

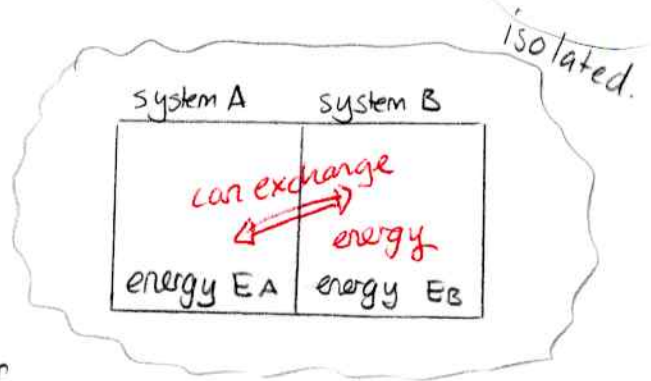
Tues: Read 4.3

Next HW Friday 10

Equilibrium states and statistics

We have considered interacting systems in the context of statistical likelihood of states. For interacting Einstein solids we saw that there were many macrostates available and these all occurred with different probabilities. We can potentially use this to describe which way energy flows. Typically the simplest situation involves a pair of interacting systems that are isolated from everything else. If they are isolated then:

- the total number of particles, N , is fixed
- the total energy, E , is fixed.



Letting N_A, N_B be the number of particles in A, B and E_A, E_B be the energy of A and B, we arrive at a typical description of the macrostates of the system:

Macrostate of A \sim specify N_A, E_A
 Macrostate of B \sim specify N_B, E_B

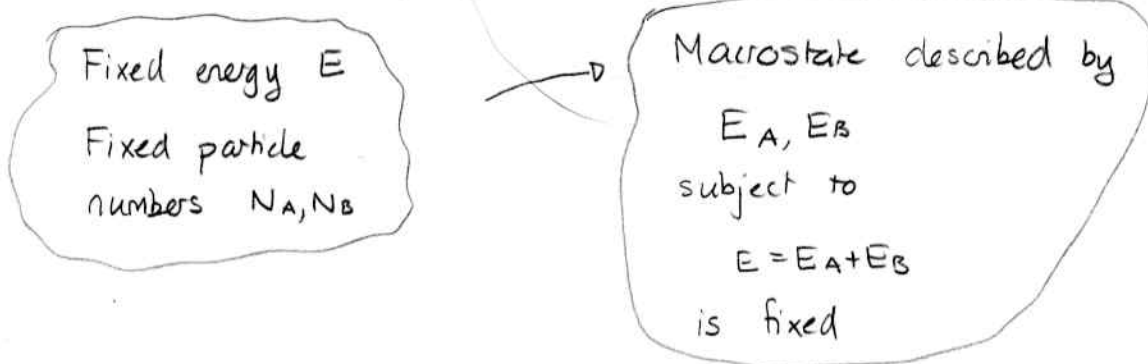
Taken together these constitute a macrostate for the combined system:

Macrostate of system \sim specify N_A, N_B, E_A, E_B

Since the system is isolated it is subject to the constraint:

$$E = E_A + E_B$$

is fixed. Additionally we will initially consider situations where the various systems cannot exchange particles. So N_A, N_B are fixed. So the macrostate description involves



For any macrostate of the system there are many possible microstates. Then a crucial assumption is that

For an isolated system with energy E , the probabilities with which any microstate (having energy E) occurs are all the same.

Let the multiplicity of microstates for the entire system be

$\Omega(N, E)$ = number of microstates for combined system of N particles (N_A in A , N_B in B) and total energy E

When the energy can be apportioned between subsystems then there are multiple macrostates with the same total energy. In this case let

$\Omega(N_A, N_B, E_A, E_B)$ = multiplicity of macrostate N_A, N_B, E_A, E_B
= number of microstates that represent this macrostate.

In general for composite systems:

$$\Omega(N_A, N_B, E_A, E_B) = \Omega_A(N_A, E_A) \Omega_B(N_B, E_B)$$

where

$\Omega_A(N_A, E_A)$ = multiplicity for system A with N_A, E_A .

and similarly for Ω_B . Then the probability with which various macrostates can occur is

$$\text{Prob}(N_A, N_B, E_A, E_B) = \frac{\Omega(N_A, N_B, E_A, E_B)}{\Omega(N, E)}$$

\rightarrow number of microstates for macrostate
 \rightarrow total number of microstates with energy E

provided $E_A + E_B = E$

This gives:

$$\text{Prob}(\underbrace{N_A, N_B, E_A, E_B}_{\text{macrostate}}) = \frac{\Omega_A(N_A, E_A) \Omega_B(N_B, E_B)}{\Omega(N, E)}$$

provided $N = N_A + N_B$ and $E = E_A + E_B$

This can be illustrated with an imaginary example, where the total energy for the two systems is 1000J. The macrostates are determined by how this energy is apportioned between A and B. Then the macrostate for which $\Omega_A \Omega_B$ is largest will be the most likely.

	System A E_A	System B E_B	Ω_A	Ω_B	$\Omega_A \Omega_B$
each row = one macrostate	100J	900J	1	10	10
	200J	800J	3	9	27
	300J	700J	6	8	48
	400J	600J	10	7	70
	\vdots	\vdots	\vdots	\vdots	\vdots

This leads to one additional assumption.

For a system where many macrostates are possible, the equilibrium state of the system is the most probable macrostate.

So the scheme is:

Describe microstates and macrostates of system

For given particle number and energy E , the multiplicity $\Omega(E, N)$ is total number of microstates

Assumption

For an isolated system all microstates with a given N and energy E are equally likely

Counting / binomial coeff...

Determine probability of each macrostate with total energy E

Assumption

Equilibrium macrostate is most probable state

As an example, we applied this to two interacting Einstein solids. Then for a single Einstein solid a macrostate is described by N and q , where q is the number of energy units. The energy is $E = \hbar\omega (q + N/2)$

So

$$\Rightarrow \frac{E}{\hbar\omega} - N/2 = q$$

macrostate
 N, E

describe via N and
 $q = \frac{E}{\hbar\omega} - N/2$

Multiplicity

$$\Omega(N, q) = \binom{N+q-1}{q}$$

We then used the formalism above to describe a pair of interacting Einstein solids.

This model showed:

- 1) the most probable macrostate (equilibrium state) is the state for which the energy per particle for the two subsystems is approximately equal

$$\frac{E_A}{N_A} \approx \frac{E_B}{N_B}$$

- 2) if the pair of systems is not initially in an equilibrium state then the energy flows from the system with a higher energy per particle to that with a lower energy per particle.

We compare this to a heat flow situation in the thermodynamics of monoatomic ideal gases.

Gas A	Gas B
particles N_A	particles N_B
temp T_A	temp T_B

$$E_A = \frac{3}{2} N_A k T_A$$

energy/particle $\Rightarrow \frac{E_A}{N_A} = \frac{3}{2} k T_A$

$$\frac{E_B}{N_B} = \frac{3}{2} k T_B$$

Assume initially that $T_A > T_B$

Second Law of Thermodynamics predicts energy flows from higher to lower temp $\Rightarrow A \rightarrow B$

Statistical analysis predicts energy flows from higher E/N to lower E/N

Agree

The second law is usually phrased in terms of entropy and we hope that aspects of the statistical analysis can also be converted into statements about entropy.

Entropy and statistics

To make the connection we note that in heat transfer processes

- * entropy must increase
- * likelihood of a state must increase.

Thus we postulate:

The entropy of a system is given by

$$S(E, N) = k \ln \Omega(E, N)$$

where $\Omega(E, N)$ is the multiplicity of the macrostate described by E, N

We now need to show:

- 1) this has desired properties for thermodynamic entropy
 - is additive
 - gives correct equilibrium state
- 2) this generates entropies matching thermodynamic entropies for various systems
 - ideal gases
 - oscillating solids, ...

1 Entropy conditions for maximum likelihood state

Consider a composite system which contains two subsystems, labeled A and B. Suppose

$$S_A = k \ln \Omega_A$$

$$S_B = k \ln \Omega_B.$$

a) Show that

$$S = S_A + S_B.$$

b) Show that the most likely macrostate satisfies

$$\frac{\partial S_A}{\partial E_A} = \frac{\partial S_B}{\partial E_B}.$$

Answer: a)
$$\begin{aligned} S &= k \ln \Omega \\ &= k \ln(\Omega_A \Omega_B) \\ &= \underbrace{k \ln \Omega_A} + \underbrace{k \ln \Omega_B} \\ &= S_A + S_B \end{aligned}$$

b) The most likely macrostate is that for which $\Omega = \Omega_A(E_A) \Omega_B(E_B) = \Omega_A(E_A) \Omega(E - E_A)$ is most probable. This is the maximum entropy state.

Thus we need

$$\frac{\partial S}{\partial E_A} = 0 \quad \Rightarrow \quad \frac{\partial S_A(E_A)}{\partial E_A} + \frac{\partial S_B(E - E_A)}{\partial E_A} = 0$$

$$\Rightarrow \quad \frac{\partial S_A}{\partial E_A} + \frac{\partial S_B}{\partial E_B} \frac{\partial (E - E_A)}{\partial E_A} = 0$$

$$\Rightarrow \quad \frac{\partial S_A}{\partial E_A} = \frac{\partial S_B}{\partial E_B} \quad \square$$

With the entropy defined in this way we immediately get the following:

If an isolated system consists of subsystems A, B, C, D, ... then the entropy of the composite system is:

$$S = S_A + S_B + S_C + \dots$$

where $S_A =$ entropy of A.

The entropy as defined in thermodynamics has this property.

The statistical model also shows that:

For an isolated system, the equilibrium state is that for which the entropy is a maximum.

since for most probable state Ω is largest

These two results immediately give

The statistical definition of entropy and equilibrium state is such that if A, B, C, ... interact their equilibrium state will satisfy

$$\frac{\partial S_A}{\partial E_A} = \frac{\partial S_B}{\partial E_B} = \frac{\partial S_C}{\partial E_C} = \dots$$

With the definition from thermodynamics that $1/T = \frac{\partial S}{\partial E}$ this gives that the statistical model predicts that in equilibrium the temperatures will be the same.

So the model is:

Statistical model

~ describe macrostates/microstates

~ determine multiplicities $\Omega(E, N)$

Postulates: * For an isolated system and given energy E
all microstates are equally probable

* Equilibrium state = most probable macrostate

Entropy

$$S(E, N) = k \ln[\Omega(E, N)]$$

Entropy: adds
max for equilibrium state

$$\left(\frac{\partial S}{\partial E}\right)_N = \frac{1}{T}$$

Thermodynamics

Determining multiplicities for discrete systems

Multiplicities for discrete systems often involve factorials. For the Einstein solid

$$\Omega(N, q) = \frac{(N+q-1)!}{q!(N-1)!}$$

When N, q are large we need an approximate method for evaluating these. Stirling's approximation gives

$$\text{If } N \text{ is sufficiently large then} \\ N! \approx N^N e^{-N} \sqrt{2\pi N}$$

and this gives

$$\ln(N!) \approx N \ln N - N + \frac{1}{2} \ln(2\pi N)$$

2 Stirling's approximation

For each of the following, compare:

- $N!$ to the result from Stirling's approximation and
- $\ln N!$ to the result from Stirling's approximation.

- $N = 4$
- $N = 16$
- $N = 64$

Answer:

N	$N!$	Stirling	% diff
4	24	23.5	2.1%
16	2.092×10^{13}	2.081×10^{13}	0.52%
64	1.26887×10^{89}	1.2672×10^{89}	0.13%

N	$\ln(N!)$	Stirling	% diff
4	3.179	3.157	0.70%
16	30.67	30.67	0.00%
64	205.17	205.17	0.00%