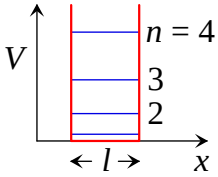
2. Density of states for molecular motions

classical limit: $\Delta E << E$ (microcanonical), $\Delta E << k_B T$ (canonical)

2.1 Translational density of states

[1-D (one-dimensional) translation]

a particle (mass m) in a 1-D box (length l):



eigenvalue: $\varepsilon(n) = \frac{h^2}{8m}\frac{n^2}{l^2}$ (n = 1, 2, 3, ...) (2.1.1)

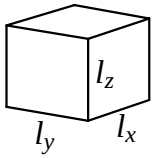
density of states: $\rho_{trans}^{(1D)}(\varepsilon) = \frac{dn}{d\varepsilon} = \frac{\sqrt{2m}}{h} l \varepsilon^{-1/2}$ (2.1.2)

[3-D translation]

a particle (mass m) in a 3-D box ($l_x \times l_y \times l_z$) ... independent in x, y, and z directions

eigenvalue: $\varepsilon(n_x, n_y, n_z) = \varepsilon_x + \varepsilon_y + \varepsilon_z = \frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right)$

(n_x, n_y, n_z = 1, 2, 3, ...) (2.1.3)



density of states: $\rho_{trans}^{(3D)}(\varepsilon) = \iiint_{\varepsilon=\varepsilon_x+\varepsilon_y+\varepsilon_z} \frac{dn_x}{d\varepsilon_x}\frac{dn_y}{d\varepsilon_y}\frac{dn_z}{d\varepsilon_z} d\varepsilon$

$$= \left(\frac{\sqrt{2m}}{h}\right)^3 l_x l_y l_z \int_0^{\varepsilon} \int_0^{\varepsilon-\varepsilon_z} (\varepsilon - \varepsilon_z - \varepsilon_y)^{-1/2} \varepsilon_y^{-1/2} d\varepsilon_y \varepsilon_z^{-1/2} d\varepsilon_z = 2\pi \left(\frac{\sqrt{2m}}{h}\right)^3 l_x l_y l_z \varepsilon^{1/2} \quad (2.1.4)$$

$l_x l_y l_z$ = volume:

density of states per unit volume: $\rho_{trans}^{\circ\,(3D)}(\varepsilon) = 2\pi\left(\frac{\sqrt{2m}}{h}\right)^3 \varepsilon^{1/2} = c_{trans}\varepsilon^{1/2}$ (2.1.5)

[3-D relative translation]

Relative translation of particle A and B: m (mass) → μ (reduced mass)

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (2.1.6)$$

$$\rho_{trans}^{\circ\,(3D)}(\varepsilon) = 2\pi\left(\frac{\sqrt{2\mu}}{h}\right)^3 \varepsilon^{1/2} = c_{trans}\varepsilon^{1/2} \quad (2.1.7)$$

note:

1-D translation → activated complex in the TST

2-D translation → diffusion of an adsorbed molecule on a surface

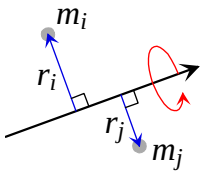
3-D translation → reaction producing two molecules

Problem-2.1

1) Derive the expression for the density of states per unit area of 2-D translation.
2) Derive the 3-D translational energy distribution for canonical ensemble (Maxwell-Boltzmann distribution) at temperature T from equation (2.1.5).

2.2 Rotational density of states

[Rotational motion]



moment of inertia: $I = \sum_{i=1}^{n} m_i r_i^2$ (2.2.1)

(m_i: mass of ith atom, r_i: distance of ith atom from rotation axis)

rotational constant: $B = \dfrac{h^2}{8\pi^2 I}$ (2.2.2)

⟨Rotational symmetry number⟩

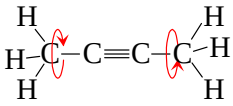
σ = number of indistinctive (same atoms are indistinctive) rotational conformation

ex.) $\sigma(N_2)=2$, $\sigma(HCl)=1$, $\sigma(CO_2)=2$, $\sigma(H_2O)=2$, $\sigma(NH_3)=3$, $\sigma(C_2H_4)=4$, $\sigma(CH_4)=12$

⟨Rigid rotor approximation⟩

I is constant (*i.e.*, independent on the speed of rotation, the vibrational states, or *etc.*)

[1-D Rotator]



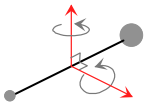
e.g. intramolecular rotation of $H_3C\text{-}C{\equiv}C\text{-}CH_3$:

eigenvalue: $\varepsilon(J) = BJ^2$ (J = 0, ±1, ±2, ...), degeneracy: $g(J) = 1$ (2.2.3)

$J' \equiv |J| \rightarrow \varepsilon(J') = BJ'^2$ (J' = 0, 1, 2, ...), $g(J') = 2$ [*but* $g(0) = 1$] (2.2.4)

density of states: $\rho_{rot}^{(1D)}(\varepsilon) = \dfrac{g(J')}{\sigma}\dfrac{dJ'}{d\varepsilon} = \dfrac{1}{\sigma\sqrt{B}}\varepsilon^{-1/2}$ (2.2.5)

[2-D Rotator]



e.g. linear molecules [N_2, CO_2, *etc.*]:

eigenvalue: $\varepsilon(J) = BJ(J+1)$ (J = 0, 1, 2, ...), degeneracy: $g(J) = 2J + 1$ (2.2.6)

density of states: $\rho_{rot}^{(2D)}(\varepsilon) = \dfrac{g(J)}{\sigma}\dfrac{dJ}{d\varepsilon} = \dfrac{1}{\sigma B}$ (2.2.7)

[3-D Rotator]

e.g. non-linear molecules

a) Spherical top ... $I_A = I_B = I_C$ [CH_4, SF_6]:

eigenvalue: $\varepsilon(J) = BJ(J+1)$ (J = 0, 1, 2, ...), degeneracy: $g(J) = (2J+1)^2$ (2.2.8)

density of states: $\rho_{rot}^{(3D)}(\varepsilon) = \dfrac{g(J)}{\sigma}\dfrac{dJ}{d\varepsilon} = \dfrac{2}{\sigma B^{3/2}}\left(\varepsilon + \dfrac{B}{4}\right)^{1/2} \sim \dfrac{2}{\sigma B^{3/2}}\varepsilon^{1/2}$ (2.2.9)

b) Symmetric top ... $I_A = I_B \neq I_C$ *or* $I_A \neq I_B = I_C$ [NH_3, CH_3]: (approximation)
Asymmetric top ... $I_A \neq I_B \neq I_C$ (H_2CO, HCO): (approximation)

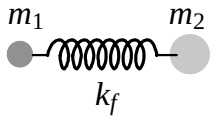
density of states: $\rho_{rot}^{(3D)}(\varepsilon) \sim \dfrac{2}{\sigma B_{av}^{3/2}}\varepsilon^{1/2}$, $B_{av} = (ABC)^{1/3}$ (2.2.10)

[Summary]

$n_r \equiv$ rotational degree of freedom (dimension of rotation)

$$\rho_{rot}^{(n_r)}(\varepsilon) \sim c_{rot}^{(n_r)} \varepsilon^{\frac{n_r}{2}-1}, \quad c_{rot}^{(n_r)} = \frac{\Gamma(n_r)}{\sigma B_{(\mathrm{av})}^{n_r/2}} \tag{2.2.11}$$

2.3 Vibrational density of states



[Vibrational motion]

$$-k_f x = \mu \frac{d^2x}{dt^2} \quad (k_f: \text{force constant}, \mu: \text{reduced mass}) \tag{2.3.1}$$

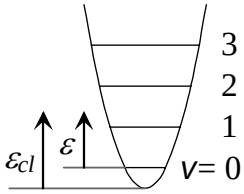
〈Harmonic oscillator approximation〉

k_f is constant (*i.e.*, independent of deviation x)

Solution to the classical mechanics:

$$x = x_0 \sin(2\pi\nu t + \varphi), \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k_f}{\mu}} \quad (\nu: \text{frequency } [\mathrm{s}^{-1}]) \tag{2.3.2}$$

[One vibrator]



eigenvalue: $\varepsilon_{cl}(n) = \left(n + \frac{1}{2}\right)h\nu, \quad \varepsilon(n) = nh\nu$ (2.3.3)

density of states: $\rho_{vib-cl}^{(1)}(\varepsilon_{cl}) = \frac{dn}{d\varepsilon} = \frac{1}{h\nu}$ (2.3.4)

[n_v Vibrators]

Number of vibrators: $n_v = 3\,n_{atom} - 6$ (non-linear molecule), $n_v = 3\,n_{atom} - 5$ (linear molecule)

two vibrators: $\rho_{vib-cl}^{(2)}(\varepsilon_{cl}) = \int_0^{\varepsilon_{cl}} \frac{1}{h\nu_1}\frac{1}{h\nu_2} d\varepsilon_2 = \frac{1}{h\nu_1}\frac{1}{h\nu_2}\varepsilon_{cl}$

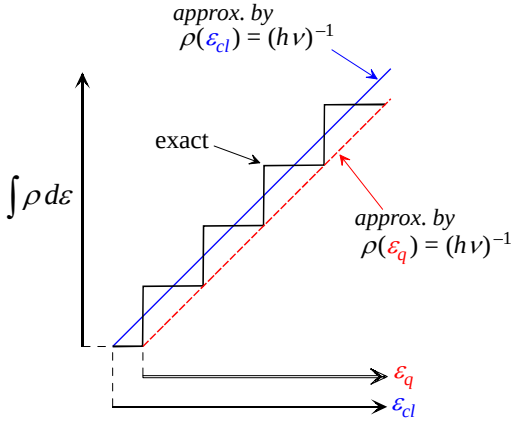
three vibrators: $\rho_{vib-cl}^{(3)}(\varepsilon_{cl}) = \int_0^{\varepsilon_{cl}} \int_0^{\varepsilon_{cl}-\varepsilon_3} \frac{1}{h\nu_1}\frac{1}{h\nu_2} d\varepsilon_2 \frac{1}{h\nu_3} d\varepsilon_3 = \frac{1}{2}\frac{1}{h\nu_1}\frac{1}{h\nu_2}\frac{1}{h\nu_3}\varepsilon_{cl}^2$

.....

n_v vibrators: $\rho_{vib-cl}^{(n_v)}(\varepsilon_{cl}) = \frac{1}{\Gamma(n_v)\prod_{i=1}^{n_v} h\nu_i}\varepsilon_{cl}^{n_v-1} = c_{vib-cl}^{(n_v)}\varepsilon_{cl}^{n_v-1}$ (2.3.5)

note:

1) Density of states is crude approximation (fig. 2) for vibration since $h\nu \sim$ 200–3000 cm^{-1}.
2) in eq. 2.3.5, ε_{cl} is the energy from the classical origin.
3) $\Gamma(n) = (n-1)!, \quad \Gamma(1) = \Gamma(2) = 1$



Problem-2.2 ———