9/1

Last time:

Microstate is labeled by the index $r = 1, 2, \ldots$ that identifies a cell in phase space (classical) or a set of quantum numbers.

Example: 2 spins $1/2$. They have 4 microstates

	$\uparrow\uparrow$	$\uparrow\downarrow$	$\downarrow\uparrow$	$\downarrow\downarrow$
r	1	2	3	4

<u>Statistical Ensemble</u>: Large number of replicas of the system that we are considering.

We do not know what every part of the system is doing. But we may know a macroscopic property such as the energy or the magnetization and we will find how many microscopic states of the system are compatible with the macroscopic property.

A <u>macrostate</u> is composed by all the <u>microstates</u> compatible with the macroscopic property of the system.

The microscopic states in the macrostate are called accessible states.

We can calculate the probability that different values of a macroscopic property has by comparing the accessible states with all the possible microstates.

Ex: let's calculate the total magnetic moment M in our example of 2 spins ½.

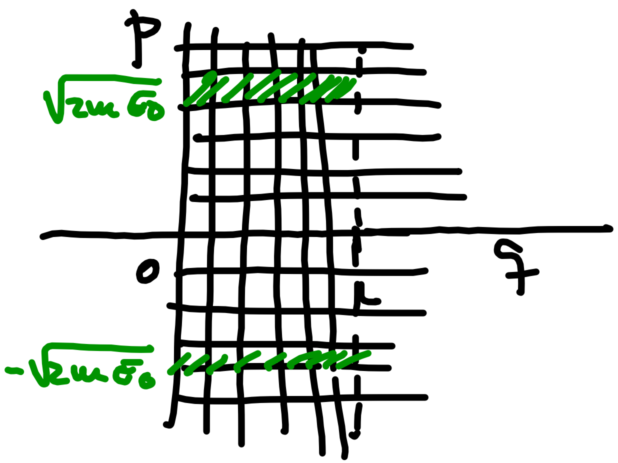
$\bar{\mu}$ is the magnetic moment per spin

r	m_1	m_2	M
1	+	+	2μ
2	+	−	0
3	−	+	0
4	−	−	-2μ

• The most likely value of M is 0.

- If I know that $M=0$ then only 2 of the 4 states are accessible.
- If $M = 2\mu$ there is only one accessible state.

Ex: One free particle in a box of length L in 1D: (classical)



$$0 \le q \le L$$

$$\epsilon = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

1) If we know that
$\epsilon = \epsilon_0 \Rightarrow p = \pm\sqrt{2m\epsilon_0}$

2) If we know that $\epsilon \le \epsilon_0$ all states between $0 \le q \le L$ and $|p| \le \sqrt{2m\epsilon_0}$ are accessible.

Basic Postulates:

- Isolated system: it cannot exchange neither energy nor particles with its surroundings.

E = constant

N = constant

1) The probability of finding the system in any of its accessible states is the same. In this case the system is in thermodynamical equilibrium.

"An isolated system in equilibrium is equally likely to be in any of its accessible states"

A-12 : The H (eta) Theorem : Time dependence of P_r (probability of microstate r).

Consider a quantum system with accessible states labeled by r.

① $\sum_r P_r(t) = 1$ at any time t.

$W_{sr} = W_{rs}$ is the probability that the system will go from accessible microstate r to accessible microstate s or vice versa.

$$W_{sr} = c\langle s|H|r\rangle = c^*\langle r|H|s\rangle^* = c\langle r|H|s\rangle = W_{rs}$$

hermiticity of H and W_{sr} has to be real,

Calculate

(2)

$$\frac{dP_r}{dt} = \underbrace{\sum_s P_s W_{sr}}_{\text{this makes } P_r \text{ increase}} - \underbrace{\sum_s P_r W_{rs}}_{\text{this term reduces } P_r} = \sum_s (P_s - P_r) W_{rs}$$

Define

$$H = \overline{\ln P_r} \equiv \sum_r P_r \ln P_r$$

$$\frac{dH}{dt} = \sum_r \left(\frac{dP_r}{dt} \ln P_r + \frac{P_r}{P_r} \frac{dP_r}{dt} \right) =$$

$$= \sum_r \frac{dP_r}{dt} (\ln P_r + 1) \overset{2}{=}$$

$$= \sum_r \sum_s (P_s - P_r) w_{rs} (\ln P_r + 1) = \quad 3$$

$$= \sum_s \sum_r (P_r - P_s) w_{sr} (\ln P_s + 1) \quad 4$$

$$2 \frac{dH}{dt} = 3 + 4$$

$$2\frac{dH}{dt} = \sum_{r,s} \Big[w_{sr}(P_r - P_s)(\ln P_s + 1) + $$

$$+ w_{rs}(P_s - P_r)(\ln P_r + 1) \Big] = \qquad w_{rs} = w_{sr}$$

$$= \sum_{r,s} w_{rs} \Big[-(P_s - P_r)(\ln P_s + 1) + (P_s - P_r)(\ln P_r + 1) \Big]$$

$$= -\sum_{r,s} W_{rs} (P_s - P_r)(\ln P_s - \ln P_r)$$

$$\frac{dH}{dt} = -\frac{1}{2} \sum_{r,s} w_{rs} (P_s - P_r)(\ln P_s - \ln P_r) \leq 0$$

Since $(P_s - P_r)$ has the same sign that $(\ln P_s - \ln P_r)$

H always decreases with time - H-theorem.

When $\frac{dH}{dt} = 0$ equilibrium has been achieved.

It means that $P_r = P_s$ = constant for all r, s.

• Equal probability for each accessible state.

Later we will see that

$$S = -k \underbrace{\sum_r P_r \ln P_r}_{H} = -kH \quad \therefore \quad \frac{dS}{dt} \geq 0$$

S : entropy.

Example: spin 1/2 system.

If $M=0$ and we have two spins.

2 accessible states: $\uparrow\downarrow$ $\quad$ $\downarrow\uparrow$

$P=\frac{1}{2}$ $\quad$ $P=\frac{1}{2}$

If $N=4$ (instead of 2) and $M=0$.

$$\binom{4}{2} = \frac{4!}{2!\,2!} = \frac{4\times 3}{2} = 6 \text{ states with } P=\frac{1}{6}.$$

For N spins with $M=0$ I have

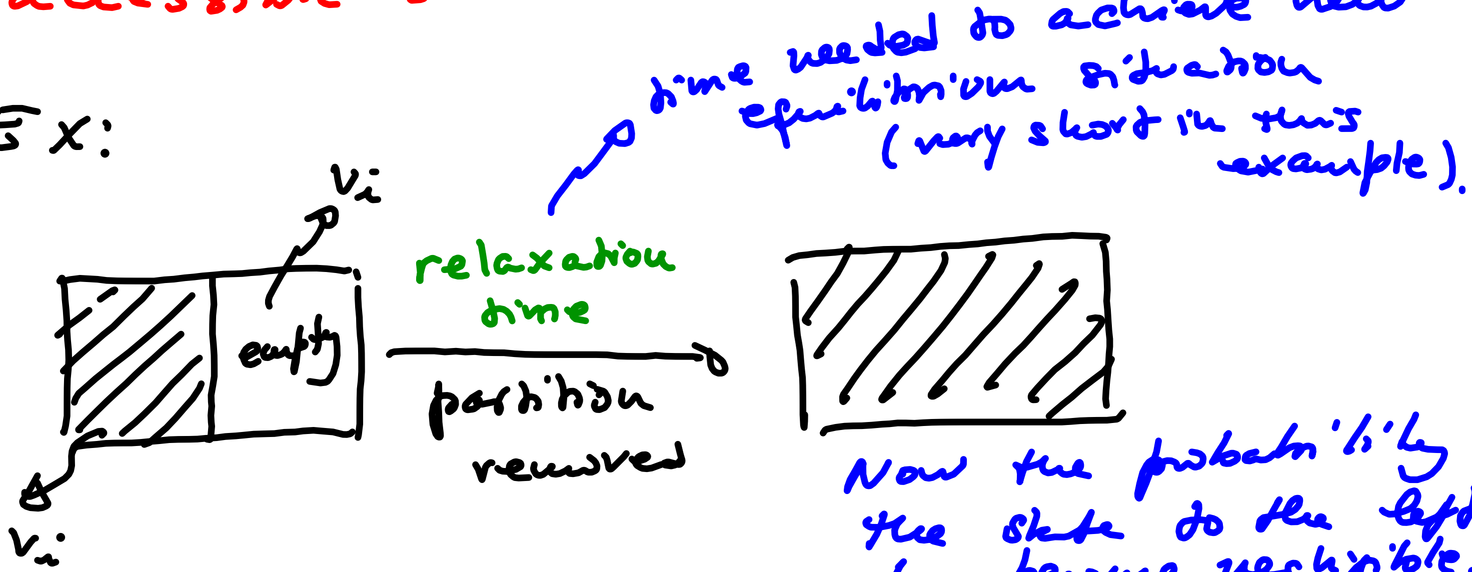
$$\binom{N}{\frac{N}{2}} = \frac{N!}{\left[\left(\frac{N}{2}\right)!\right]^2}$$

so the probability of each is

$$P=\frac{\left[(N/2)!\right]^2}{N!}$$

We see that the probability of each accessible state decreases as the system becomes larger. A system in equilibrium is constantly jumping among all its equally accessible states.

Ex:



Now the probability of the state to the left has become negligible.

Probability Calculations:

$\Omega(E)$: Total number of accessible states between E and $E+dE$.

How many states in this range have also $y = y_k$? (y is another macroscopic property such as magnetization).

$\Omega(E; y_k)$ is the number of states with y_k and Energy between E and $E+dE$.

The probability of encountering y_k in our system is given by:

$$P(y_k) = \frac{\Omega(E; y_k)}{\Omega(E)}$$

Then we can calculate $\bar{y} = \langle y \rangle$:

$$\bar{y} = \frac{\sum_k y_k \, \Omega(E; y_k)}{\Omega(E)}$$

Ex: 2 spins ½:

r	m_1	m_2	M
1	+	+	2μ
2	+	−	0
3	−	+	0
4	−	−	-2μ

- What is the probability that $m_1 = +$ if $M = 2\mu$?

  1

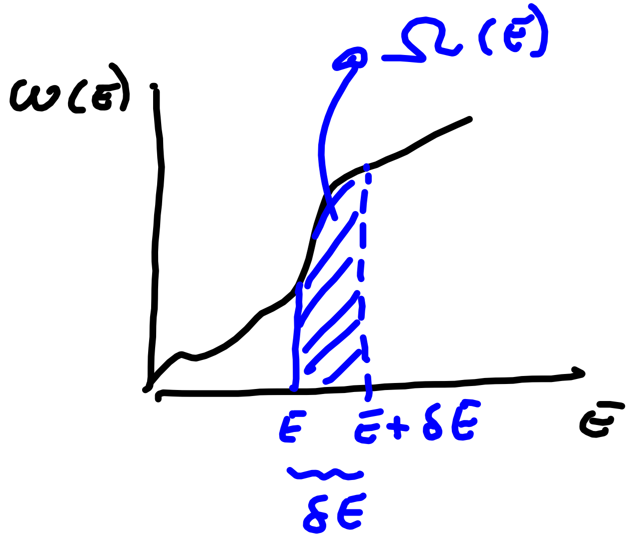
- What if $M = 0$?

  $\frac{1}{2}$

Density of states: $\omega(E)$

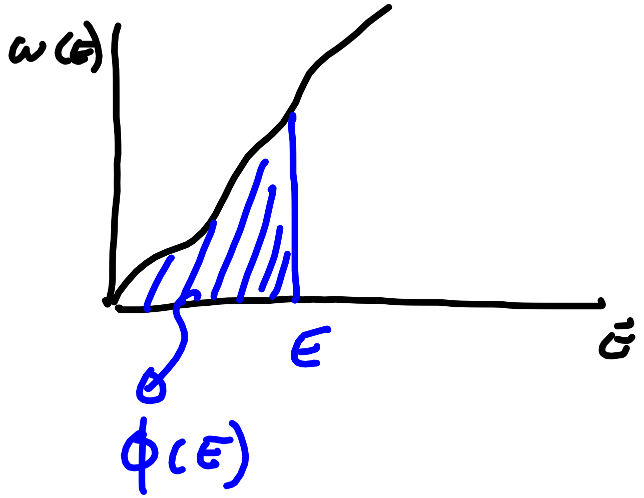
$\omega(E)$ is the number of states in an interval of energy δE such that

$$\Omega(E) = \omega(E)\underbrace{\delta E}_{\text{no } E \text{ dependent}}$$



Since δE is very small $\omega(E)$ is almost constant in the interval δE.

How does $\omega(E)$ depend on E in a generic macroscopic system?



$\phi(E)$ = number of states with energy smaller than E.

Assume that the macroscopic system has f degrees of freedom.

$\phi_i(\varepsilon) \propto \varepsilon^{\alpha}$ $\qquad \alpha \approx 1$ $\qquad$ the # of states increases more or less with ε.

$\varepsilon \approx \frac{E}{f}$ $\qquad E$ is assumed to be equally distributed among the degrees of freedom.

Then

$$\phi(E) \cong \phi_1(\varepsilon)\,\phi_2(\varepsilon)\dots\phi_f(\varepsilon) \approx \varepsilon^f \approx \frac{E^f}{f^f} \qquad (1)$$

$$\Omega(E) \approx \phi(E+\delta E) - \phi(E) = \frac{\partial \phi}{\partial E}\,\delta E \overset{(1)}{=}$$

$$= \frac{\partial(E^f/f^f)}{\partial E}\,\delta E = f\,\frac{E^{f-1}}{f^f}\,\delta E \propto E^f \quad \text{if } f >> 1.$$

The density of states increases very rapidly with E.

Ex: Ideal gas. (classical limit).

N particles in a volume V.

$$E = K + \underbrace{U}_{\to 0 \text{ for ideal gas}} + \underbrace{E_{int}}_{\to 0 \text{ for monoatomic gas.}}$$

$$K = \frac{1}{2m} \sum_{i=1}^{N} \underbrace{\bar{p}_i \cdot \bar{p}_i}_{\sum_{i=1}^{N} p_{i\alpha} p_i^{\alpha}}$$ kinetic energy

$\bar{p}_i \cdot \bar{p}_i = |p_i^2|$

$\alpha = 1, 2, 3$.

$(\bar{p}_i)^2$: defines a sphere of radius $\bar{p}$ in f dimensional space.

$\therefore$ $2mE = \sum_{i=1}^{N} \sum_{\alpha=1}^{3} p_{i\alpha}^2$ $\qquad$ p : radius.

In phase space we have coordinates $\{q_i\}$ and $\{p_i\}$

6N coordinates

$$\Omega(E) \simeq \int_E^{E+\delta E} \cdots \int d^3p_1 \cdots d^3p_N \underbrace{\int_{-\infty}^{\infty} d^3q_1 \cdots d^3q_N}_{V^N}$$