# Lecture 2 - Statistical Mechanics

## Aims

Aims to relate the macroscopic thermodynamic properties of a system to the microscopic / atomistic constituents & degrees of freedom.

- **Macrostate:** as defined by state variables & functions
- **Microstate:** single/many particle eigenstates of the Hamiltonian of the system. $H\psi_i = E_i\psi_i$

**Fundamental** assumption **of statistical mechanics:**

At fixed N, V, E a system is equally likely to be found in any microstate of energy $E_i = E$.

## Boltzmann Entropy

$$S(N, V, E) = k_B \ln \Omega(N, V, E)$$

where $\Omega(N, V, E)$ is the number of microstates with energy $E_i = E$.

Entropy is maximised in equilibrium (2nd law of thermodynamics).

Assume the full system is closed and let $E = E_1 + E_2$ be constant. The subsystems are weakly interacting, such that $\Omega_i \equiv \Omega_i(E_i)$.

### Derivation

How can we express the total number of microstates?

$$\Omega = \Omega_1(E_1) \cdot \Omega_2(E_2) = \Omega_1(E_1)\Omega_2(E - E_1)$$

In equilibrium, Entropy (S) is maximised, which means $\Omega$ is maximised.

Therefore, $\frac{d\Omega}{dE_1} = 0$.

Using the chain rule:

$\frac{d\Omega}{dE_1} = \frac{d\Omega_1}{dE_1}\Omega_2 + \Omega_1\frac{d\Omega_2}{dE_1}$

$= \frac{d\Omega_1}{dE_1}\Omega_2 - \Omega_1\frac{d\Omega_2}{dE_2} = 0$

This leads to:

$\frac{1}{\Omega_1}\frac{d\Omega_1}{dE_1} = \frac{1}{\Omega_2}\frac{d\Omega_2}{dE_2}$

Which can be rewritten as:

$\frac{d}{dE_1}\ln\Omega_1 = \frac{d}{dE_2}\ln\Omega_2$

Let's define a quantity $\beta = \frac{d}{dE}\ln\Omega$. This quantity must be equal between systems in equilibrium.

From thermodynamics, we know the Maxwell relation:

$dS = \frac{1}{T}dU + \frac{p}{T}dV$

$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}$ (with $dE = dU$)

Connecting this to our definition of $\beta$:

$\beta = \frac{d}{dE}\ln\Omega = \frac{1}{k_B}\frac{dS}{dE}$

$\implies \beta = \frac{1}{k_B T}$

## Summary and Boltzmann Distribution

1. $\beta$ is equal between systems in thermal equilibrium.

2. $\beta = \frac{1}{k_B T}$, giving a microscopic understanding of entropy and temperature.

Now, consider a small subsystem (1) in contact with a very large heat reservoir (subsystem 2).

Let $E = E_i + E_R$ be the total constant energy, where $E_i$ is the energy of the subsystem in state $i$, and $E_R$ is the reservoir energy.

The total number of states is $\Omega = \sum_i \Omega_R(E - E_i)$. We sum over individual states, not energy levels.

The probability, $p(i)$, of observing the subsystem in a specific state $i$ with energy $E_i$ is:

$p(i) = \frac{\Omega_R(E - E_i)}{\sum_j \Omega_R(E - E_j)}$

Assuming the reservoir is infinitely large ($E_i \ll E$), we can do a Taylor expansion of $\ln \Omega_R(E - E_i)$:

$\ln \Omega_R(E - E_i) \approx \ln \Omega_R(E) - \frac{\partial \ln \Omega_R(E)}{\partial E} E_i$

$\ln \Omega_R(E - E_i) \approx \ln \Omega_R(E) - \beta E_i$

Exponentiating this gives:

$\Omega_R(E - E_i) \approx \Omega_R(E) e^{-\beta E_i} \approx C \cdot e^{-\beta E_i}$

Substituting this back into the probability equation, we get the **Boltzmann Distribution**:

$p(i) = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}$

## Observables and the Partition Function

For any observable quantity $A$, its average value is:

$\langle A \rangle = \sum_i p_i A_i = \frac{1}{Z} \sum_i A_i e^{-\beta E_i}$

where Z is the **Partition Function**:

$Z = \sum_i e^{-\beta E_i}$

### Summary

- Statistical mechanics connects microstates to the macro state.

- It gives a microscopic connection to entropy and temperature.

- Important concepts:

  - Boltzmann distribution

  - Partition function