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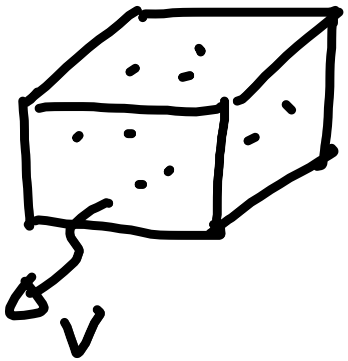
Macrostates and microstates.



N identical particles inside V.

$N \sim 10^{23}$

Thermodynamic limit:

$N \to \infty$

$V \to \infty$

$n = \frac{N}{V} = \text{constant}$

density of particles.

Extensive properties: depend on the volume and N. Proportionally increases.

Ex: Energy, volume, entropy

Intensive properties: independent of N and V.

Ex: temperature, pressure, density, ...

Energy: (non-interacting particles)

$$E = \sum_i n_i \varepsilon_i$$

n_i: # of particles with energy ε_i.

ε_i: possible values of the energy for one single particle

$$N = \sum_i n_i$$

Statistical mechanics is applied to both quantum and classical systems.

Microstate: a particular state with a given $\{n_i\}$ and $\{\varepsilon_i\}$ identified with $\psi(r_1, r_2, \ldots, r_N)$ solution of Schrödinger equation for a system with energy E and N particles.

Ex: system of 3 spins in a magnetic field.

$H \uparrow$

$$+ \quad + \quad -$$

$$-\mu H \quad -\mu H \quad +\mu H$$

$N = 3$

$E = -\mu H$

This is a microstate with $N=3$ and $E=-\mu H$

Macrostate: all the microstates of a system with a well defined energy E and N particles.

Example: $N=3$ $E=-\mu H$ spin system in H-field

$+\ +\ -$
$+\ -\ +$
$-\ +\ +$

these 3 microstates form the macrostate with $E=-\mu H$ and $N=3$.

Equal a priori probability: (postulate) at any time t a system is equally likely to be in any of the microstates that are consistent with its macrostate.

Total number of possible microstates
for macrostate (E, N, V):

$\Omega(E, N, V)$

All the properties of
a system can be
obtain if we know Ω.

However, calculating Ω may be very
hard.

Statistics and Thermodynamics:

- Physical meaning of $\Omega(\underbrace{E, N, V}_{\text{all extensive variables.}})$.

energy can be exchanged between A_1 and A_2

$A^{(0)}$ isolated system

$\Omega_1(N_1, V_1, \bar{E}_1)$

$\Omega_2(N_2, V_2, \bar{E}_2)$

What are going to be $\bar{E}_1$ and $\bar{E}_2$ when equilibrium is reached?

$E^{(0)} = \bar{E}_1 + \bar{E}_2 =$ constant (no interaction energy)

$$A^{(0)} = A_1 + A_2$$

$$\Omega^{(0)} = \Omega_1(E_1)\,\Omega_2(E_2) = \Omega_1(E_1)\,\Omega_2(E^{(0)} - E_1)$$

$$= \Omega^{(0)}(E^{(0)}, E_1)$$

We need to find out for what value of E_1 the system $A^{(0)}$ will be in thermodynamic equilibrium.

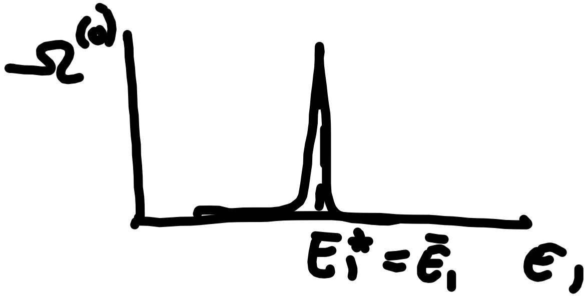
Example: $E^{(0)} = 15$

A_1: m_i	A_1: E_i	A_2: m_i'	A_2: E_i'
2	4	3	7
5	5	8	8
10	6	16	9
17	7	26	10
25	8	40	11
# of microstates	energy of macrostate		

E_1	E_2	$\Omega_1(E_1)$	$\Omega_2(E_2)$	$\Omega^{(0)}(E_1)$
4	11	2	40	80
5	10	5	26	130
6	9	10	16	160*
7	8	17	8	136
8	7	25	3	75

$\Omega^{(0)} = 160$ in equilibrium

then $E_1 = 6$ and $E_2 = 9$.



$\Omega_1(E_1)\,\Omega_2(E_2)$

$$\left.\frac{\partial \Omega^{(0)}}{\partial E_1}\right|_{E_1=\bar{E}_1} = \left.\frac{\partial \Omega_1(E_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} \Omega_2(\bar{E}_2) +$$

$$+\,\Omega_1(\bar{E}_1)\left.\frac{\partial \Omega_2(E_2)}{\partial E_2}\right|_{E_2=\bar{E}_2} \underbrace{\left.\frac{\partial E_2}{\partial E_1}\right|_{E_1=\bar{E}_1}}_{-1} = 0$$

Since $E_2 = E^{(0)} - E_1$

$$\frac{\partial E_2}{\partial E_1} = -1$$

Then

$$\frac{\partial \Omega_1(E_1)}{\partial E_1}\bigg|_{E_1=\bar{E}_1} \Omega_2(\bar{E}_2) = \frac{\partial \Omega_2(E_2)}{\partial E_2}\bigg|_{E_2=\bar{E}_2} \Omega_1(\bar{E}_1)$$

or

$$\frac{1}{\Omega_1(\bar{E}_1)} \frac{\partial \Omega_1(E_1)}{\partial E_1}\bigg|_{E_1=\bar{E}_1} = \frac{1}{\Omega_2(\bar{E}_2)} \frac{\partial \Omega_2(E_2)}{\partial E_2}\bigg|_{E_2=\bar{E}_2}$$

or

$$\frac{\partial \ln \Omega_1(E_1)}{\partial E_1}\bigg|_{E_1=\bar{E}_1} = \frac{\partial \ln \Omega_2(E_2)}{\partial E_2}\bigg|_{E_2=\bar{E}_2}$$

Define

$$\beta = \left.\frac{\partial \ln \Omega(E)}{\partial E}\right|_{E=\bar{E},N,V} \qquad (1)$$

Then at equilibrium

$$\boxed{\beta_1 = \beta_2}$$

$\therefore$ β_i for systems A_1 and A_2 become equal at equilibrium.