Diatomic Molecules: Partition Functions
Partition Function of a Diatomic Molecule

• Consider a diatomic molecule inside a box at temperature T, so the energy of the \( i^{th} \) microstate of this molecule can be expressed as –

\[
\mathcal{E}_i = \mathcal{E}_{\text{tr}} + \mathcal{E}_{\text{rot}} + \mathcal{E}_{\text{vib}} + \mathcal{E}_e + \mathcal{E}_n \quad \text{(i)}
\]

where \( \mathcal{E}_{\text{tr}} \) is the translational energy of the centre of mass of the molecule, \( \mathcal{E}_{\text{rot}} \) is the energy associated with the rotation of the constituent atoms in the molecule about the centre of mass, \( \mathcal{E}_{\text{vib}} \) is the energy associated with the vibrations of the two atoms along the line joining them, \( \mathcal{E}_e \) is the energy of atomic electrons and \( \mathcal{E}_n \) is the energy of the atomic nucleus.

Figure: Diatomic molecule having identical atoms
So, the partition function of a single diatomic molecule can be written as –

\[ Z_D = \sum_{\text{states}} e^{-\beta \varepsilon_i} \] ...........(ii)

from (i),

\[ Z_D = \sum_{\text{states}} (e^{-\beta \varepsilon_{\text{tr}}})(e^{-\beta \varepsilon_{\text{rot}}})(e^{-\beta \varepsilon_{\text{vib}}})(e^{-\beta \varepsilon_{\text{e}}})(e^{-\beta \varepsilon_{\text{n}}}) \]

\[ Z_D = Z_{\text{tr}} Z_{\text{rot}} Z_{\text{vib}} Z_{\text{e}} Z_{\text{n}} \] ...........(iii)

where \( Z_{\text{tr}}, Z_{\text{rot}}, Z_{\text{vib}}, Z_{\text{e}} \) and \( Z_{\text{n}} \) 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 –

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

Therefore, one particle translational partition function is -

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

After solving, we get the translational partition function

\[
Z = \frac{(2\pi mkT)^{3/2}}{h^3} abc = \frac{V}{h^3} \left( 2\pi mkT \right)^{3/2} \quad ........(vi)
\]
So, partition function for a gas of $N$ diatomic molecules is –

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

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,

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

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

$$Z_{rot} = \sum_J g_{rot} \exp \left(\frac{-J(J+1)h^2}{8\pi^2 I k T}\right)$$
Rotational levels are degenerate and this degeneracy arises due to space quantization of angular momentum. There are \((2J+1)\) allowed orientations. So, \(g_{\text{rot}} = (2J+1)\)

\[
Z_{\text{rot}} = \sum_{J} (2J + 1) \exp\left(\frac{-J(J+1)\hbar^2}{8\pi^2 I k T} \right) = \sum_{J} (2J + 1) \exp\left(\frac{-J(J+1)\theta_{\text{rot}}}{T} \right) \quad \ldots\ldots (viii)
\]

Where \(\theta_{\text{rot}} = \frac{\hbar^2}{8\pi^2 I k}\) is the rotational temperature.

**Case I: High temperature limit:** When \(T \gg \theta_{\text{rot}}\)

\[
Z_{\text{rot}} = \int_{0}^{\infty} (2J + 1) \exp\left(\frac{-J(J+1)\theta_{\text{rot}}}{T} \right) dJ
\]

After solving, we get \(Z_{\text{rot}} = \frac{T}{\theta_{\text{rot}}} = \frac{8\pi^2 I k T}{\hbar^2}\)

For a gas of \(N\) diatomic molecules,

\[
Z_{\text{rot}} = \left(\frac{8\pi^2 I k T}{\hbar^2}\right)^N
\]
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 -

\[ S_{rot} = Nk \ln \frac{8\pi^2 I k T}{h^2} + Nk \]

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

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

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

\[ F_{rot} = E_{rot} - TS_{rot} = -NkT \ln \frac{8\pi^2 I k T}{h^2} \]
Case II: Low temperature limit: When $T << \theta_{rot}$
Rotational partition function can be written as –

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

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

- \textit{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, $\sigma$. It specifies the number of indistinguishable orientations that a molecule have.

- For a homo-nuclear diatomic molecule, $\sigma=2$ whereas for hetero-nuclear diatomic molecule, $\sigma=1$. Accordingly, we divide the rotational partition function by $\sigma$. 

$$8\ldots531 + 62 = -TT \theta \theta \theta \theta \theta e Z$$
**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 –

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

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

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

Helmholtz free energy:

$$F_{vib} = -NkT \ln Z_{vib} = \frac{N\hbar \nu}{2} + NkT \ln(1 - e^{-\hbar \nu/kT})$$

Entropy:

$$S_{vib} = -\left(\frac{\partial F_{vib}}{\partial T}\right) = Nk \left[ -\ln(1 - e^{-\hbar \nu/kT}) + \frac{\hbar \nu/kT}{e^{\hbar \nu/kT-1}} \right]$$
Specific heat at constant volume:

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

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

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

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,

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

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

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,

\[ Z_n \cong g_{gr}(n, s) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (xi) \]

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


3. *Elementary Statistical Mechanics* by Gupta & Kumar

4. *Statistical Mechanics* by K. Huang

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