PHYS4006: Thermal and Statistical Physics

Lecture Notes
Part – 1 (Unit-III & IV)

Classical and Quantum Statistics: MB, BE & FD Statistics

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So far, we have dealt with the laws of thermodynamics (including Thermodynamic potentials, Phase transitions, Carnot’s cycle, Properties of He I and He II etc.) and basic postulates of Statistical Mechanics (highlighting concept of phase space, Microstates & macrostates, Ensemble theory, Boltzmann entropy relation).

Before the advent of quantum mechanics, Maxwell, Boltzmann, Gibbs etc, applied statistical methods with the help of classical physics. These methods are collectively known as Classical statistics or **Maxwell-Boltzmann (MB) Statistics**.

These statistics were successful in explaining pressure, temperature etc. of gaseous systems but couldn’t explain some experimental results like the energy distribution in case of black-body radiation, specific heat at low temperature etc.

Such phenomena were successfully explained by S.N. Bose, Albert Einstein, Enrico Fermi, P.A. Dirac where they had made use of some new statistics with the help of newly discovered quantum theories.

These new statistics are known as Quantum Statistics and can be divided as:

i. **Bose-Einstein (BE) statistics**
ii. **Fermi-Dirac (FD) statistics**

Maxwell-Boltzmann (MB) Statistics

The basic postulates associated with the MB statistics are-

- **The particles of the system are *identical* and *distinguishable*.**
- **The phase space can be divided into a very large number of cells.**
- **There is no restriction on the number of particles which can occupy a single phase cell.**
- **The available volume of the phase space cell can be very small and may even approach zero.**
- **The total number of particles in the system remains constant.**
- **The total energy of the system remains constant.**

Let us consider a system composed of n distinguishable, non-interacting particles. Out of these n particles, n_1, n_2,…...n_i…..n_k represent number of molecules in the energy levels ε_1, ε_2…. ε_i….. ε_k, respectively corresponding to g_1, g_2…..g_i……g_k cells. The thermodynamic probability for the macrostate (n_1, n_2,…...n_i…..n_k) according to classical statistics is given by -

$$W_{(n_1, n_2, \ldots\ldots n_k)} = \frac{n! \left(g_1\right)^{n_1} \left(g_2\right)^{n_2} \ldots\ldots \left(g_i\right)^{n_i} \ldots\ldots\ldots \left(g_k\right)^{n_k}}{n_1! n_2! \ldots\ldots n_i! \ldots\ldots n_k!}$$

$$W_{(n_1, n_2, \ldots\ldots n_k)} = n! \prod_{i=1}^{k} \frac{\left(g_i\right)^{n_i}}{n_i!}$$

Taking natural logarithm and applying Stirling’s approx. ln(x!)=xln(x)-x, we get,

$$\ln(W) = n \ln n + \sum_{i=1}^{k} n_i \ln g_i - \sum_{i=1}^{k} n_i \ln n_i$$

For the most probable state : $d(\ln(W)) = 0$

$$d(\ln(W)) = \sum_{i=1}^{k} \ln\left(\frac{g_i}{n_i}\right) dn_i = 0$$

We have the constraints:

$$\sum_{i=1}^{k} n_i = N = \text{constant} \quad \sum_{i=1}^{k} n_i\varepsilon_i = U = \text{constant}$$

Differentiating $$\sum_{i=1}^{k} dn_i = 0 \quad \sum_{i=1}^{k} \varepsilon_i dn_i = 0$$

Using the method of Lagrange’s undetermined multipliers and after solving, we get

$$\sum_{i=1}^{k} \left\{ \ln\left(\frac{g_i}{n_i}\right) - \alpha - \beta\varepsilon_i \right\} dn_i = 0$$

This equation holds only if,

$$\ln\left(\frac{g_i}{n_i}\right)-\alpha-\beta\varepsilon_i=0$$

Now, the Maxwell-Boltzmann distribution function is given by,

$$n_i=g_i e^{-\alpha}e^{-\beta\varepsilon_i}\qquad (i=1,2,3,.....k)$$

This equation gives the number of gas molecules in the ith cell and known as Maxwell-Boltzmann law of energy distribution.

simply, $$N=\sum_i n_i=\sum_i\left(g_i e^{-\alpha}e^{-\beta\varepsilon_i}\right)=e^{-\alpha}\sum_i g_i e^{-\beta\varepsilon_i}=A.Z$$

where, $A=e^{-\alpha}$ *and* $Z=\sum_i g_i e^{-\beta\varepsilon_i}$

Occupation index, $$\boxed{f_i=\frac{n_i}{g_i}=\frac{N}{Z}e^{-\beta\varepsilon_i}}$$

This Boltzmann distribution applies to systems which have **distinguishable** particles and N, V and U are fixed. The Maxwell-Boltzmann Distribution is applicable only to dilute gases.

$$A = \frac{N}{Z} \Rightarrow n_i = \frac{N g_i e^{-\beta \varepsilon_i}}{\sum_i g_i e^{-\beta \varepsilon_i}}$$

$$\mathrm{Pr}obability, P(\varepsilon_i) = \frac{n_i}{N} = \frac{g_i e^{-\beta \varepsilon_i}}{\sum_i g_i e^{-\beta \varepsilon_i}}$$

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

The quantity Z represents the sum of the Boltzmann factor $Z = e^{-\beta \varepsilon_i} = e^{-\varepsilon_i / kT}$ Over all the accessible states and is called the **partition function** *(derived from German term Zustandssummae)*. The quantity Z indicates how the gas molecules of an assembly are distributed or partitioned among the various energy levels. The distribution function proportional to the Boltzmann factor is known as the *canonical distribution*.

Evaluation of Constants: g, α and β

- To evaluate g_i, let us imagine a very small interval of energy lying between ε and (ε+dε). If n(ε) denotes the number of molecules lying in the energy interval (ε-1/2) and (ε+1/2), then

$$n(\varepsilon) = g(\varepsilon)e^{-\alpha}e^{-\beta\varepsilon}$$

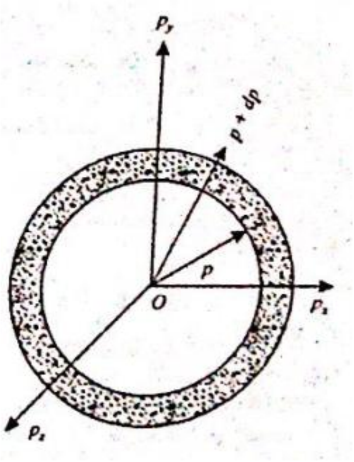
where $g(\varepsilon)$ gives the number of cells in the phase space corresponding to unit energy interval.

Now,

$$n(p) = g(p)e^{-\alpha}e^{-\beta p^2/2m}$$

where $\varepsilon = p^2/2m$ and $n(p)$ gives the number of molecules in unit momentum interval between (p-1/2) and (p+1/2).

Number of molecules in the momentum interval p and (p+dp) is given by



$$n(p)dp = g(p)e^{-\alpha}e^{-\beta p^2/2m}dp$$

Now,

$$g(p)dp = \frac{volume\ in\ phase\ space\ corresponding\ to\ momentum\ interval\ p\ and\ (p+dp)}{h^3}$$

$$g(p)dp = \frac{\iiint dxdydz \iiint dp_x dp_y dp_z}{h^3}$$

$$g(p)dp = \frac{V}{h^3}\iiint dp_x dp_y dp_z$$

After substitution, we get

$$n(p)dp = \frac{4\pi V p^2}{h^3}e^{-\alpha}e^{-\beta p^2/2m}dp$$

Evaluation of α

Let p_{max} be the maximum value of momentum that any molecule can have

$$n = \int_0^{p_{max}} n(p)\, dp = \frac{4\pi V}{h^3} e^{-\alpha} \int_0^{\infty} p^2\, e^{\frac{-\beta p^2}{2m}}\, dp$$

After integration, we get $$e^{-\alpha} = \frac{nh^3}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2}$$

Finally, we get $$n(p)dp = 4\pi n\left(\frac{\beta}{2\pi m}\right)^{3/2} p^2\, e^{-\frac{\beta p^2}{2m}} dp$$

Evaluation of β

Since, $n(p)dp = 4\pi n\left(\frac{\beta}{2\pi m}\right)^{3/2} p^2 e^{-\frac{\beta p^2}{2m}} dp$

In terms of energy,

$$n(\varepsilon)\,d\varepsilon = 4\pi n\left(\frac{\beta}{2\pi m}\right)^{3/2}(2m\varepsilon)\,e^{-\beta\varepsilon}\left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon = \frac{2n}{\sqrt{\pi}}\beta^{3/2}\varepsilon^{1/2}e^{-\beta\varepsilon}d\varepsilon$$

This relation gives the number of molecules lying in the energy interval ε and (ε+d ε) in terms of β.

So, total energy of these molecules = ε n(ε) dε

Hence, total energy of the system consisting of all the molecules,

$$U = \int_0^\infty \varepsilon\, n(\varepsilon)\,d\varepsilon = \frac{2n}{\sqrt{\pi}}\beta^{3/2}\int_0^\infty \varepsilon^{3/2}e^{-\beta\varepsilon}d\varepsilon = \frac{3n}{2\beta}$$

For an ideal gas, each molecule possesses an average K.E. = 3/2kT, where k is Boltzmann’s constant.

Therefore, total energy of n molecules = 3/2nkT

$$U = \frac{3n}{2\beta} = \frac{3}{2}kT \quad or \quad \beta = \frac{1}{kT}$$

1. **Maxwell-Boltzmann’s law of distribution of energies:**

$$n(\varepsilon)\,d\varepsilon = \frac{2n}{\sqrt{\pi}}\left(\frac{1}{kT}\right)^{3/2}\varepsilon^{1/2}e^{\frac{-\varepsilon}{kT}}\,d\varepsilon$$

2. Maxwell-Boltzmann's law of distribution of momentum:

$$n(p)\,dp = 4\pi n\left(\frac{1}{2\pi mkT}\right)^{3/2} p^2 e^{\frac{-p^2}{2mkT}}\,dp$$

3. Maxwell-Boltzmann's law of distribution of speeds:

Put p = mv

$$n(v)\,dv = 4\pi n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{\frac{-mv^2}{2kT}}\,v^2 dv$$

The most probable speed v_{mp} of a particle is that value of the speed v for which the number of particles with speed between v and (v+dv) is a maximum,

$$\frac{dn(v)}{dv} = 0$$

which gives,

$$v_{mp} = \sqrt{\frac{2kT}{m}}$$

Root mean square (rms) speed of a system of particles is that speed whose square is the average of the squares of the speeds of the particles.

$$v^2{}_{rms} = \frac{\int_0^\infty v^2\, n(v)dv}{\int_0^\infty n(v)dv} = \frac{3kT}{m} \quad \Rightarrow \quad v_{rms} = \sqrt{\frac{3kT}{m}}$$

The average thermal speed of a particle is-

$$\bar{v} = \frac{\int_0^\infty v\, n(v)dv}{\int_0^\infty n(v)dv} = \sqrt{\frac{8kT}{m\pi}}$$

Thus,

$$\Rightarrow \quad v_{rms} \rangle \bar{v} \rangle v_{mp}$$

References: Further Readings

1. *Statistical Mechanics* by R.K. Pathria

2. *Statistical Mechanics* by K. Huang

3. *Statistical Mechanics* by B.K. Agrawal and M. Eisner

4. *Thermal Physics (Kinetic theory, Thermodynamics and Statistical Mechanics)* by S.C. Garg, R.M. Bansal and C.K. Ghosh

5. *Heat, Thermodynamics and Statistical Physics* by C.L. Arora

Assignment

1) Use statistical definition of entropy to show that the difference in entropy between a state of volume V_i and a state of volume V_f (temperature and number of molecules remains constant) is equal to nR $\log(V_f/V_i)$.

2) Consider a system of N paramagnetic atoms each having magnetic moments M, are placed in magnetic field (B). N atoms are aligned parallel to B and (N-n) atoms are aligned anti-parallel to B. Then, find (i) internal energy of the system, (ii) entropy of the system and (iii) thermodynamic temperature of the system.

3) An electron gas obeys the M-B statistics. Calculate the average thermal energy (in eV) of an electron in the system at room temperature (300 K).

4) Six distinguishable particles are distributed over three non-degenerate levels of energies 0, ε and 2ε. Calculate the total number of microstates of the system. Find the total energy of the distribution for which the probability is a maximum.

5) Calculate the fraction of oxygen molecules within 1% of the most probable velocity at N.T.P. What is the effect of changing (i) the gas to hydrogen & (ii) the temperature to 500ºC?

6) A system can take only three different energy states $\varepsilon_1=0$, $\varepsilon_2=1.38\times10^{-21}$ joule and $\varepsilon_3=2.76\times10^{-21}$ joule. These states occur in 2, 5, 4 different ways, respectively. Deduce the probability that at temperature 100 K, the system may be (i) in one of the microstates of energy, ε_3 and (ii) in ground state ε_1. ($k=1.38\times10^{-23}$ joule/K).

Thank You

For any questions/doubts/suggestions and submission of assignment
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