Chapter 15

The Heat Capacity of a Diatomic Gas

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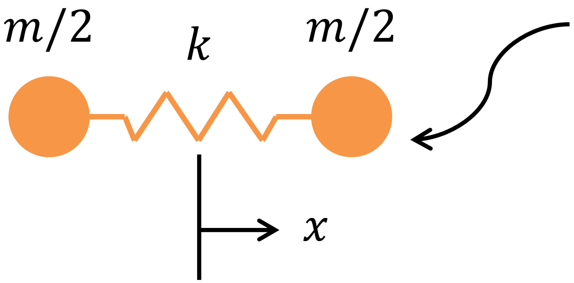
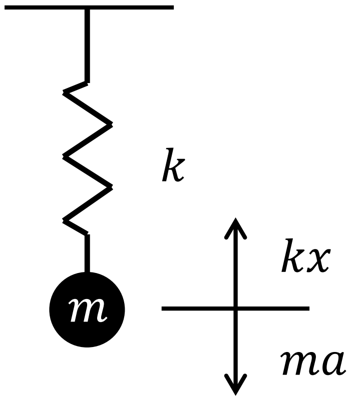
15.1 Introduction

- One dimensional Harmonic Oscillator
  - Vibrational motion of a diatomic molecule with its frequency υ



N_2 or O_2
(diatomic gas)



$$m\ddot{x} + kx = 0$$

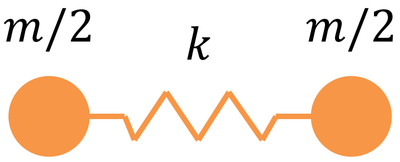
$$\ddot{x} + \omega^2 x = 0$$

$$x = A\sin(\omega t) \qquad \omega = \sqrt{\frac{k}{m}} \quad T = \frac{2\pi}{\omega} = \frac{1}{\upsilon}$$

15.1 Introduction

- One dimensional Harmonic Oscillator

  - Vibrational motion of a diatomic molecule with its frequency υ



$$\epsilon_{kinetic} = \frac{1}{2}mv^2$$

$$\epsilon_{potential} = \frac{1}{2}kx^2$$

$$\frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 = c$$

※ Potential energy

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}(4\pi^2 m\upsilon^2)x^2 = 2\pi^2 m\upsilon^2 x^2$$

15.1 Introduction

※ Schrödinger equation for vibrational mode

$$\frac{\nabla^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}(\varepsilon-2\pi^2 m v^2 x^2)\psi=0$$

$$\begin{cases}\psi(x\to\pm\infty)=0\\ \left(\frac{d\psi}{dx}\right)_{x=0}=0\end{cases}$$

$$z=\sqrt{\frac{4\pi^2 vm}{h}}x$$

15.1 Introduction

$$\frac{d^2\psi}{dx^2} + (\alpha - z^2)\psi = 0 \qquad \alpha = \frac{2\varepsilon}{h\nu}$$

$$\psi = ce^{-\frac{z^2}{2}}w$$

$$\frac{d^2w}{dz^2} - 2z\frac{dw}{dz} + (\alpha - 1)w = 0$$

15.1 Introduction

- Hermite polynomial

$$\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + 2ny = 0$$

$$\mathrm{y} = H_n(x) = (-1)^n e^{x^2}\frac{d^n}{dx^n}\left[e^{-x^2}\right]$$

$$\therefore \alpha - 1 = 2\mathrm{n}$$

$$\therefore \boldsymbol{\varepsilon} = \left(\frac{\mathbf{1}}{\mathbf{2}} + \boldsymbol{n}\right)\boldsymbol{h\nu}$$

energy levels are nondegenerate

one energy level – one solution

$$\boldsymbol{\psi = Ce^{-\frac{z^2}{2}}H_n(Z)}$$

$$Z = \sqrt{\frac{4\pi^2 \nu m}{h}}\,x$$

$$C = \left[\sqrt{\frac{4\pi^2 \nu m}{h}}\,\frac{1}{2^n n!}\right]^{\frac{1}{2}}$$

15.2 The Quantized Linear Oscillator

- Single particle energy level

$$\varepsilon_j = \left(j + \frac{1}{2}\right)h\nu \qquad\qquad j = 0,1,2\ \cdots$$

- The partition function

$$Z = \sum_{j=0}^{\infty} g_j e^{-\frac{\varepsilon_j}{kT}} = \sum_{j=0}^{\infty} e^{-\left(j+\frac{1}{2}\right)\frac{h\nu}{kT}} \qquad nondegenerate:\ g_j = 1\ for\ all\ j$$

$$= e^{-\theta/2T} + e^{-3\theta/2T} + e^{-5\theta/2T} + \cdots = \boldsymbol{\frac{e^{-2\theta/T}}{1 - e^{-\theta/T}}} \qquad \left(\theta = \frac{h\nu}{k}\right)$$

- The Boltzmann distribution

$$\frac{N_j}{N} = e^{-\frac{\varepsilon_j}{kT}} e^{\frac{\theta}{2T}}(1 - e^{-\frac{\theta}{T}}) \qquad\qquad \left(\frac{N_j}{g_j} = \frac{N}{Z} e^{-\frac{\varepsilon_j}{kT}}\right)$$

$$= e^{-\frac{1}{kT}\left(j+\frac{1}{2}\right)h\nu}\ e^{\frac{\theta}{2T}}(1 - e^{-\frac{\theta}{T}})$$

$$= e^{-\frac{j\theta}{T}}\ (1 - e^{-\frac{\theta}{T}})$$

15.2 The Quantized Linear Oscillator

- Internal energy

$$U = NkT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_v$$

$$= NkT^2 \frac{\partial}{\partial T}\left[-\frac{\theta}{2T} - \ln\left(1 - e^{-\frac{\theta}{T}}\right)\right]$$

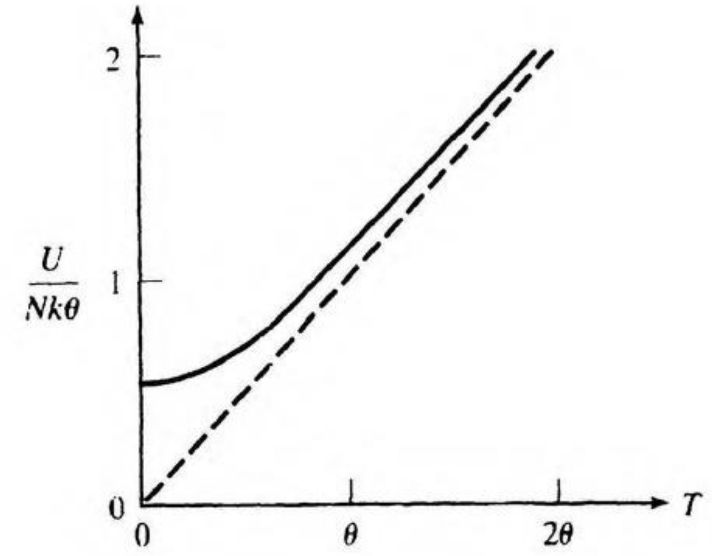
$$= NkT^2 \left[\frac{\theta}{2T^2} - \frac{-e^{-\frac{\theta}{T}}}{1 - e^{-\frac{\theta}{T}}}\frac{\theta}{T^2}\right]$$

$$= Nk\theta\left[\frac{1}{2} + \frac{1}{e^{\theta/T} - 1}\right]$$

$$\approx Nk\theta\left(\frac{1}{2} + \frac{T}{\theta}\right)$$

$$\approx NkT \quad \textbf{if} \ \frac{T}{\theta} \gg 1$$

$$\approx Nk\theta/2 \ \textbf{if} \ \frac{T}{\theta} \ll 1$$



15.3 Vibrational Modes of Diatomic Molecules

- Heat capacity of vibrational energy

$$C_V = \left(\frac{\partial U}{\partial T}\right)_v = Nk\theta \frac{-e^{\theta/T}(-\theta/T^2)}{(e^{\theta/T}-1)^2} = Nk\left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{(e^{\theta/T}-1)^2}$$

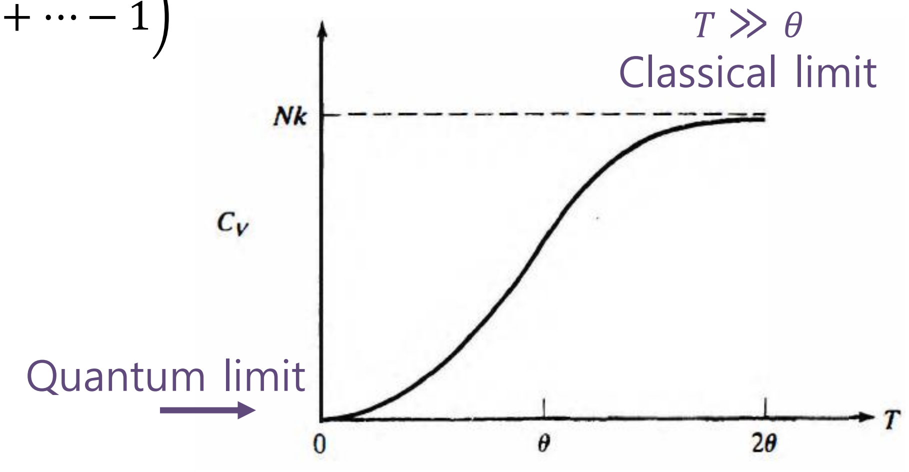
at high temperature $\theta/T \ll 1$,

$$C_V = Nk\left(\frac{\theta}{T}\right)^2 \frac{1+\theta/T+\frac{1}{2}(\theta/T)^2+\cdots}{\left(1+\theta/T+\frac{1}{2}(\theta/T)^2+\cdots-1\right)^2}$$

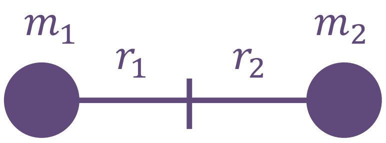
$$= Nk\left(\frac{\theta}{T}\right)^2 \frac{1}{(\theta/T)^2} = \boldsymbol{Nk}$$

at low temperature $\theta/T \gg 1$,

$$C_V = Nk\left(\frac{\theta}{T}\right)^2 \frac{1}{e^{\theta/T}} \quad \rightarrow \quad \mathbf{0}$$



15.4 Rotational modes of diatomic molecules



Rigid Rotator

$$m_1 r_1 = m_2 r_2$$

$$r = r_1 + r_2$$

Reduced mass

Moment of inertia

$$I = m_1 {r_1}^2 + m_2 {r_2}^2 = \frac{m_1 m_2}{m_1 + m_2} r^2$$

$$E = \frac{1}{2} I \omega^2$$

※ Spherical polar coordinates

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r\frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial r}\left(\sin\theta\frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi}{\partial \emptyset^2} + \frac{8\pi^2 mE}{r^2}\psi = 0$$

- The quantized energy levels

$$\varepsilon_l = l(l+1)\frac{h^2}{8\pi^2 I} = l(l+1)\frac{h^2}{2\, I} \qquad l = 0, 1, 2, \cdots$$

- Degenerate

$$g_l = 2l + 1$$

15.4 Rotational modes of diatomic molecules

- Partition function of rotational energy

$$Z = \sum_{j=0}^{\infty} g_j e^{-\epsilon_j/kT} = \sum_{j=0}^{\infty} (2l+1) e^{-l(l+1)h\theta_{rot}/T} \qquad (\theta_{rot} = \frac{h^2}{8\pi^2 Ik})$$

When $T \gg \theta_{rot}$, it can be approximated as

$$Z = \int_0^{\infty} e^{-\theta_{rot}/Tx} dx = \frac{T}{\theta_{rot}}, T \gg \theta_{rot} \qquad {}^{*}\left\{ \begin{array}{c} x \equiv l(l+1) \\ dx = (2l+1)dl \end{array} \right.$$

In contrast, when T<<θ_{rot}, it becomes

$$Z = 1 + 3e^{-2\theta_{rot}/T} + 5e^{-6\theta_{rot}/T} \dots \approx 1 + 3e^{-2\theta_{rot}/T}$$

$$\ln(Z) = \ln(1 + 3e^{-\frac{2\theta_{rot}}{T}}) \approx 3e^{-\frac{2\theta_{rot}}{T}}$$

Rotational characteristic temperature ~ 10 K

15.4 Rotational modes of diatomic molecules

- Rotational energy

For $T \gg \theta_{rot}$,

$$U = NkT^2 \left(\frac{\partial \ln(Z)}{\partial T}\right)_V = NkT^2 \left(\frac{\partial \ln(T/\theta_{rot})}{\partial T}\right)_V = NkT$$

For $T \ll \theta_{rot}$,

$$U = NkT^2 \left(\frac{\partial \ln(Z)}{\partial T}\right)_V = NkT^2 \left(\frac{\partial \ln(3e^{-2\theta_{rot}/T})}{\partial T}\right)_V = 6Nke^{-2\theta_{rot}/T}$$

15.4 Rotational modes of diatomic molecules

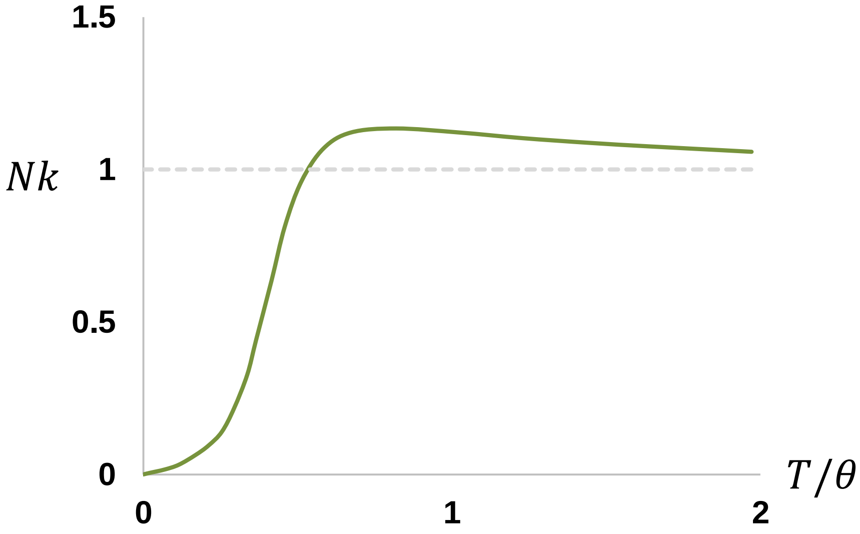
- Heat capacity of rotational energy

For $T \gg \theta_{rot}$,

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = Nk$$

For $T \ll \theta_{rot}$,

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3Nk\left(\frac{\theta_{rot}}{T}\right)^2 e^{-2\theta_{rot}/T}$$



15.6 The total heat capacity

- Total heat capacity

$$C_v = C_{v,tr} + C_{v,rot} + C_{v,vib}$$