

Partition function

$$\eta_i = g_i e^{-\beta(\epsilon_i - \mu)}$$

$$\text{or } \eta_i = e^{\beta\mu} (g_i e^{-\beta\epsilon_i})$$

$$N = e^{\beta\mu} \sum (g_i e^{-\beta\epsilon_i})$$

$$P_i(\epsilon_i) = \frac{\eta_i}{N} = \frac{g_i e^{-\beta\epsilon_i}}{\sum g_i e^{-\beta\epsilon_i}}$$

∴ Partition function is defined as:

$$Z = \sum_i g_i e^{-\beta\epsilon_i}$$

for a continuous energy distribution:

$$Z = \int_0^\infty D(\epsilon) e^{-\beta\epsilon} d\epsilon$$

For non-degenerate system:

$$Z = \sum_i e^{-\beta\epsilon_i}$$

$$\approx Z = \int_0^\infty e^{-\beta\epsilon} d\epsilon$$

Mean values

$$\bar{A} = \sum P_i A_i$$

Energy: $\bar{E} = \sum P_i \epsilon_i$

$$= \frac{\sum_i g_i e^{-\beta\epsilon_i} \epsilon_i}{Z} = \frac{1}{Z} \sum g_i \epsilon_i e^{-\beta\epsilon_i}$$

$$Z = g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2} + \dots$$

$$\frac{\partial Z}{\partial \beta} = -\epsilon_1 g_1 e^{-\beta\epsilon_1} + \dots$$

$$\therefore \bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$\boxed{\bar{E} = -\frac{\partial \ln Z}{\partial \beta}}$$

$$\bar{E}^2 = \frac{\sum g_i e^{-\beta\epsilon_i} \epsilon_i^2}{Z} = \frac{1}{Z} \sum g_i \epsilon_i^2 e^{-\beta\epsilon_i}$$

$$Z = g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2} + \dots$$

$$\frac{\partial Z}{\partial \beta} = -g_1 \epsilon_1 e^{-\beta\epsilon_1} + \dots$$

$$\frac{\partial^2 Z}{\partial \beta^2} = +g_1 \epsilon_1^2 e^{-\beta\epsilon_1} + \dots$$

$$\boxed{\bar{E}^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}}$$

Pressure:

$$\bar{p} = \sum P_i p_i$$

$$p = \left(\frac{\partial E}{\partial V} \right)_{T, N}$$

$$\bar{p} = \frac{1}{Z} \sum g_i e^{-\beta G_i} \left(-\frac{\partial G_i}{\partial V} \right)_{T, N} =$$

$$Z = g_1 e^{-\beta G_1} + g_2 e^{-\beta G_2} + \dots$$

$$\left(\frac{\partial Z}{\partial V} \right)_{T, N} = (g_1 e^{-\beta G_1}) \beta \left(\frac{\partial E}{\partial V} \right) + \dots$$

$$\text{or } \bar{p} = \frac{1}{\beta} \frac{1}{Z} \left(\frac{\partial Z}{\partial V} \right)$$

$$\text{or } \boxed{\bar{p} = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)_{T, N}}$$

Chemical potential

$$\bar{\mu} \equiv \left(\frac{\partial E}{\partial N} \right)_{T, V}$$

$$\therefore \boxed{\bar{\mu} = -\frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial N} \right)_{T, V}}$$

Entropy

In general, partition function is a function of T, V, N .

$$\text{i.e. } Z = Z(T, V, N)$$

$$d(\ln Z) = \left(\frac{\partial \ln Z}{\partial \beta} \right)_{V, N} d\beta + \left(\frac{\partial \ln Z}{\partial V} \right)_{T, N} dV + \left(\frac{\partial \ln Z}{\partial N} \right)_{T, V} dN$$

Also,

$$d(\ln Z) = -\bar{E} d\beta + \beta \bar{p} dV - \beta \bar{\mu} dN$$

$$\therefore d(\ln Z + \beta \bar{E}) = \beta [d\bar{E} + \bar{p} dV - \bar{\mu} dN] = \beta T ds$$

$$\therefore \text{or } ds = \frac{1}{\beta T} d(\ln Z + \beta \bar{E})$$

$$\text{or } ds = k_B \ln Z + \frac{\bar{E}}{T} + s_0$$

$$\therefore \boxed{S = k_B \ln Z + \frac{\bar{E}}{T}}$$

$$\text{or } \cancel{E} - T \bar{S} = \bar{E} - T S$$

Also,

$$\bar{E} - T S = \boxed{F = -k_B \ln Z}$$

$$\boxed{F = -k_B T \ln Z}$$

We have,

$$G = F + PV = U - TS + PV$$

$$dG = dF + PdV + VdP$$

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$$G = F + PV$$

$$\bar{P} = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)_{T, N}$$

$$= \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)$$



$$G = \frac{1}{\beta} \left[\ln Z - \left(\frac{\partial \ln Z}{\partial \ln V} \right)_{T, N} \right] \quad \text{Where } F = -k_B T \ln Z.$$

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$$H = U + PV$$

$$= \frac{1}{\beta} \left[\frac{\partial \ln Z}{\partial \beta} + V \left(\frac{\partial \ln Z}{\partial V} \right)_{T, N} \right]$$

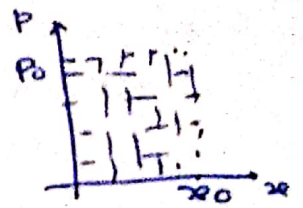
$$H = \frac{1}{\beta} \left[\frac{\partial \ln Z}{\partial \ln T} + \frac{\partial \ln Z}{\partial \ln V} \right]$$

Phase Space

- To specify dynamical configuration of any assembly of particles, we need 6 coordinates: x, y, z, p_x, p_y, p_z .
 - Canonical conjugate variables: measurement of Δx affects other
 - $\Delta x \Delta p_x \equiv$ given by Heisenberg uncertainty principle
 - f : degree of freedom $= 3$
 - \rightarrow Dimension of phase space $= 3 \times 2 = 6$
 - \rightarrow general 2f dimensions of phase space.
 - Volume element in phase space = cell = $\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z$
 - The two dimensional plane $(x, p_x) \rightarrow$ phase space.
 - The smallest volume element: $\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z$
 - $= \Delta x \Delta p_x \Delta y \Delta p_y \Delta z \Delta p_z$
 - $= h^3$
 - In general volume element in phase space: $(dx dy dz \dots d q) (dp_x dp_y dp_z \dots dp_f)$
- $$\text{volume element} = h^f$$
- In classical statistics: h can be any small const. It can be very small as no restriction on no. of cells \Rightarrow distinguishable.
 - In Q.S., h is Planck's constant \Rightarrow indistinguishable particles

In 2-D space, the no. of states is given by

$$\gamma = \frac{\text{Total area}}{\text{area of 1 small box}} = \frac{20 \times 10}{h^2}$$



Similarly, no. of states available in 6-dimensional phase space:

$$\gamma = \frac{\text{total 6-dim. volume}}{dx dy dz dx dy dz} = \frac{V_r V_p}{h^3}$$

or no. of states available in 6-D volume element $dx dy dz dx dy dz$ will be:

$$\text{No. of states} = \frac{dx dy dz dx dy dz}{h^3} = \frac{dx dy dz dx dy dz}{h^3}$$

Ex 11.3

(a) $\Delta x = 10^{-5} \text{ m}$, $p = -10^{-25} \text{ to } 10^{-25} \text{ kg m s}^{-1}$

$$\gamma = \frac{\Delta V}{h} = \frac{10^{-5} \times 2 \times 10^{-25}}{6.63 \times 10^{-34}} = 3000$$

(b) $r = 10^{-14} \text{ m}$, $p = 10^{-19} \text{ kg m s}^{-1}$

$$\gamma = \frac{(4/3 \pi r^3) \times (4/3 \pi p^3)}{h^3} = 600$$

Prob 11.4

(a) $\Delta x = 0.1 \text{ \AA}$, $v \leq 10^7 \text{ m/s}$

$$\therefore \gamma = \frac{0.1 \times 10^{-10} \times 9 \times 10^{-31} \times 10^7}{6.63 \times 10^{-34}}$$

(b) $\gamma = \frac{2 \times 10^{-6} \times (4 \times 10^{-3} \times 10^{-2})^3}{h^3} = \frac{128 \times 10^{-6-15}}{216 \times 10^{-42}}$

Total available states can be sum of all available states for the particles.

\therefore we have $\int \frac{dx dy dz dx dy dz}{h^3}$

If the interaction of particles with the neighbours can be ignored, the particles will have access to the entire volume of the phase space. If the system is confined to volume V and integration is carried out over all momenta directions (i.e. $d^3p = p^2 dp \sin \theta d\theta d\phi$; $\cos \theta = \mu$).

$$\iiint \frac{dx dy dz dx dy dz}{h^3} = \frac{V}{h^3} 4\pi \int p^2 dp$$

\therefore no. of cells within momenta p and $p+dp$: $\frac{4\pi V}{h^3} p^2 dp$
 or $g(p) dp = \frac{V}{h^3} 4\pi p^2 dp$

Similarly,

$g(v) dv$: no. of cells with velocity v and $v+dv$
 $\&$ $g(\epsilon) d\epsilon$: " " " " energy " ϵ and $\epsilon+d\epsilon$

$$\therefore E = \frac{p^2}{2m}$$

$$dp = \sqrt{\frac{m}{2E}} dE.$$

$$\therefore g(E) dE = \frac{4\pi V}{h^3} 2mE \sqrt{2m} \frac{1}{2} E^{-1/2} dE.$$

$$\boxed{g(E) dE = \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2} dE} \quad \text{--- (1)}$$

Density of states: no. of accessible states per unit energy. It is denoted by $D(E) = \left(\frac{dn(E)}{dE}\right)$.

\therefore Total no. of accessible states: $\int D(E) dE$.
 \rightarrow over entire range of available energies.

from eqn (1) " " " " = $\int g(E) dE$.

\therefore we can say that Dos is given by:

$$\boxed{D(E) = \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2} dE.}$$

We know that $g(p) dp = \frac{V}{h^3} 4\pi p^2 dp$.

In relativistic case, $E = \sqrt{p^2 c^2 + m_0^2 c^4}$.

$$E^2 = m_0^2 c^4 + p^2 c^2.$$

$$\boxed{p^2 = \frac{E^2}{c^2} - m_0^2 c^2}$$

for photons, $m_0 = 0$

$$\therefore p^2 = E^2/c^2$$

$$\therefore g(E) dE = \frac{0 V}{h^3} 4\pi \frac{E^2}{c^3} dE = \frac{4\pi V}{c^3 h^3} E^2 dE$$