Modern

Day 25

<u>Today</u>

I Last time

II Example of multiplicity

III Boltzmann's procedure

I • $2^{nd}$ law

$$\Delta S_{tot} \geq 0$$

- equality holds for reversible processes

• Microstate
→ describe every particle

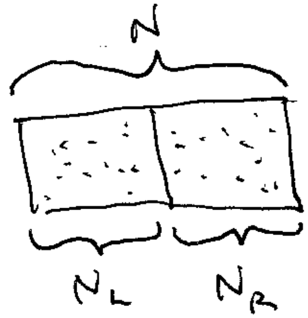
• Macrostate
→ characterized by thermal variables

• Entropy: $S = k \ln \Omega$

$k$ = Boltzmann's constant

$\Omega$ = # of microstates corresponding to a given macrostate

II Binary model




$$\Omega(N, N_L) = \binom{N}{N_L} = \frac{N!}{N_L!\,(N-N_L)!}$$

• Stirling's Approximation

$$n! \approx \sqrt{2\pi n}\, e^{-n} n^n \quad (\text{for large } n)$$

Let $N_L = \frac{N}{2} + s$ and $\frac{2s}{N} \equiv x \ll 1$

We found

$$\Omega(N, s) \approx \sqrt{\frac{N}{2\pi}} \frac{2^N}{\left(\frac{N}{2}\right)\sqrt{1-x^2}\,(1-x^2)^{N/2}} \left(\frac{1-x}{1+x}\right)^s$$

Recall $e^x = 1 + x + \frac{x^2}{2!} + \dots \approx 1 + x$

$e^{-x} \approx 1 - x \quad e^{-x^2} \approx 1 - x^2 \quad (1+x^2)^{\frac{N+1}{2}} \approx (1-x^2)^{N/2}$

Then

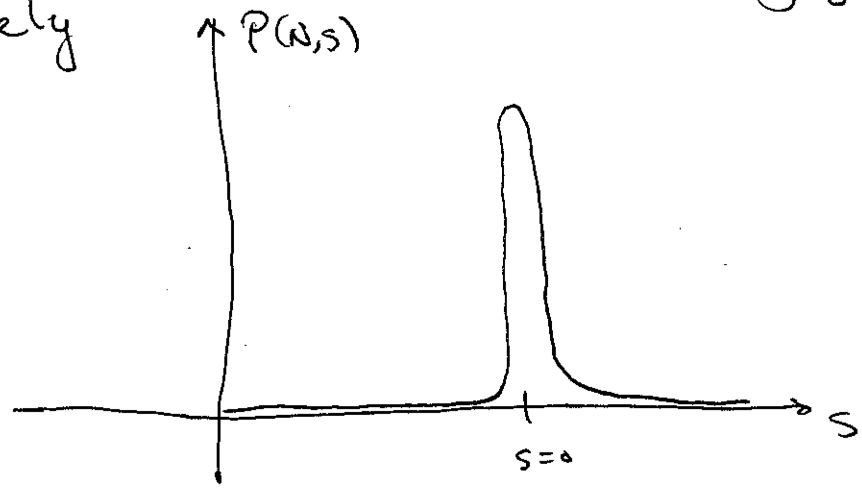
$$\Omega(N,s) \approx \sqrt{\frac{2}{\pi N}} \; \underbrace{\frac{2^N}{(e^{-x^2})^{\frac{N}{2}}} \left(\frac{e^{-x}}{e^{x}}\right)^{s}}$$

$$= e^{N\frac{x^2}{2}} \cdot e^{-2xs}$$

$$= e^{-2s^2/N}$$

$$\Rightarrow \boxed{\Omega(N,s) = \sqrt{\frac{2}{\pi N}}\; 2^N e^{-\frac{2s^2}{N}}}$$

to the fact that the equilibrium configuration (nearly $N/2$ particles in each half) is overwhelmingly likely




What is the probability of macrostate $(N,s)$ ?

$$P(N,s) = \frac{\Omega}{2^N} = \sqrt{\frac{2}{\pi N}}\; e^{-\frac{2s^2}{N}}$$

~~Switch to $x$ (fraction imbalance)~~

[Review session (send e-mail about time)]

This is a gaussian distribution.

For large N the peak is very narrow and this corresponds

III Having found $\Omega$ one can in fact describe all of the thermodynamics of the system using Boltzmann's procedure.

Today we will give an overview of this procedure, which we fully develop over the next few discussions.

The steps of the procedure are:

Multiplicity: $\Omega$

$\downarrow$

Entropy: $S = k \ln \Omega$

$\downarrow$

Temperature: $T = \dfrac{1}{\left(\frac{\partial S}{\partial U}\right)_V}$

$\downarrow$

Boltzmann Probability: $\underset{\text{state } j}{P(j)} = \dfrac{e^{-E_j/kT}}{Z}$ $\leftarrow$ energy of state $j$

Here $Z$ is the partition function

The 1st law states

$$\text{đ}Q = dU + \text{đ}W$$

$$= dU + P\,dV$$

Dividing through by the temperature

$$\frac{\text{đ}Q}{T} = \frac{1}{T}dU + \frac{P}{T}dV$$

or

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

and is defined by a sum over all states

$$Z = \sum_j e^{-E_j/kT}$$

It guarentees that

$$\sum_j P(j) = 1.$$

Let's first understand the temperature claim: recall ~~our~~ definition $dS = \frac{\text{đ}Q}{T}$

If we consider a process in which the volume is held constant then we learn that

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

$V$ $\nearrow$ indicates what is held fixed

or

$$T = \frac{1}{\left(\frac{\partial S}{\partial U}\right)_V}.$$

We'll start to investigate the probability step next time.