PHYS4006: Thermal and Statistical Physics

Lecture Notes
Part - 3 (Unit - IV)

Diatomic Molecules: Partition Functions

Dr. Neelabh Srivastava
(Assistant Professor)
Department of Physics
Mahatma Gandhi Central University
Motihari-845401, Bihar
E-mail: neelabh@mgcub.ac.in

Programme: M.Sc. Physics
Semester: 2nd

Partition Function of a Diatomic Molecule

- Consider a diatomic molecule inside a box at temperature T, so the energy of the of ith microstate of this molecule can be expressed as –

$$\varepsilon_i = \varepsilon_{tr} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_e + \varepsilon_n \quad ....(i)$$

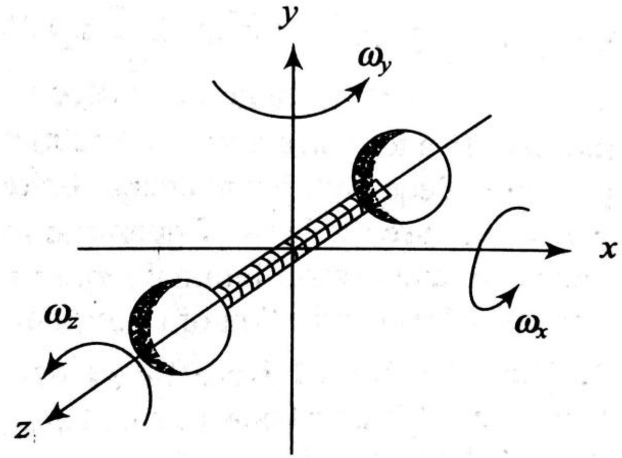

Figure: Diatomic molecule having identical atoms

where ε_{tr} is the translational energy of the centre of mass of the molecule, ε_{rot} is the energy associated with the rotation of the constituent atoms in the molecule about the centre of mass, ε_{vib} is the energy associated with the vibrations of the two atoms along the line joining them, ε_e is the energy of atomic electrons and ε_n is the energy of the atomic nucleus.

So, the partition function of a single diatomic molecule can be written as –

$$Z_D = \sum_{(states)} e^{-\beta\varepsilon_i} \quad ....(ii)$$

from (i),

$$Z_D = \sum_{(states)} \left(e^{-\beta\varepsilon_{tr}}\right)\left(e^{-\beta\varepsilon_{rot}}\right)\left(e^{-\beta\varepsilon_{vib}}\right)\left(e^{-\beta\varepsilon_{e}}\right)\left(e^{-\beta\varepsilon_{n}}\right)$$

$$Z_D = Z_{tr} Z_{rot} Z_{vib} Z_e Z_n \quad ....(iii)$$

where Z_{tr}, Z_{rot}, Z_{vib}, Z_e and Z_n denote the translational, rotational, vibrational, electronic and nuclear partition functions respectively.

Consider a gas consisting of N molecules and each particle is free to move throughout the volume. For a perfect gas, as the particles are indistinguishable, partition function is-

$$Z_D = \frac{Z^N}{N!}$$

where Z is single particle partition function.

Translational Motion: Consider a single diatomic molecule. It will have three translational degrees of freedom. Consider a molecule of mass m enclosed in a rectangular box of sides a, b and c with volume abc. The translational energy is –

$$\varepsilon_i = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \quad \text{........}(iv)$$

Therefore, one particle translational partition function is -

$$Z = \sum_{n_x=1}^{\infty} \exp\left(\frac{-h^2 n_x^2}{8ma^2kT}\right) \sum_{n_y=1}^{\infty} \exp\left(\frac{-h^2 n_y^2}{8mb^2kT}\right) \sum_{n_z=1}^{\infty} \exp\left(\frac{-h^2 n_z^2}{8mc^2kT}\right) \quad \text{........}(v)$$

After solving, we get the *translational partition function*

$$Z = \frac{(2\pi mkT)^{3/2}}{h^3} abc = \frac{V}{h^3}(2\pi mkT)^{3/2} \quad \text{........}(vi)$$

So, partition function for a gas of N diatomic molecules is –

$$Z_{tr} = \frac{V^N}{h^{3N} N!} \left(2\pi mkT\right)^{3N/2} \quad \text{........}(vii)$$

Total translational energy of N diatomic molecules is

$$E_{tr} = kT^2 \frac{\partial \ln Z_{tr}}{\partial T} = \frac{3}{2} NkT$$

Rotational Motion: The energy level of a diatomic molecule according to a rigid rotator model is given by,

$$\varepsilon_{rot} = \frac{J(J+1)h^2}{8\pi^2 I} \quad , J = 0, 1, 2.......$$

where I is moment of inertia and J is rotational quantum number. The rotational partition function is

$$Z_{rot} = \sum_J g_{rot} \exp\left(\frac{-J(J+1)h^2}{8\pi^2 IkT}\right)$$

Rotational levels are degenerate and this degeneracy arises due to space quantization of angular momentum. There are (2J+1) allowed orientations. So, $g_{rot} = (2J+1)$

$$Z_{rot} = \sum_J (2J+1)\exp\left(\frac{-J(J+1)h^2}{8\pi^2 IkT}\right) = \sum_J (2J+1)\exp\left(\frac{-J(J+1)\theta_{rot}}{T}\right) \quad ....(viii)$$

Where $\theta_{rot} = \dfrac{h^2}{8\pi^2 Ik}$ is the rotational temperature.

<u>Case I: High temperature limit</u>: When T >> θ_{rot}

$$Z_{rot} = \int_0^\infty (2J+1)\exp\left(\frac{-J(J+1)\theta_{rot}}{T}\right) dJ$$

After solving, we get $Z_{rot} = \dfrac{T}{\theta_{rot}} = \dfrac{8\pi^2 IkT}{h^2}$

For a gas of N diatomic molecules,

$$Z_{rot} = \left(\frac{8\pi^2 IkT}{h^2}\right)^N$$

The **mean energy** of the gas will be

$$E_{rot} = kT^2 \frac{\partial \ln Z_{rot}}{\partial T} = NkT$$

Contribution to **entropy** due to rotational motion of N diatomic molecules is -

$$S_{rot} = Nk \ln \frac{8\pi^2 IkT}{h^2} + Nk$$

Contribution to **specific heat** due to rotational motion of N diatomic molecules is –

$$\left(C_V\right)_{rot} = \left(\frac{\partial E_{rot}}{\partial T}\right)_{rot} = Nk = R$$

The **Helmholtz free energy** due to rotational motion of N diatomic molecules is –

$$F_{rot} = E_{rot} - TS_{rot} = -NkT \ln \frac{8\pi^2 IkT}{h^2}$$

Case II: Low temperature limit: When $T << \theta_{rot}$

Rotational partition function can be written as –

$$Z_{rot} = 1 + 3e^{-2\theta_{rot}/T} + 5e^{-6\theta_{rot}/T} + ...$$

At low temperatures, thermal energy (kT) of the system is not sufficient enough to take the molecules to higher rotational levels.

- → ***Rotational motion disappears at low temperatures.***
- The rotational partition function for homo-nuclear diatomic molecule is one half of the rotational partition function for hetero-nuclear diatomic molecules. This difference is generally expressed in terms of **symmetry number, σ**. *It specifies the number of indistinguishable orientations that a molecule have*.
- For a homo-nuclear diatomic molecule, σ=2 whereas for hetero-nuclear diatomic molecule, σ=1. Accordingly, we divide the rotational partition function by σ.

Vibrational Motion: A diatomic molecule has only one degree of freedom corresponding to the vibrational motion of the nuclei along the axis joining them.

Vibrational motion of atoms bound in a molecule can be taken to be nearly simple harmonic. The energy level of a linear simple harmonic oscillator are non-degenerate and vibrational energy of a diatomic molecule is given by –

$$\varepsilon_{vib} = \left(n + \frac{1}{2}\right) h\nu \quad , n = 0, 1, 2 \ldots\ldots$$

So, the vibrational partition function can be written as –

$$Z_{vib} = \sum_{n=0}^{\infty} \exp\left[-\left(n + \frac{1}{2}\right)\frac{h\nu}{kT}\right]$$

$$Z_{vib} = \exp\left(\frac{-h\nu}{2kT}\right)\sum_{n=0}^{\infty} \exp\left(\frac{-nh\nu}{kT}\right)$$

After further simplification and neglecting higher order terms, we get

$$Z_{vib} = \frac{\exp\left(\frac{-h\nu}{2kT}\right)}{1-\exp\left(\frac{-h\nu}{kT}\right)} \quad ....(ix)$$

Vibrational energy: The vibrational energy of a gas of N diatomic molecules is –

$$E_{vib} = kT^2\frac{\partial \ln Z_{vib}}{\partial T} = \frac{Nh\nu}{2} + \frac{Nh\nu}{\exp\left(\frac{h\nu}{kT}\right)-1}$$

Helmholtz free energy:

$$F_{vib} = -NkT\ln Z_{vib} = \frac{Nh\nu}{2} + NkT\ln\left(1-e^{-h\nu/kT}\right)$$

Entropy:

$$S_{vib} = -\left(\frac{\partial F_{vib}}{\partial T}\right) = Nk\left[-\ln\left(1-e^{-h\nu/kT}\right) + \frac{h\nu/kT}{e^{h\nu/kT-1}}\right]$$

Specific heat at constant volume:

$$\left(C_V\right)_{vib} = \left(\frac{\partial E_{vib}}{\partial T}\right)_{vib} = \frac{N^2h^2\nu^2}{kT^2}\frac{e^{h\nu/kT}}{\left(e^{h\nu/kT}-1\right)^2}$$

$$\left(C_V\right)_{vib} = Nk\left(\frac{\theta_{vib}}{T}\right)^2\frac{e^{\theta_{vib}/T}}{\left(e^{\theta_{vib}/T}-1\right)^2}$$

- For $T \gg \theta_{vib}$, $(C_V)_{vib} \rightarrow Nk$
- For $T \ll \theta_{vib}$, $(C_V)_{vib} \rightarrow 0$

This suggests that **vibrational motion gets frozen at low temperatures.**

Electronic and Nuclear Partition functions

- Molecules can exist with electrons excited to states higher than the ground state. The energy spacings of these states vary in irregular manner. So, it is not possible to give a general expression for Z_e.

- At ordinary temperatures, most of the molecules are usually in their ground state whose energy can be taken as zero. Thus,

$$Z_e = g_{gr}(e) + g_1 \exp\{-\beta\varepsilon_1(e)\} + \ldots\ldots\ldots$$

$$Z_e \cong g_{gr}(e) \quad \ldots\ldots\ldots\ldots(x)$$

where $g_{gr}(e)$ is the degeneracy of the electronic ground state.

- The nuclear energy can be taken to be zero. Except in atomic explosions, the nuclei are not excited thermally to states above their ground state. Thus,

$$Z_n \cong g_{gr}(n,s) \quad ....(xi)$$

where, $g_{gr}(n, s)$ is the nuclear spin degeneracy.

- If in a diatomic molecule, nuclei have spins s_1 and s_2 then,

$$g_{gr}(n,s) = (2s_1 + 1)(2s_2 + 1)$$

Assignment

- Use the concept of partition function
  - to determine the specific heat capacity of Hydrogen.
  - to determine the specific heat capacity of Solids.

References: Further Readings

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

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

3. *Elementary Statistical Mechanics* by Gupta & Kumar

4. *Statistical Mechanics* by K. Huang

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

Thank You

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