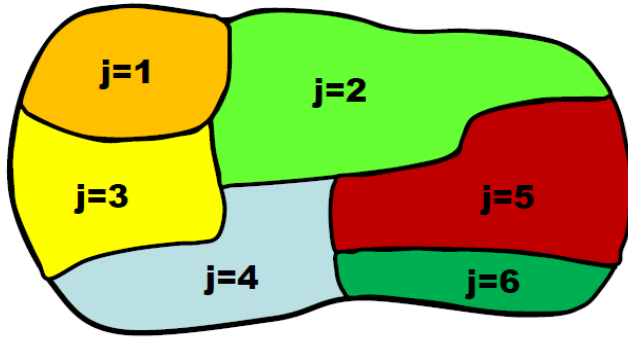# MICROCANONICAL ENSEMBLE

We now find the total number of microstates for a large system by combining **M** sub-systems. We do this for a <u>completely closed system</u>. Note that closed systems conserve total energy – so if the system starts with some energy **E**, only microstates with that energy will be accessible at future times.

<u>KEY POINT</u>: The total number Ω of microstates for the whole system is given by

$$\Omega = \prod_{j=1}^{M} \Omega_j = \Omega_1 \Omega_2, \cdots \Omega_M$$

so that

$$\ln \Omega = \sum_{j=1}^{M} \ln \Omega_j = \ln \Omega_1 + \ln \Omega_2, + \cdots + \ln \Omega_M$$

<u>Example 1</u>: For a system of **N** spins with spin **s** (each having **2s + 1** states) the total number of microstates is Ω = (2s + 1)^N (so that ln Ω = N ln (2s+1)). Thus the log of the multiplicity is additive. If each spin in the system was different, with value s_j for j = 1,2,...N, then we get ln $\Omega = \Sigma_j$ ln (2s_j + 1), again additive.

> Thus the log of the number of microstates is an <u>additive</u> quantity – ie., it is an <u>extensive variable</u>

The argument is a little more messy when we deal with particles with continuously varying quantum numbers, or where the spectrum is unbounded – we shall do this later.
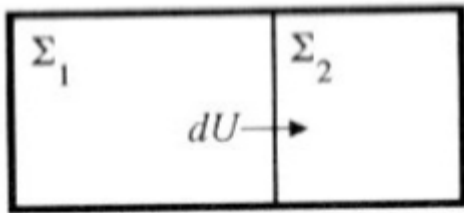
MICROSTATES & ENTROPY

Let's look again at our thought expt with a closed box (no heat or energy passes through any wall), in thermal eqlbm at temperature **T**. We have a massless moveable partition, & work can be done on the contents of box 2 by those of box 1.

We do this reversibly. The total system stays in an energy eigenstate, total energy is conserved, and each sub-system cycles between different energy eigenstates.

For an infinitesimal <u>reversible</u> motion of the wall we then have

$$d \ln \Omega = \frac{d\Omega}{\Omega} = d \ln \Omega_1 + d \ln \Omega_2 = 0$$

However we also have

$$d \ln \Omega = \left(\frac{\partial \ln \Omega_1}{\partial U_1} \right)_V dU_1 + \left(\frac{\partial \ln \Omega_2}{\partial U_2} \right)_V dU_2$$

or, using $dU_1 = -dU_2 = dU$ we have

$$d \ln \Omega = \left[\left(\frac{\partial \ln \Omega_1}{\partial U_1} \right)_V - \left(\frac{\partial \ln \Omega_2}{\partial U_2} \right)_V \right] dU = 0$$

so that

$$\left(\frac{\partial \ln \Omega_1}{\partial U_1} \right)_V = \left(\frac{\partial \ln \Omega_2}{\partial U_2} \right)_V$$

Notice how closely this argument parallels that in our thermodynamic discussion of the same example (cf eqtns (9)-(11) of Ch. 1). There we saw that the common temperature **T** for the 2 boxes is defined by

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

Hence that we find that **S** is proportional to **ln** Ω. We will therefore write, for this "closed box" scenario, that
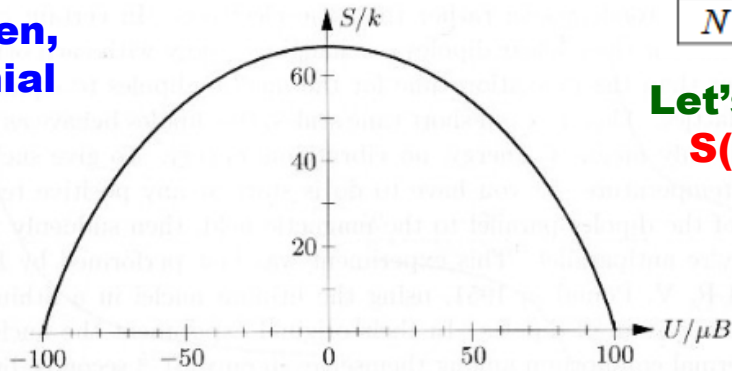
$$\boxed{S \equiv k_B \ln \Omega}$$

If we use Kelvin units for **T**, we have

$$k_B \equiv 1.38 \times 10^{-23} \, J/K$$

EXAMPLE 2: N SPIN-1/2 PARTICLES

Recall that the number of states varies really fast with energy. Suppose that N=100; then the number of states $\Omega_N(n)$ varies as we have already seen, as a binomial function.

n	E_n	Ω_n
N	$-N\mu B$	1
$N-2$	$-(N-2)\mu B$	$C^N_1 = N$
$N-4$	$-(N-4)\mu B$	$C^N_2 = N(N-1)/2$
$N-100 = 0$	0	$C^N_{50} \sim 10^{29}$

Let's take the log of $\Omega_N(n)$; this just gives $S(E)/k_B$, where $S(E)$ is the entropy as a function of the energy E (written at left as U). From the graph we see that dS/dU = 1/T changes sign - we interpret this later.

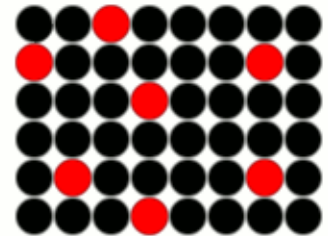## EXAMPLE 3: ENTROPY of MIXING:

We mix together 2 atomic species in a lattice, with N_A of species A, & N_B of species B, with $N_A + N_B = N$. If the mixture is random, we again have a binomial distribution of configurations. If we let $x = N_A/N$, we have

$$\Omega = \frac{N!}{(xN)![(1-x)N]!}$$

so that

$$\ln\Omega \quad \sim \quad -xN\ln x - (1-x)N\ln(1-x)$$

and the details go through as before

If the energy of all these configurations is the same, then they are all equally likely. If they are not, then only ones with the same energy as the initial energy will be allowed. How this works depends on what the Hamiltonian of the system happens to be.

EXAMPLE 4: 1-d POLYMER

This is just a 1-d tethered string, as shown. We have a total number **N** sub-units or "links", each of length **l**; all configurations have the same energy **U**. This is yet again a binomial distribution – the net extension **L** is like the excess of heads over tails, or the net spin, and we get for large **N** that the number of microstates corresponding to different configurations is
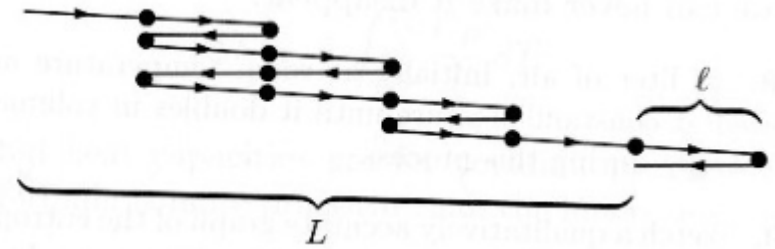
$$\Omega(L) = \Omega_0 \exp\left[-\frac{L^2}{2Nl^2}\right]$$ implying a configurational entropy $S_{con}(L) = S(0) - \frac{k_B L^2}{2Nl^2}$

We can try pulling on one end of the system – a simple thermodynamic analysis shows that if we apply a force **f**, then since **U** = const, and since

$dU = TdS + fdL$ we have $dF = -SdT + fdL$ & hence $f = \left(\frac{\partial F}{\partial L}\right)_T = -T\left(\frac{\partial S_{con}}{\partial L}\right)_T = \frac{k_B T}{Nl^2} L$

which is just Hooke's Law (extension proportional to force). This is a pretty amazing result which gives a MICROSCOPIC result for Young's modulus **Y** = **L/f**. It tells us the force is fighting entropy in the system – it is fighting against an "entropic force".

Role of Vibrations: there can also be vibrational excitations (called phonons when quantized). Without discussing their origin or mechanics, we can still say a few things.

The total entropy is now

$$S = S_{vib} + S_{con}$$

We shall evaluate **S_{vib}** in the next chapter

Suppose we slowly stretch the polymer, so the total entropy doesn't change. Then △**S** = 0, and

$$\Delta S_{vib} = -\Delta S_{con} = \frac{k_B L \Delta L}{Nl^2}$$

The polymer heats up (ie., energy and entropy go into the vibrations).

1. In line with the basic axioms of probability, the number of microstates for a composite system is given by the product of the number of microstates for each of the sub-systems.

2. The logarithm of the # of microstates is then ADDITIVE over the sub-systems – it is therefore an extensive quantity.

3. The log of the number of microstates is proportional to the entropy S.

4. Entropy S therefore has a characteristic form as a function of energy. For a system which can be mapped to a set of spin-1/2 spins, this has a characteristic inverse parabola shape.

KEY RESULT

$$S \equiv k_B \ln \Omega$$