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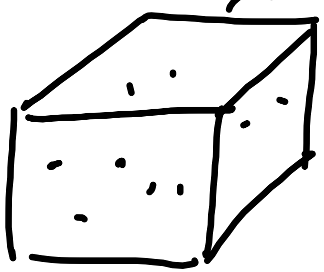
Macrostates and microstates



V: volume

N identical particles.

$N \sim 10^{23}$

Thermodynamic limit: $N \to \infty$
$V \to \infty$

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

density.

Extensive properties:
Increase proportionally to V and N.

Energy
mass
Entropy

C : heat capacity

Intensive properties: independent of V and N.

n, T, p, c (specific heat).

Energy: (consider non-interacting particles).

$$E = \sum_i n_i \, \varepsilon_i$$

E: total energy.

n_i: # of particles with energy ε_i

ε_i: one of many possible values of the energy that one particle can have.

$$N = \sum_i n_i$$

- Stat. Mech. can be applied to either quantum or classical systems.

Quantum mechanically ε_i are discrete and E is discrete but $\Delta E \ll E$ then E usually can be seen as continuous.

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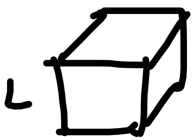
Quantum particle in a box with $\psi = 0$ at the boundaries.

1D 

$$\varepsilon_n = \frac{n^2 h^2}{8 m L^2} \qquad n = 1, 2, \ldots$$

3D 

$V = L^3$

$$\varepsilon_i = \varepsilon_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2 m L^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$n_i = 1, 2, \ldots$$

Microstate: a particular state with a given $\{n_i\}$ and $\{\varepsilon_i\}$ each is identified by $\psi(r_1, \ldots, r_N)$ which is a solution of the Schrödinger eq.

Example : system of 3 spins in H field.

$H \uparrow \quad + \quad + \quad -$ $\qquad E = -\mu H \qquad N = 3$

Macrostate : N, V, and E
are all the microstates compatible with the external parameters.

Example: 3 spins, $E = -\mu H$

$H \uparrow$
$+ + -$
$+ - +$
$- + +$

3 microstates constitute the macrostate.

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Equal a-priori probability postulate:

At any time t a system is equally likely to be in any of the microstates consistent with it macrostate.

Key issue in Stat Mech is to be able to calculate $\Omega(N, V, E)$ which is the number of microstates for the macrostate with E, V, N.

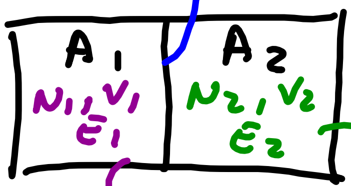
Statistics and Thermodynamics.

Physical meaning of $\Omega(N, V, E)$.

only E can be exchange

$A^{(0)}$ isolated system

(constant
$E = E^0$
$V = V^0$
$N = N^0$)



$\Omega_2(N_2, V_2, E_2)$

$\Omega_1(N_1, V_1, E_1)$

$\Omega_0(N^0, V^0, E^0) = \Omega_1 \Omega_2$

A_1 and A_2 are separately in equilibrium.
we need to find the value of Ω_1 and Ω_2 when they reach equilibrium with each other.

$$E^{(0)} = E_1 + E_2 = \text{constant}$$

$$A^{(0)} \equiv A_1 + A_2 \quad \text{(no interaction energy).}$$

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

For what value of E_1 the system A^0 reaches equilibrium?

We need to find the value of E_1 that maximizes $\Omega^{(0)}$ so that the system spends all its time in the large number of microstates compatible with E_1^*.

E_1^* is the value of E_1 that maximizes Ω^0.

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Example: $E^{0} = 15$

A_1		A_2						
m_1	E_1	m_2	E_2	E_1	E_2	$\Omega_1(E_1)$	$\Omega_2(E_2)$	$\Omega^{(0)}(E_1)$
2	4	3	7	4	11	2	40	80
5	5	8	8	5	10	5	26	130
10	6	16	9	6	9	10	16	160
17	7	26	10	7	8	17	8	136
25	8	40	11	8	7	25	3	75

most likely.

$E_1^{*} = 6$

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

$$\left.\frac{\partial \Omega^{(0)}}{\partial E_1}\right|_{E_1=E_1^*} = \left.\frac{\partial \Omega_1(E_1)}{\partial E_1}\right|_{E_1=E_1^*} \Omega_2(E_2^*) +$$

$$+ \Omega_1(E_1^*) \left.\frac{\partial \Omega_2(E_2)}{\partial E_2}\right|_{E_2=E_2^*} \frac{\partial E_2}{\partial E_1} = 0$$

$$E_2 = E^0 - E_1 \Rightarrow \frac{\partial E_2}{\partial E_1} = -1$$

Then

$$\left.\frac{\partial \Omega_1(E_1)}{\partial E_1}\right|_{E_1=E_1^*} \Omega_2(E_2^*) = \left.\frac{\partial \Omega_2(E_2)}{\partial E_2}\right|_{E_2=E_2^*} \Omega_1(E_1^*)$$

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or

$$\frac{1}{\Omega_1}\frac{\partial \Omega_1}{\partial E_1}\bigg|_{E_1=E_1^*} = \frac{1}{\Omega_2}\frac{\partial \Omega_2}{\partial E_2}\bigg|_{E_2=E_2^*}$$

or

$$\frac{\partial \ln \Omega_1(E_1)}{\partial E_1}\bigg|_{E_1=E_1^*} = \frac{\partial \ln \Omega_2(E_2)}{\partial E_2}\bigg|_{E_2=E_2^*}$$

Define

$$\beta = \frac{\partial \ln \Omega(E)}{\partial E}\bigg|_{E=E^*,N,V} \qquad (1)$$

Then at equilibrium between A^1 and A^2: $\beta_1 = \beta_2$.

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Zeroth law of thermodynamics: a common parameter T that characterizes 2 or more systems in thermal equilibrium.

Then we expect that β and T (temperature) will be related.

From thermodynamics we know that

$$dE = T\,dS - P\,dV + \mu\,dN \qquad E = E(S,V,N)$$

then

$$\left.\frac{\partial E}{\partial S}\right|_{V,N} = T \Rightarrow \boxed{\left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{1}{T}} \quad (2)$$

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Compare:

$$\frac{\partial \ln \Omega}{\partial E} = \beta$$

with

$$\left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{1}{T}$$

$$S \propto \ln \Omega \quad \Rightarrow \quad S = c \ln \Omega$$

and

$$\frac{1}{T} \propto \beta \qquad \frac{1}{T} = c\beta$$

or

$$\frac{\Delta S}{\Delta(\ln \Omega)} = \frac{1}{\beta T} = c$$

Boltzmann noticed this and defined

$c = k$ Boltzmann's constant.

Then

$$S = k \ln \Omega(N, V, T) \qquad \text{I}$$

$$k = \frac{1}{\beta T} \Rightarrow \beta = \frac{1}{kT} \qquad \text{II}$$

I determines the absolute value of the entropy S in terms of the # of microstates.

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We see that if $\Omega = 1 \Rightarrow S = 0$.

$\Omega = 1$ single microstate it happens when the system at $T=0$ is in its ground state.

Third law of thermodinamics: if $T \to 0$ then $S \to 0$. (or S very small in case of degenerate ground states).

Second law: the energy available in the universe becomes less and less available to be transformed into work $\therefore$ S meassures disorder or chaos in a system.

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S always increases or stays the same.

Then the largest Ω is the most disordered the system is and the least information we have about it.

More relationships:

Assume that the wall between A_1 and A_2 can move. Then $V_1 + V_2 = V^0 =$ constant.

Find maximum of Ω with respect to the volume V_1 then you will find that

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the maximum occurs when

$$\left.\frac{\partial \ln \Omega_1}{\partial V_1}\right|_{N_1, E_1, V_1 = V_1^*} = \left.\frac{\partial \ln \Omega_2}{\partial V_2}\right|_{N_2, E_2, V_2 = V_2^*}$$

define

$$\eta = \left.\frac{\partial \ln \Omega}{\partial V}\right|_{N, E, V = V^*}$$

then $\eta_1 = \eta_2$ in equilibrium.

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If the barreer now allows particles to go through we have $N_1 + N_2 = N^0 =$ constant and Ω^0 will have a maximum at $N_1 = N_1^*$.

$$\left.\frac{\partial \ln \Omega}{\partial N_1}\right|_{V_1, E_1, N_1 = N_1^*} = \left.\frac{\partial \ln \Omega}{\partial N_2}\right|_{V_2, E_2, N_2 = N_2^*}$$

define

$$\xi = \left.\frac{\partial \ln \Omega}{\partial N}\right|_{V, E, N = N^*}$$

$\xi_1 = \xi_2$ at equilibrium.

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