Non-Quantized Energy Values

(*) For the System of Spin Half particles the energy states were quantized

(*) We will now generalize the discussion when energy is not necessarily quantized.

(*) We will start with an example.

N molecules in a box

→ Consider N gas molecules in a volume V.

→ The energy of the gas molecules will depend upon

@ The potential energy of the N gas molecules determined the position $r_1, r_2, \dots r_N$ of the molecules

Gas molecules in a Box

$(*)$ The kinetic energy of the molecules determined by their respective momenta; $p_1, p_2, \dots p_N$

$(*)$ The internal energy of each molecule characterized by the internal configuration coordinates $Q_1, \dots Q_N$ and momentum coordinates $P_1, \dots P_N$.

Density of states

$\rightarrow$ Suppose $\Lambda(E)$ denotes the density of states. which is the number of states that the system can take when the total energy is between E and $E + \delta E$.

Density of states

→ Clearly

$$\Omega(E) \propto \int_E^{E+\delta E} \int \cdot \int \cdots \int dr_1 \, dr_2 \cdots dr_N \, dp_1 \cdots dp_N \, dQ_1 \cdots dQ_N \, dP_1 \, dP_2 \cdots dP_N$$

where we integrate over all of the space that satisfy the constraint of total energy between E and $E+\delta E$

Ideal gas approximation

→ Suppose the gas molecules do not have any interaction energy. Then

$$\Gamma(E) \propto \left(\int\limits_{E}^{E+\delta E}\int\int \cdots \int dp_1 \cdots dp_N \, d\theta_1 \cdots d\theta_N \, d\rho_1 \cdots d\rho_N \right)$$

$$\int\limits_{r_i}\int \cdots \int \cdots \, dr_1 \cdots dr_N$$

$$= \left[\int\limits_{E}^{E+\delta E}\int\int \cdots \int dp_1 \cdots dp_N \, d\theta_1 \cdots d\theta_N \, d\rho_1 \cdots d\rho_N \right)$$

$$\int dr_1 \int dr_2 \cdots \int d\theta_N$$

Towards Ideal gas

$$= \int_{E}^{E+\delta E} \int dp_1 \cdots dp_N \, d\theta_1 \cdots d\theta_N dp_1 \cdots dp_N$$

$$(V^N)$$

→ Suppose, the molecules do not have any internal degrees of freedom and their internal energy $E_{int} = 0$.

Then

$$\Omega(E) \propto V^N \left[\int_{E}^{E+\delta E} \int dp_1 \cdots dp_N \right]$$

Limit of an ideal gas.

$\rightarrow \quad \mho(E) \propto V^N \displaystyle\int \cdots \int_{E}^{\overline{E+\delta E}} dp_1 \cdots dp_N$

Suppose each molecule i with momentum $\vec{P_i} = p_{i\cdot 1}\vec{e_x} + p_{i_2}\vec{e_y} + p_{i_3}\vec{e_3}$

has energy $E_i = \displaystyle\sum_{j=1}^{3} \frac{1}{2m} p_{ij}^2$

$\rightarrow$ Total Energy is
$$E = \sum_{i=1}^{N} \sum_{j=1}^{3} \frac{1}{2m} p_{ij}^2 .$$

Limit of an ideal gas

$$\rightarrow \therefore \Lambda(E) \propto V^N \int \cdots \int_E^{E+\delta E} dp_1 \cdots dp_N$$

and

$$\int \int \cdots \int_E^{E+\delta E} dp_1 \cdots dp_N \quad \text{is the}$$

measure of the set

$$\left\{ (p_1, p_2 \cdots p_N) \,\middle|\, E < \sum_{i=1}^{N} \sum_{j=1}^{3} \frac{p_{ij}^2}{2m} \leq E+\delta E \right\}$$

which is the volume of a shell in
3N dimensional space.

Limit of an Ideal Gas

$$\Omega(E) \propto V^N \int \cdot \int \cdots \int \cdot \, dp_1 \cdots dp_N \bigg|_E^{E+\delta E}$$

$$\underbrace{\qquad\qquad\qquad\qquad}_{\chi(E)}$$

$$\rightarrow \chi(E) = \int \int \cdots \int \cdot \, dp_1 \cdots dp_N \cdot \bigg|_E^{E+\delta E}$$

$$= \mu \left\{ p_{ij} : i=1 \cdots N, j=1 \cdots 3 \; ; \; E \leq \sum_i \sum_j \frac{p_{ij}^2}{2m} \leq E+\delta E \right\}$$

$$= \mu \left\{ p_{ij} : i=1 \cdots N, j=1 \cdots 3 \; ; \; (2mE) \leq \sum_i \sum_j p_{ij}^2 \leq 2m(E+\delta E) \right\}$$

Limit of an ideal gas

$\Rightarrow \quad \Omega(E) \propto V^N \chi(E)$

$\chi(E)$ is the volume of a shell of
an hypersphere between the radius
$R(E) \doteq \sqrt{2mE}$ and $R(E+\delta E)$.

$\rightarrow$ Volume of a hypersphere of dimension f with radius
$R(E) \propto (R(E))^f$

$\Rightarrow \quad \chi(E) = \left[\dfrac{d}{dE} (R(E))^f \right] \delta E$

Limit of an ideal gas

$$\Rightarrow \quad \chi(E) = \left[\frac{d}{dE} (2mE)^{f/2} \right] \delta E$$

$$= \left(\frac{f}{2} (2mE)^{\frac{f}{2}-1} \right) \delta E$$

$$\Rightarrow \quad \Omega(E) \propto V^N_{\frac{3N}{2}} (2mE)^{3N/2-1} \delta E \quad ; f = 3N$$

$$\Rightarrow \quad \Omega(E) = B \, V^N E^{3N/2}$$

$\uparrow$ is a constant independent of N, V.

Limit of an ideal gas

→ Evidently

$\Lambda(E)$ increases rapidly with E

⊛ Consider $N \approx$ Avagadros number

$$\Lambda(E) = B V^N E^{3N/2}$$

Generalisation

- Suppose the system has f degrees of freedom

→ Let $\phi_i(\varepsilon)$ be the number of ways in which the ith d.o.f $''$ can have energy $\leq \varepsilon$

→ $\Phi(E)$ be the number of ways in which the entire system can have energy $\leq E$

Density of states.

Then
$$\phi(E) \leq \phi_1(E/f) \, \phi_2(E/f) \cdots \phi_f(E/f)$$
where the RHS is the number of ways in which the total energy is less than or equal to E with each d.o.f having to satisfy the added constraint to have energy less than E/f.

→ Assume that $\phi_i(\varepsilon) = \phi_j(\varepsilon)$

Density of states

- $\phi(E) \leq \left[\phi_1 (E/f) \right]^f$

- We will assume

$$\phi(E) \approx \phi_1 (E/f)^f$$

$\Omega(E) =$ Number of states of System between
  E and $E + \delta E$

$$= \frac{d\phi(E)}{dE} \delta E = \delta E \, f \left[\frac{\partial \phi_1(\varepsilon)}{\partial \varepsilon} \Big|_{\varepsilon = E/f} \right] \frac{1}{f} \left[\phi_1 (E/f) \right]^{f-1}$$

$$= \left(\partial \phi_1(\varepsilon)/\partial \varepsilon \right)_{\varepsilon = E/f} \left[\phi_1 (E/f) \right]^{f-1} \delta E$$

Density of states

$$\Rightarrow \quad \Lambda(E) = \left.\frac{\partial \phi_1(\varepsilon)}{\partial \varepsilon}\right|_{\varepsilon = E/f} \phi_1(E/f)^{f-1} \, \delta E$$

$$= \left(\left.\frac{\partial \phi_1(\varepsilon)}{\partial \varepsilon}\right|_{\varepsilon = E/f} \delta E\right) \left[\phi_1\left(E/f\right)\right]^{f-1}$$

→ It is evident that a Small increase in ϕ_1 will lead to a large increase in Λ due to the large exponent $(f-1)$ in $\left[\phi_1(E/f)\right]^{f-1}$. (Note that $\partial \phi/\partial \varepsilon > 0$).

Density of states

$$\Rightarrow \ln \Lambda(E) = (f-1) \ln \Phi_1 + \ln\left[\frac{\partial \Phi_1}{\partial \varepsilon} \delta E\right]$$

$$\approx f \ln \Phi_1 \qquad \text{for } f \text{ large.}$$

If the energy E of the system
is not too close to the ground state
[in which case $\Phi_1(\varepsilon) \approx 1$ and
$\ln \Phi_1 \approx 0$].

$$\Rightarrow \qquad \Lambda(E) = \Phi_1^f \propto E^f$$

Density of states

→ Thus

$\Omega(E)$ is an EXTREMELY rapidly increasing function of energy.

Thermal Interaction

→ In describing a macroscopic system it is in general possible to specify macroscopically measurable independent parameters $x_1, x_2 \cdots x_n$ which are known to affect the equation of motion. (i.e. appear in the Hamiltonian)

→ Applied magnetic field, volume of a system

→ If a particular quantum state has energy E_r. then $E_r = E_r(x_1, x_2, \cdots x_n)$.

Macroscopic State

→ The macroscopic state or the macrostate is defined by specifying external parameters and any other constraints imposed on the system.

→ Corresponding to a macrostate, the system can be in any one of a very large number of microstates

Thermal Interaction

→ A and A' are two macroscopic Systems

→ $A^{(0)} = A \cup A'$ is isolated (closed) System.

→ Suppose all possible external parameters remain fixed; thus, the energy levels of the System A and System A' remain fixed. [External magnetic field of Spin 1/2 example]

Thermal Interaction

→ Every System A and A' that are prepared in accordance with the Specification will have energy transfer with different (A, A') elements having different energy transfer.

→ Mean Energies can be discussed.

→

Heat

→ The mean Energy transferred from one system to the other as a result of purely thermal interactions is called heat

→ The change $\overline{\Delta E}$ of the mean energy of System A is called the heat Q absorbed by the system.

$$Q = \overline{\Delta E}$$

Conservation

→ Since Energy of $A^{(0)}$ is conserved

$$\overline{\Delta E} + \overline{\Delta E'} = 0$$

$\overline{\Delta E'}$ is the mean change in energy of A'.

$$\therefore \quad Q + Q' = 0 \quad \text{or} \quad Q = -Q'$$

Thermal Equilibrium.

→ Suppose A had energy E_i initially
and A' had energy E_i'. Then

$$E + E' = E_i' + E_i = E^{(0)} = \text{constant}$$

as $A^{(0)}$ is closed.

→ In thermal equilibrium all accessible states
of the closed system are equally
likely.

Most probable configuration

→ Number of accessible states of A
If energy of A is between E and $E + \delta E$
= $\Lambda(E)$.

→ For each accessible state of A with
energy E, A' will have $\Lambda'(E')$ with
$E' = E^{(0)} - E$ accessible states

→ Total number of accessible states for
$A^{(0)} \propto \Lambda(E) \, \Lambda'(E')$

Most probable Configuration

⤳ As all $\underset{\wedge}{\text{accessible}}$ states are equally likely
the most probable energy configuration
is the one that has the most
number of accessible states which is
obtained by setting

$$\frac{\partial}{\partial E}\left[\mathcal{N}(E)\, \mathcal{N}'(E')\right) = \frac{\partial}{\partial E}\mathcal{N}(E)\,\mathcal{N}'(E-E') = 0$$

which has the same solution as

$$\frac{\partial}{\partial E}\left(\ln \mathcal{N}(E)\, \mathcal{N}(E^{(o)}-E')\right) = \frac{\partial}{\partial E}\ln \mathcal{N}(E) + \frac{\partial}{\partial E}\ln \mathcal{N}'(E') = 0$$

Most probable energy Configuration

$$\Rightarrow \quad \frac{\partial}{\partial E} \ln \mathcal{N}(E) - \frac{\partial}{\partial E'} \ln \mathcal{N}'(E') = 0$$

$$\Rightarrow \quad \boxed{\frac{\partial}{\partial E} \ln \mathcal{N}(E) = \frac{\partial}{\partial E'} \ln \mathcal{N}'(E')}$$

$\rightarrow$ Defining $\quad \sigma(E) = \ln \mathcal{N}(E)$

we have $\qquad \dfrac{\partial \sigma(E)}{\partial E} = \dfrac{\partial \sigma'(E')}{\partial E'}$

Most Probable Energy Configurations

$\rightarrow$ Let

$\beta = \dfrac{\partial \ln \nu}{\partial E}$ and

$\sigma - \ln \nu$.

$kT = 1/\beta \quad ; \quad \tau = 1/\beta.$

$S = k \ln \nu$

$\Rightarrow \quad \dfrac{1}{T} = k\beta = k \dfrac{\partial \ln \nu}{\partial E} = \dfrac{\partial S}{\partial E}$

Thus, the most probable energy configuration occurs when $S + S'$ is maximized or when $T = T'$.