PHYS 3014: Statistical Mechanics

Lecture Notes
Part 14

Grand Partition Function of Boltzmann Gas, Bose Gas and Fermi Gas

Dr. Ajai Kumar Gupta
Professor
Department of Physics
Mahatma Gandhi Central University
Motihari-845401, Bihar
E-mail: akgupta@mgcub.ac.in

Programme: B. Sc. Physics
Semester: VI

Grand Partition function of Boltzmann, Bose and Fermi gas

The grand partition function is

$$Z(T, V, \mu) = \sum_{r,s} \exp(-\alpha N_r - \beta E_s) \quad \text{--- (1)}$$

where N_r is the no. of particles of the state having energy E_s. If N_i is the number of particles in the energy state E_i of the system then

$$E_i = \sum_a n_{a,i} \epsilon_a$$
$$N_i = \sum_a n_{a,i} \quad \text{--- (2)}$$

where $n_{a,i}$ is the number of particles present in an energy level of energy ϵ_a.

The grand partition function of the system

$$Z(T, V, \mu) = \sum_i \exp \sum_a (\mu \beta n_{a,i} - n_{a,i} \epsilon_a) \quad \text{--- (3)}$$

$$Z(T,\mu,V) = \sum_i e^{\mu\beta N_i} \cdot \exp(-\beta E_i)$$

$$= \sum_i e^{-\mu\beta N_i} \sum_i \exp(-\beta E_i)$$

$$= \sum_i e^{\mu\beta N_i}\, Z(T,V,N_i)$$

$Z(T,V,N_i)$ = Canonical partition function of N_i particles.

$$Z(T,V,\mu) = \sum_i (e^{\mu\beta})^{N_i} \frac{1}{\lfloor N_i} Z(T,V,1)$$

$$= \exp\left[e^{\mu\beta} \cdot Z(T,V,1)\right]$$

$Z(T,V,1)$ = Single particle canonical partition function.

So we also have from eqn ③

$$Z = \sum_{n_1} \exp[\beta n_1(\mu-\epsilon_1)] \cdot \sum_{n_2} \exp[\beta n_2(\mu-\epsilon_2)] \cdots\cdots$$

The $\sum_n \exp n\beta(\mu-\epsilon_a) = \xi_a$ is called as partition function for single level ϵ_a.

For M-B gas, any number of particle can accomodate any energy level, and particles are distinguishable.

$$\mathcal{Z}(T,V,\mu) = \exp\left[e^{\mu\beta} z(T,V,1)\right]$$

$\therefore$ grand potential

$$\phi(T,V,\mu) = -kT \ln \mathcal{Z}(T,V,\mu)$$

$$= -kT \sum_i e^{-\beta(\epsilon_i-\mu)}$$

$$= \sum_i \phi_i$$

$\therefore$ average number of particles in an energy level ϵ_i is

$$\bar{n}_i = -\frac{\partial \phi_i}{\partial \mu} = +kT \frac{\partial}{\partial \mu}\left[e^{-\beta(\epsilon_i-\mu)}\right]$$

$$= kT \cdot \beta e^{-\beta(\epsilon_i-\mu)}$$

$\therefore$ $\bar{n}_i = e^{-\beta(\epsilon_i-\mu)}$ M-B Statistics.

For Bose-Gas,

particles are indistinguishable and any number of particle can accomodate any energy state. configuration set $\{n_1, n_2, \cdots\}$ is specifying the states of the gas. So we have to consider all possible number of particles in each single particle state i.e

$n_r = 0, 1, 2, 3, \cdots$, for each r.

The grand partition function of Bose gas is

$$\mathcal{Z}(T, V, \mu) = \left[\sum_{n_1} \exp \beta n_1 (\mu - \epsilon_1)\right] \cdot \left[\sum_{n_2} \exp \beta n_2 (\mu - \epsilon_2)\right] \cdots$$

$$= \left(\sum_{n_1=0}^{\infty} e^{\beta n_1 (\mu - \epsilon_1)}\right)\left(\sum_{n_2=0}^{\infty} e^{\beta n_2 (\mu - \epsilon_2)}\right) \cdots$$

$$= \left(\frac{1}{1 - e^{\beta(\mu - \epsilon_1)}}\right)\left(\frac{1}{1 - e^{\beta(\mu - \epsilon_2)}}\right) \cdots$$

$$= \prod_r \left\{\frac{1}{1 - e^{\beta(\mu - \epsilon_r)}}\right\}$$

$\therefore \ln \mathcal{Z}(T,V,\mu) = -\sum_r \ln\{1-e^{\beta(\mu-\epsilon_r)}\}$

The grand potential of the system

$$\phi(T,V,\mu) = -KT\ln \mathcal{Z}(T,V,\mu)$$

$$= KT\sum_r \ln\{1-e^{\beta(\mu-\epsilon_r)}\}$$

$$= \sum_r \phi_r$$

ϕ_r is the grand potential for r^{th} state.

$\therefore$ average number of particles in energy state of energy ϵ_i is

$$\bar{n}_i = -\frac{\partial \phi_i}{\partial \mu} = -KT\frac{\partial}{\partial \mu}\ln\{1-e^{\beta(\mu-\epsilon_i)}\}$$

$$= -KT \cdot \frac{1}{1-e^{\beta(\mu-\epsilon_i)}} \cdot \{-e^{\beta(\mu-\epsilon_i)}\} \cdot \beta.$$

$$\therefore \quad \bar{n}_i = \frac{1}{e^{\beta(\epsilon_i-\mu)}-1} \qquad \text{B-E statistics.}$$

For Fermi gas,
particles are indistinguishable and any energy state can accomodate only one particle. Configuration set $\{n_1, n_2, \cdots\}$ is specifying the state of the gas. So we have to consider all possible number of particles in each single state i.e $n_r = 0, 1$ for each r.

Grand partition function

$$\mathcal{Z}(T,V,\mu) = \left(\sum_{n_1=0}^{1} e^{\beta n_1(\mu-\epsilon_1)}\right)\left(\sum_{n_2=0}^{1} e^{\beta n_2(\mu-\epsilon_2)}\right) \cdots$$

$$= \left[1+e^{\beta(\mu-\epsilon_1)}\right]\cdot\left[1+e^{\beta(\mu-\epsilon_2)}\right]\cdots$$

$$= \prod_r \left[1+e^{\beta(\mu-\epsilon_r)}\right]$$

$$\therefore \ln \mathcal{Z}(T,V,\mu) = \sum_r \ln\left\{1+e^{\beta(\mu-\epsilon_r)}\right\}$$

$\therefore$ grand potential of the system

$$\phi(T,V,\mu) = -KT \ln Z(T,V,\mu)$$

$$= -KT \sum_r \ln\{1+e^{\beta(\mu-\epsilon_r)}\}$$

$$= \sum_r \phi_r$$

where $\phi_r = -KT \ln\{1+e^{\beta(\mu-\epsilon_r)}\}$ is the grand potential of rth quantum state.

$\therefore$ average number of particles in ith quantum state is

$$\bar{n}_i = -\frac{\partial \phi_i}{\partial \mu} = KT \frac{\partial}{\partial \mu} \ln\{1+e^{\beta(\mu-\epsilon_i)}\}$$

$$= KT \cdot \frac{1}{1+e^{\beta(\mu-\epsilon_i)}} \cdot \beta \cdot e^{\beta(\mu-\epsilon_i)}$$

$$\therefore \quad \bar{n}_i = \frac{1}{e^{\beta(\epsilon_i-\mu)}+1} \qquad \text{F-D statistics.}$$

Single Particle density of states

For obtaining thermodynamic and statistical quantities, summation over many states is taken. For large volume, the sum over all one particle states can be rewritten in terms of integral

i.e. $\sum_{k} \longrightarrow \int g(\epsilon)\,d\epsilon$

$g(\epsilon)$ is called as one particle density of states. $g(\epsilon)\,d\epsilon$ is the density of states lying between energy ϵ and $\epsilon + d\epsilon$.

In consistent with the wave-particle duality, if a particle is confined in one dimensional box of length L, then the wave function associated with the particle must vanishes at the wall of the box. In three dimension, it must vanishes at the faces of the cube. This condition leads to the formation of standing waves in the box. The condition for a standing wave in one dimension is

$$\lambda = \frac{2L}{n}, \quad n = 1, 2, 3, \cdots \text{ etc.}$$

λ is the wavelength associated with particle.

wave vector $K = \frac{2\pi}{\lambda}$

So the condition is

$$K = \frac{n\pi}{L}$$

In 3-dimension, the condition will be

$$K = (n_x, n_y, n_z)\frac{\pi}{L}, \quad n_x, n_y, n_z \text{ are +ive integers}$$

Each combination of permissible n_x, n_y, n_z will represent a state. In number space, defined by n_x, n_y, n_z, the volume of a single state is unity. So the number of permissible states in the number space will be that contained in the positive octant of a sphere of radius n. where $n^2 = n_x^2 + n_y^2 + n_z^2$.

In K-space, the number of states with wave-vector smaller than or equal to K is

$$\Gamma(K) = \frac{1}{8} \cdot \frac{\frac{4}{3}\pi K^3}{\left(\frac{\pi}{L}\right)^3}$$

or the number of states with wave vector lying between K and K+dK will be

$$g(k)\,dk = \Gamma(k+dk) - \Gamma(k)$$

$$= \frac{d\Gamma(k)}{dk}\,dk$$

$$= \frac{L^3}{2\pi^2}\,k^2\,dk$$

$$= \frac{V}{2\pi^2}\,k^2\,dk \qquad \because V = L^3$$

$$\because\ \epsilon = \frac{\hbar^2 k^2}{2m}$$

or

$$\sqrt{\frac{2m}{\hbar^2}}\,\epsilon^{1/2} = k \Rightarrow dk = \sqrt{\frac{2m}{\hbar^2}}\cdot\frac{1}{2}\,\epsilon^{-1/2}\,d\epsilon$$

or

$$g(k)\,dk = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}\,\frac{1}{2}\,d\epsilon$$

$$= \frac{2\pi V}{h^3}\,(2m)^{3/2}\,\epsilon^{1/2}\,d\epsilon$$

$$= g(\epsilon)\,d\epsilon$$

$$g(\epsilon) = \frac{d\Gamma}{d\epsilon} = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2}$$

is one particle density of states.

References:

- Statistical Mechanics by R. K. Pathria
- Statistical Mechanics by B. K. Agarwal and M. Eisner
- An Introductory Course of Statistical Mechanics by P. B. Pal
- Elementary Statistical Physics by C. Kittel
- Fundamentals of Statistical and Thermal Physics by F. Reif
- Statistical and Thermal Physics by R. S. Gambhir and S. Lokanathan

Thank You

For any questions/doubts/suggestions and submission of assignments

Write at E-mail: akgupta@mgcub.ac.in