$$

- This gives average entropy per system to be

$$\bar{S} = \frac{S}{N} = k_B(\ln N + \beta\bar{E} - C)$$

- Now using $\frac{1}{T} = \left(\frac{\partial\bar{S}}{\partial\bar{E}}\right)_V$ gives $\beta = \frac{1}{k_B T}$