Method of Ensembles: Partition Functions

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▪In earlier lectures, we have discussed the concept of Ensembles viz. Microcanonical, Canonical and Grand-canonical.

▪Herein, we will use that concept in deriving the thermodynamical functions of a thermodynamic system.

▪Before we proceed, let us recall the concept of partition function .

The Maxwell-Boltzmann distribution function is given by,

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

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

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

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

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.

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

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

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

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

The quantity Z represents the sum of the Boltzmann factor $\qquad Z = e^{-\beta \varepsilon_i} = e^{-\varepsilon_i / kT}$
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 energy term in the expression for partition function does not mean only the translational component but also may contain the components corresponding to other degrees of freedom too e.g. rotational, vibrational and electronic too.

- This partition function can be used for calculating the various thermodynamical properties of ensembles having independent systems (obeying classical laws) irrespective of whether the ensembles have distinguishable or indistinguishable independent systems.

- Consider an assembly of classical gas where the distribution of energy states is considered to be continuous. So, the number of energy levels in the momentum range p and (p+dp) is given by -

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

Number of energy levels between energy range ε and (ε+dε) is given by –

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

Since, the distribution of energy states is continuous, therefore

$$Z = \sum_i g_i e^{-\varepsilon_i/kT} = \int_0^\infty g(\varepsilon)\, d\varepsilon\, e^{-\varepsilon/kT}$$

$$Z = \frac{2\pi V (2m)^{3/2}}{h^3} \int_0^\infty \varepsilon^{1/2}\, e^{-\varepsilon/kT}\, d\varepsilon$$

After solving, we get

$$Z = \frac{2\pi V (2m)^{3/2}}{h^3} \frac{\sqrt{\pi}}{2} (kT)^{3/2}$$

$$\boxed{Z = \frac{V}{h^3} (2\pi m k T)^{3/2}}$$

This gives the **translational partition function** for a gas molecule.

Partition Function and its relation Thermodynamic Quantities

1. with Entropy (S):

Consider an assembly of ideal gas molecules obeying M-B distribution law and according to Boltzmann's entropy relation –

$$S = k \ln W = k \ln \Omega \quad ....(i)$$

The maximum thermodynamic probability is given by -

$$W = N! \prod_i \frac{g_i^{n_i}}{n_i!} \quad ....(ii)$$

Taking logarithms and apply Stirling's approximation, we get

$$\ln W = N \ln N + \sum_i \left(n_i \ln g_i - n_i \ln n_i \right) \quad ....(iii)$$

According to M-B distribution law

$$n_i = g_i e^{-\alpha} e^{-\beta \varepsilon_i} = g_i A e^{-\beta \varepsilon_i}$$

Now, from eqn. (iii)

$$\ln W = N \ln N + \sum_i n_i \ln g_i - \sum_i n_i \ln g_i - \sum_i n_i \ln A + \sum_i n_i \beta \varepsilon_i$$

Putting,

$$\sum_i n_i = N \quad and \quad \sum_i n_i \varepsilon_i = E$$

$$\ln W = N \ln N - N \ln A + \beta E = N \ln \frac{N}{A} + \beta E$$

$$\ln W = N \ln Z + \beta E$$

$$\because \quad S = k \ln W = k\left(N \ln Z + \beta E\right) = Nk \ln Z + \frac{kE}{kT}$$

$$S = Nk \ln Z + \frac{E}{T} \quad ....(iv)$$

but for an ideal gas, $\qquad E = \frac{3}{2} NkT \quad ....(v)$

from (iv) and (v),

$$\boxed{S = Nk \ln Z + \frac{3}{2} Nk} \quad ....(vi)$$

2. with Helmholtz Free Energy (F):

$$\because \quad F = E - TS = E - T\left(Nk \ln Z + \frac{E}{T} \right)$$

$$\boxed{F = -NkT \ln Z} \quad ....(vii)$$

3. with Total Energy (E):

Average energy of a system of N particles is given by,

$$\overline{E} = \frac{E}{N} = \frac{\sum_i n_i \varepsilon_i}{\sum_i n_i} = \frac{\sum_i g_i A \varepsilon_i e^{-\beta \varepsilon_i}}{\sum_i g_i A_i e^{-\beta \varepsilon_i}}$$

$$\overline{E} = \frac{\sum_i g_i \varepsilon_i e^{-\beta \varepsilon_i}}{Z} \quad ....(viii)$$

Since, partition function

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

For isothermal-isochoric transformation,

$$\left(\frac{\partial Z}{\partial T} \right)_V = \frac{1}{kT^2} \sum_i g_i \varepsilon_i e^{-\varepsilon_i / kT}$$

$$kT^2 \left(\frac{\partial Z}{\partial T} \right)_V = \sum_i g_i \varepsilon_i e^{-\varepsilon_i / kT} = Z\overline{E} \Rightarrow \quad \overline{E} = \frac{kT^2}{Z} \left(\frac{\partial Z}{\partial T} \right)_V$$

Total energy,

$$E = N\overline{E} \Rightarrow \quad \boxed{E = \frac{NkT^2}{Z} \left(\frac{\partial Z}{\partial T} \right)_V = NkT^2 \left[\frac{\partial}{\partial T} (\log Z) \right]_V} \quad ....(ix)$$

4. with Enthalpy (H):

Enthalpy is given by,

$$H = E + PV = E + RT \qquad \text{(for an ideal gas, PV=RT)}$$

$$H = NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + RT \quad ....(x)$$

5. with Gibb's Potential (G):

$$\because \quad G = H - TS = NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + RT - TS$$

putting the value of S from eq^n. (iv) in above, we get

$$G = NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + RT - T\left(Nk\ln Z + \frac{E}{T}\right)$$

$$G = NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + RT - NkT\ln Z - E$$

putting the value of E from eqⁿ. (ix), we get

$$G = NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + RT - NkT\ln Z - NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V$$

$$\boxed{G = RT - NkT\ln Z} \quad ....(xi)$$

6. with Pressure (P) of the gas:

$$\therefore \quad \boxed{P = -\left(\frac{\partial F}{\partial V}\right)_V = NkT\left[\frac{\partial}{\partial V}(\log Z)\right]_V} \quad ....(xii)$$

7. with Specific heat at constant volume, (C_V):

$$\therefore \quad C_V = \left(\frac{\partial E}{\partial T}\right)_v = \frac{\partial}{\partial T}\left[NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V\right]$$

$$\boxed{C_V = Nk\left[2T\frac{\partial}{\partial T}(\log Z) + T^2\frac{\partial^2}{\partial T^2}(\log Z)\right]_V} \quad ....(xiii)$$

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. *Statistical Mechanics* by Satya Prakash

Thank You

**For any questions/doubts/suggestions and submission of assignment
write at E-mail: neelabh@mgcub.ac.in**