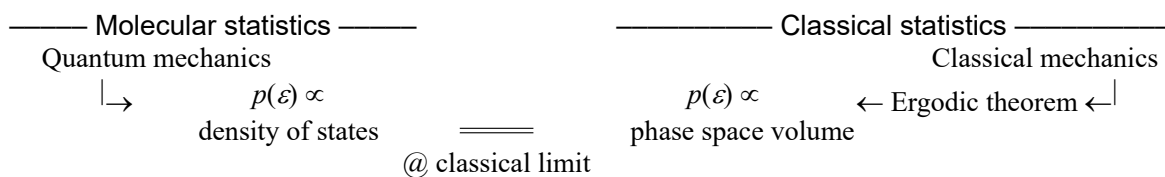


3. External Nuclear Motions



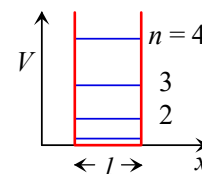
3.1 Translational motion

⟨1D translation⟩

for a particle with mass, m , in a 1D box of length l :

· Energy levels:

$$\varepsilon_n = \frac{h^2 n^2}{8m l^2}, \quad n = 1, 2, 3, \dots \quad (3.1)$$



· Density of states and partition function:

$$\rho_{\text{trans}}^{(1D)}(\varepsilon) = \frac{dn}{d\varepsilon} = \frac{\sqrt{2m}}{h} l \varepsilon^{-1/2} \quad (3.2)$$

$$q_{\text{trans}}^{(1D)}(T) = \int_0^\infty \rho_{\text{trans}}^{(1D)}(\varepsilon) \exp(-\varepsilon/k_B T) d\varepsilon = \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} l \quad (3.3)$$

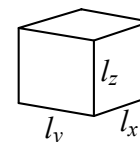
⟨3D translation⟩

for a particle with mass, m , in a 3D box of size $l_x \times l_y \times l_z$:

motions in x , y , and z coordinates: \rightarrow independent

· Density of states:

$$\begin{aligned} \rho_{\text{trans}}^{(3D)}(\varepsilon) &= \iiint_{\varepsilon=\varepsilon_x+\varepsilon_y+\varepsilon_z} \frac{dn_x}{d\varepsilon_x} \frac{dn_y}{d\varepsilon_y} \frac{dn_z}{d\varepsilon_z} d\varepsilon \\ &= \left(\frac{2m}{h^2} \right)^{3/2} l_x l_y l_z \int_0^\varepsilon \int_0^{\varepsilon-\varepsilon_z} (\varepsilon - \varepsilon_y - \varepsilon_z)^{-1/2} \varepsilon_y^{-1/2} d\varepsilon_y \varepsilon_z^{-1/2} d\varepsilon_z = 2\pi \left(\frac{2m}{h^2} \right)^{3/2} l_x l_y l_z \varepsilon^{1/2} \end{aligned}$$



since $l_x l_y l_z$ is volume, density of states per unit volume:

$$\rho_{\text{trans}}^\circ(\varepsilon) = 2\pi \left(\frac{2m}{h^2} \right)^{3/2} \varepsilon^{1/2} \quad (3.4)$$

· Partition function per unit volume:

$$q_{\text{trans}}^\circ(T) = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \quad (3.5)$$

⟨Relative translation⟩

· in (3.4) and (3.5): $m \rightarrow \mu$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (3.6)$$

Problem-3

Derive 3D translational energy distribution for canonical ensemble (Maxwell-Boltzmann distribution) at temperature T from equation (3.4).

3.2 External rotation

⟨Rotational constant⟩

· Moment of inertia:

$$I = \sum_{i=1}^n m_i r_i^2 \quad (3.7)$$

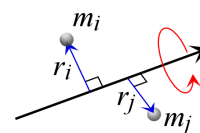
m_i : mass of i^{th} atom, r_i : distance of i^{th} atom from rotation axis

cf.) for diatomic molecule: $I = \mu r^2$ (μ : reduced mass, r : inter nuclear distance)

· Rotational constant:

$$B = \frac{\hbar^2}{2I} \quad (3.8)$$

$$\hbar = h / 2\pi$$



⟨2D rotation⟩

(linear molecules, e.g., H₂, O₂, CO₂, etc.)

· Energy levels:

$$\varepsilon_J = BJ(J+1), \quad J = 0, 1, 2, \dots \quad (3.9)$$

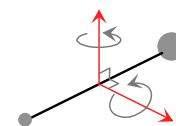
degeneracy: $g_J = 2J + 1$

· Density of states and partition function:

$$\rho_{\text{rot}}^{(2D)}(\varepsilon) = \frac{g_J}{\sigma} \frac{dJ}{d\varepsilon} = \frac{1}{\sigma B} \quad (3.10)$$

$$q_{\text{rot}}^{(2D)}(T) = \frac{1}{\sigma} \frac{k_B T}{B} \quad (3.11)$$

σ : rotational symmetry number



⟨3D Rotation⟩

(non-linear molecules)

· Density of states and partition function (with isomer correction):

$$\rho_{\text{rot}}^{(3D)}(\varepsilon) = \frac{2n_{\text{isom}}}{\sigma(ABC)^{1/2}} \varepsilon^{1/2} \quad (3.12)$$

$$q_{\text{rot}}^{(3D)}(T) = \frac{\pi^{1/2} n_{\text{isom}}}{\sigma} \left(\frac{k_B T}{A} \frac{k_B T}{B} \frac{k_B T}{C} \right)^{1/2} \quad (3.13)$$

n_{isom} : number of (optical) isomers

⟨Rotational symmetry number⟩

· nuclear-spin state \leftrightarrow rotational state with specific symmetry

(e.g., ortho-H₂ \leftrightarrow odd- J states, para-H₂ \leftrightarrow even- J states)

· ρ_{rot} or q_{rot} must be divided by σ (rotational symmetry number)

point group	σ	point group	σ	point group	σ
C_1, C_i, C_s	1	$C_{\infty v}$	1	T_d	12
C_n, C_{nv}, C_{nh}	n	$D_{\infty h}$	2	O_h	24
D_n, D_{nd}, D_{nh}	$2n$	S_{2m}	m	I_h	60

[examples]

$$\text{H}_2\text{O} (C_{2v}): \quad \sigma = 2 \cdot 1 = 2$$

$$\text{SF}_6 (O_h): \quad \sigma = 6 \cdot 4 = 24$$

$$\text{C}_2\text{H}_6 (D_{3d}): \quad \sigma = 6 \cdot 1 = 6$$

$$\text{C}_6\text{H}_6 (D_{6h}): \quad \sigma = 6 \cdot 2 = 12$$

[Exercise-3.1] Count rotational symmetry number of following molecules.

- (1) CO₂ ... $D_{\infty h}$, $\sigma = 2 \cdot 1 = 2$
 (2) CH₄ ... T_d , $\sigma = 4 \cdot 3 = 12$
 (3) C₂H₄ ... D_{2h} , $\sigma = 4 \cdot 1 = 4$
 (4) NO₃ (planar) ... D_{3h} , $\sigma = 3 \cdot 2 = 6$
 (5) CH₃I ... C_{3v} , $\sigma = 3 \cdot 1 = 3$
 (6) CHF₂Cl ... C_s , $\sigma = 1$
-

⟨Number of optical isomers⟩

- ρ_{rot} or q_{rot} must be divided by σ / n_{isom} (though n_{isom} is not rotational property)
- $n_{\text{isom}} = 2$ for chiral molecule

chiral point groups	achiral point groups	
C_1	$C_{\infty v}, D_{\infty h}$	C_i, C_s
C_n	C_{nv}, C_{nh}	S_{2m}
D_n	D_{nd}, D_{nh}	T_d, O_h, I_h

[examples]

- HFCO (C_s): achiral ($n_{\text{isom}} = 1$)
 CHFClBr (C_1): chiral ($n_{\text{isom}} = 2$)
 NH₂F (C_s): achiral ($n_{\text{isom}} = 1$)
 H₂O₂ (C_2): chiral ($n_{\text{isom}} = 2$)
-

[Exercise-3.2] Determine whether the molecule is chiral ($n_{\text{isom}} = 2$) or achiral ($n_{\text{isom}} = 1$).

- (1) HDO C_s achiral $n_{\text{isom}} = 1$
 (2) SF₆ O_h achiral $n_{\text{isom}} = 1$
 (3) NHDF C_1 chiral $n_{\text{isom}} = 2$
 (4) CH₃OH C_s achiral $n_{\text{isom}} = 1$
 (5) *gauche*-CH₂Cl-CH₂Cl C_2 chiral $n_{\text{isom}} = 2$
 (*gauche*-1,2-dichloroethane)
-