Fundamentals of Engineering Physics 2019

Week 12.

3.2. Statistical Ensemble

⊛ Usually, we do not have available a precise knowledge of the particular microscopic state in which a system of ptls is found.

⊛ A complete "macroscopic description" of a system of many ptls defines the macro(scopic) state of the system.

⊛ Such description is entirely based on specification of quantities ascertained by macroscopic measurements alone.

Eg., – Information on external parameters of the system:

"Box Size", $\vec{E}_{ext}$, $\vec{B}_{ext}$, ...

– Information about the initial preparation of the system:

"total energy" of an isolated system between "E" and "E+δE".

⊛ Accessible States of a system

- Those of its quantum states in which the system can be found without violating any conditions imposed by the information available about the system.

* In a statistical ensemble of macroscopic systems, every system is known to be in one of its accessible quantum states.

* Then, what is the probability that the system is found in any given one of these accessible states?

r	σ_1	σ_2	σ_3	σ_1'	σ_2'	M	M'
1	+	+	+	+	−	$3\mu_0$	0
2	+	+	+	−	+	$3\mu_0$	0
3	+	−	−	+	+	$-\mu_0$	$4\mu_0$
4	−	+	−	+	+	$-\mu_0$	$4\mu_0$
5	−	−	+	+	+	$-\mu_0$	$4\mu_0$

Table 3.3 Systematic enumeration of all the states, labeled by some index r, which are accessible to the system A^* when its total energy in a magnetic field **B** is equal to $-3\mu_0 B$. The system A^* consists of a subsystem A with three spins $\frac{1}{2}$, each having magnetic moment μ_0, and a subsystem A' with two spins $\frac{1}{2}$, each having magnetic moment $2\mu_0$.

Example (i)

Consider a system of four spins $\frac{1}{2}$ (each having a magnetic moment μ_0) located in an applied magnetic field **B**. The possible quantum states and associated energies of this system are listed in Table 3.2. *Suppose that this system is isolated* and known to have a total energy which is equal to $-2\mu_0 B$. The system can then be found in any one of the following four states accessible to it:

$$\{+++-\}, \qquad \{++-+\},$$
$$\{+-++\}, \qquad \{-+++\}.$$

Example (ii)

Consider a system A^* which consists of two subsystems A and A' which can interact to a small extent and thus exchange energy with each other. System A consists of three spins $\frac{1}{2}$, each having a magnetic moment μ_0. System A' consists of two spins $\frac{1}{2}$, each having a magnetic moment $2\mu_0$. The system A^* is located in an applied magnetic field **B**. We shall denote by M the total magnetic moment of A along the direction of **B**, and by M' the total magnetic moment of A' in this direction. The interaction between the spins is assumed to be almost negligible. The total energy E^* of the entire system A^* is then given by

$$E^* = -(M + M')B.$$

The system A^* consists of 5 spins and thus has a total of $2^5 = 32$ possible quantum states. Each of these can be labeled by five quantum numbers, the three numbers σ_1, σ_2, σ_3 specifying the orientations of the three magnetic moments of A, and the two quantum numbers σ_1', σ_2' specifying the orientations of the two magnetic moments of A'. Suppose that the isolated system A^* is known to have a total energy E^* equal to $-3\mu_0 B$. Then A^* must be found in any one of the five accessible states, listed in Table 3.3, which are compatible with this total energy.

† Any system which is *not* isolated can then be treated as a part of a larger system which *is* isolated.

$\boxed{\text{If an isolated system is found with equal probability in each one of its accessible states, it is in equilibrium}}$ (17)

↓ ↑

$\boxed{\text{If an isolated system is in equilibrium, it is found with equal probability in each one of its accessible states.}}$ (19)

"The Postulate of Equal A PRIORI PROBABILITIES"

$\boxed{\text{Example}}$ · An isolated system of 4 weakly interacting spins having a total energy "$-2\mu_0 B$".

- Then, "one" of 4 spins should be "down".
- There are four accessible states; $\{+,+,+,-\}$, $\{+,+,-,+\}$, $\{+,-,+,+\}$ and $\{-,+,+,+\}$.
- There is no preferred state out of those 4 accessible states.
- If the system is in equilibrium, the probability of finding it in each accessible states is equal.
- If the system is found in one of those accessible states, it will eventually reach an equilibrium state after a relaxation time.

3.4. Probability Calculations

Example: Consider a system of four spins in a magnetic field listed in Table 3.2. Suppose that the total energy of this system is known to be "$-2\mu_0 B$." Then, there are four accessible states satisfying the condition $E_{Tot} = -2\mu_0 B$.

$\{+++-\}$, $\{++-+\}$, $\{+-++\}$ and $\{-+++\}$.

- In equilibrium, the system is equally likely to be in each one of those 4 accessible states.
- Now, focus attention to the 1st spin of the system.

What is the probability P_+ that its magnetic moment points up?

$P_+ = 3/4$. Why not $P_+ = P_- = 1/2$ according to the Postulate of equal a priori probabilities? $\because$ A single spin is not isolated and is not in equilibrium.

What is the mean magnetic moment of the 1st spin?

$$\bar{M} = \frac{3}{4}(\mu_0) + \frac{1}{4}*(-\mu_0) = \frac{1}{2}\mu_0 .$$

3.5. Number of States Accessible to a Macroscopic System

⊕ Consider a macroscopic system with given external parameters.

* $\Omega(E) \equiv$ the number of states with energies lying in the interval between E and $E+\delta E$ (22)

(δE is very small in macroscopic sense, but larger than the difference in energy between adjacent quantum levels of system).

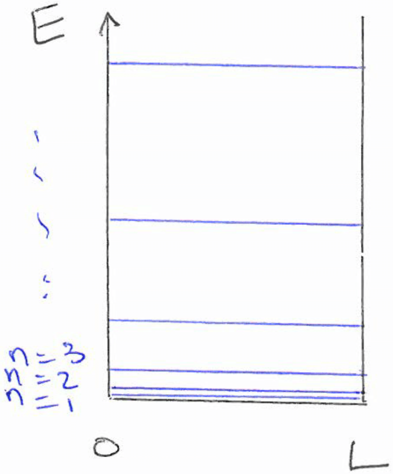
* $\Omega(E) = \rho(E)\,\delta E$ (23)

density of states (independent of δE).

* $\Phi(E) \equiv$ total number of states having energies less than E. (24).

$$\rightarrow \quad \Omega(E) = \Phi(E+\delta E) - \Phi(E) = \frac{d\Phi}{dE}\,\delta E \qquad (25).$$

* Example (i) Single Particle in a one-dimensional box



- Quantized energy levels (eigenvalues) are

  - $E = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} n^2$, where $n = 1, 2, 3, \cdots$ (26)

- For a macroscopic system, $n \gg 1$.

  - $n = \frac{L}{\pi\hbar} (2mE)^{1/2}$ (27)

- The number of states $\Phi(E)$ having energies less than E is therefore ($\because$ successive quantum states correspond to values of n differing by 1).

  - $\Phi(E) = n = \frac{L}{\pi\hbar} (2mE)^{1/2}$ (28)

and - $\Omega(E) = \left(\frac{d\Phi}{dE}\right) \delta E = \frac{L}{2\pi\hbar} (2m)^{1/2} E^{-1/2} \delta E.$ (29)

* Example (ii) $\boxed{\text{Single Ptl in 3d Box}}$ with $L = L_x = L_y = L_z$.

* $$E = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad (30)$$

where $n_x, n_y, n_z = 1, 2, 3, \cdots$

For macro-system, $n_x, n_y, n_z \gg 1$.

*

$$n_x^2 + n_y^2 + n_z^2 = \left(\frac{L}{\pi\hbar}\right)^2 (2mE) \equiv R^2$$

R : radius of a sphere in "quantum number space" (n_x, n_y, n_z).

See Fig 3.7.

* By counting a number of points with positive integer values of n_x, n_y and n_z, $\rightsquigarrow$ volume of one octant (1/8) of the sphere of radius R, we obtain

$$\Phi(E) = \frac{1}{8}\left(\frac{4}{3}\pi R^3\right) = \frac{\pi}{6}\left(\frac{L}{\pi\hbar}\right)^3 (2mE)^{3/2},$$

* $$\therefore \quad \Omega(E) = \frac{V}{4\pi^2\hbar^3}(2m)^{3/2} E^{1/2}\,\delta E \qquad (32)$$

$(V = L^3)$

⊛ For a macroscopic system consisting of many particles, we can make a very crude order-of-magnitude estimate,

* Total energy of system

$$E - E_0 \sim \underbrace{f}_{\text{number of degrees of freedom}} * (\underbrace{\epsilon - \epsilon_0}_{\text{energy corresponding to each degree of freedom}}) \qquad (34)$$

* Typically $\underbrace{\varphi(\epsilon)}_{}\propto (\epsilon - \epsilon_0)^{\alpha}$, $\alpha \sim 1$.

total number of possible values of specific quantum number (corresponding to each degree of freedom) when its associated energy is less than ϵ.

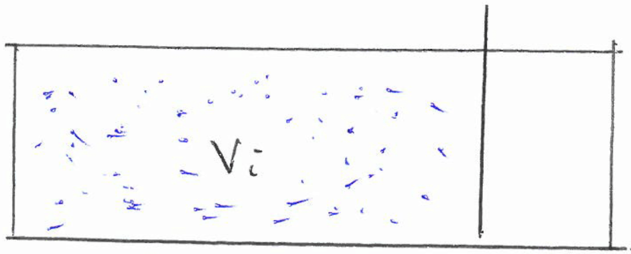
* By counting total number of possible combinations of all quantum numbers,

$\Phi(E) \sim [\varphi(\epsilon)]^f$ $\rightsquigarrow$ $\boxed{\Omega(E) \propto (E - E_0)^f}$ very approximately (38)

– extremely rapidly increasing function of "E".

(f can be $O(10^{24})$).

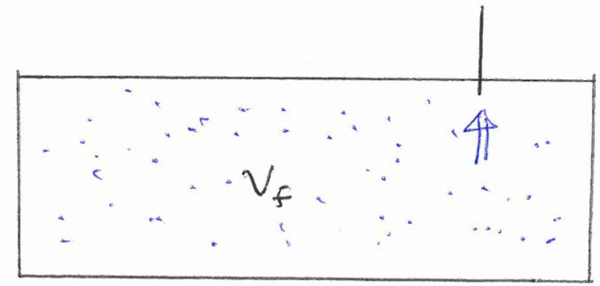
⊛ Constraints, Equilibrium, and Irreversibility



N ptls

$\xrightarrow{\text{After}}$

$\tau \gg$ relaxation time



N ptls.

⊛ Number of accessible states for each ptl ~~Ω_i~~, ω_i

ω_i ~~Ω_i~~ $\propto V_i$

in equilibrium.

⊛ Total number of accessible states of the System

$$\Omega_i = \omega_i^N \propto V_i^N$$

⊛ Number of " ;

ω_f

$\omega_f \propto V_f$

in equilibrium.

⊛ Total number of accessible states of the system

$$\Omega_f = \omega_f^N \propto V_f^N$$

⇒ Note that $\boxed{\Omega_f = \left(\frac{V_f}{V_i}\right)^N \Omega_i \ggg \Omega_i}$ for $N \ggg 1$.

⊛ In the preceeding example, the initial situation cannot be restored merely by re-imposing the former constraint while keeping the system isolated.

> "The process is irreversible if the initial situation of an ensemble of isolated systems having undergone this process cannot be restored by simply imposing a constraint."

⊛ In the example, "the removal of a partition is a irreversible process."

⊛ Immediately after the partition is removed, all ptls are still in the left part (V_i) of the box.

But system at that moment is not in equilibrium because ptls are not found with the equal probability in each of its ~~final~~ final accessible states, $\omega_f \propto V_f$.

Reading Assignments and HomeWork

(*) Read "Summary of Definitions" on page 135, and make sure you understand those.

Homework.

Problems :

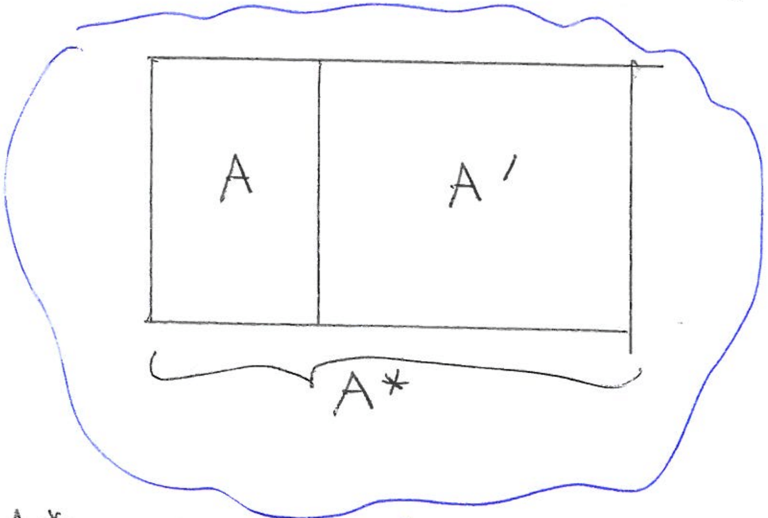
3.2 and 3.3. on page 137

3.5. on page 138,

3.8. on page 140.

Ch. 4. Thermal Interaction

4.1. Distribution of Energy between Macroscopic Systems



$A^* = A + A'$ is isolated.

Total Energy of A^* :

$$E^* = E + E' = \text{const.} \quad (1)$$

energy of "A", "A'"

$$\rightarrow \quad E = E^* - E' \quad (2)$$

⊛ What is the probability $P(E)$ that the energy of A is equal to E ?

→ Among the total number Ω^*_{tot} of states accessible to A^*, what is the number $\Omega^*(E)$ of states of A^* which are such that the subsystem A has an energy equal to E ?

$$\rightarrow \quad \underline{P(E)} = \frac{\Omega^*(E)}{\Omega^*_{tot}} = \text{const.}\ \underline{\Omega^*(E)} \quad (3)$$

⊛ $\Omega^*(E)$ can be expressed in terms of number of states accessible to A and A', respectively.

⊛ When A has an energy E, it can be in any one of its possible $\Omega(E)$ states.

→ Then system A' must have an energy $E' = E^* - E$, and can be in any one of the $\Omega'(E') = \Omega'(E^* - E)$ states accessible to it.

→ Counting every combination of possible states of A and those of A', we have

$$\boxed{\Omega^*(E) = \Omega(E)\,\Omega'(E^* - E)} \qquad (4),$$

and

$$P(E) = \text{const} * \Omega(E)\,\Omega'(E^* - E) \qquad (5)$$

⊛ Recall that $\Omega(E)$ is an extremely rapidly increasing function of E for any macroscopic system.

→ $\Omega'(E^* - E)$ is an extremely rapidly decreasing function of E
(increasing 〃 E').

⇒ Product of those two functions exhibits a very sharp maximum for some particular value of E, at $\bar{E}$.

⊛ $P(E) = C\,\Omega(E)\,\Omega'(E')$ is maximum at some $E = \bar{E}$.

$$\therefore \left.\frac{\partial P(E)}{\partial E}\right]_{\bar{E}} = 0 \quad \Rightarrow \quad \left.\frac{\partial}{\partial E} \ln P(E)\right]_{\bar{E}} = 0 .$$

– Since $\ln P(E) = \ln(\text{const}) + \ln \Omega(E) + \ln \Omega'(E')$,

$$\frac{\partial}{\partial E} \ln P = 0 \Rightarrow \frac{\partial}{\partial E} \ln \Omega(E) + (-)\frac{\partial}{\partial E'} \ln \Omega'(E') = 0 .$$

or

$$\beta(E) = \beta'(E') \qquad (8)$$

where

$$* \ \beta(E) \equiv \frac{\partial}{\partial E} \ln \Omega = \frac{1}{\Omega}\frac{\partial \Omega}{\partial E} \qquad (9)$$

$$\boxed{\frac{1}{\beta} \equiv k_B T} \quad (12);$$

T ; "absolute temperature"

k_B : Boltzmann's constant.

$$\boxed{S \equiv k_B \ln \Omega} \quad (14):$$

S : "entropy"

"quantitative measure of the degree of randomness of the system!"