

**Chapter 15**

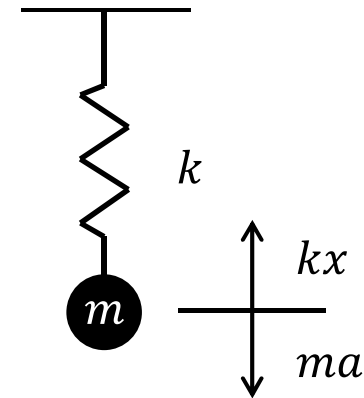
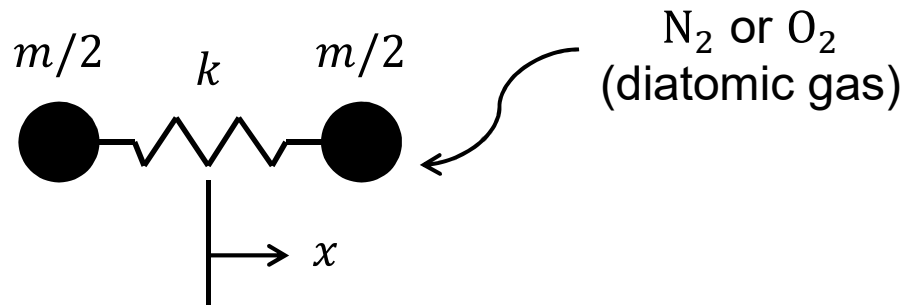
**The Heat Capacity of  
a Diatomic Gas**

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# 15.1 Introduction

- One dimensional Harmonic Oscillator
  - Vibrational motion of a diatomic molecule with its frequency  $\nu$



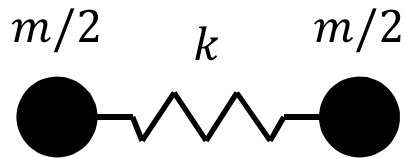
$$m\ddot{x} + kx = 0$$

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

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

# 15.1 Introduction

- One dimensional Harmonic Oscillator
  - Vibrational motion of a diatomic molecule with its frequency  $\nu$



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

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

※ Potential energy

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

# 15.1 Introduction

※ Schrödinger equation for vibrational mode

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

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} (\varepsilon - 2\pi^2 m v^2 x^2) \psi = 0 \quad \left\{ \begin{array}{l} \psi(x \rightarrow \pm\infty) = 0 \\ \left( \frac{d\psi}{dx} \right)_{x=0} = 0 \end{array} \right.$$

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

# 15.1 Introduction

$$\frac{d^2\psi}{dz^2} + (\alpha - z^2)\psi = 0 \quad \alpha = \frac{2\varepsilon}{\hbar v}$$

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

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

# 15.1 Introduction

- Hermite polynomial

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

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

$$\therefore \alpha - 1 = 2n$$

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

energy levels are nondegenerate  
one energy level = one solution

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

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

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

## 15.2 The Quantized Linear Oscillator

- Single particle energy level

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

- The partition function

$$\begin{aligned} Z &= \sum_{j=0}^{\infty} g_j e^{-\frac{\varepsilon_j}{kT}} = \sum_{j=0}^{\infty} e^{-\left(j+\frac{1}{2}\right)\frac{h\nu}{kT}} && \text{nondegenerate : } g_j = 1 \text{ for all } j \\ &= e^{-\theta/2T} + e^{-3\theta/2T} + e^{-5\theta/2T} + \dots = \frac{e^{-\theta/2T}}{1 - e^{-\theta/T}} && \text{Characteristic temperature} \\ &&& \left(\theta = \frac{h\nu}{k}\right) \end{aligned}$$

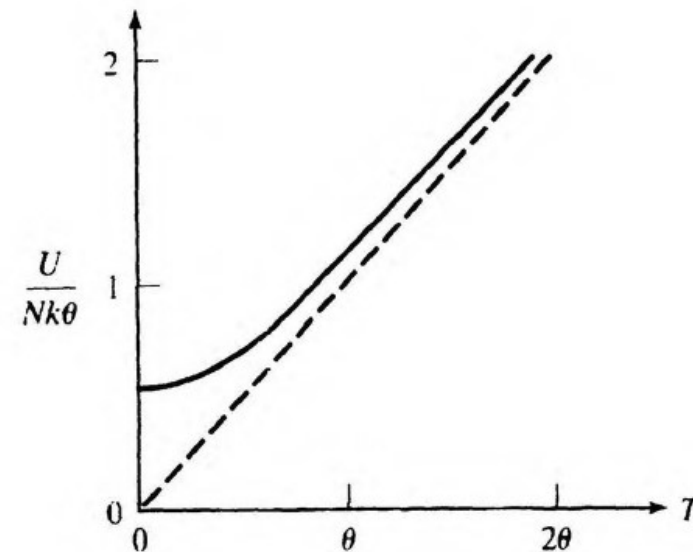
- The Boltzmann distribution

$$\begin{aligned} \frac{N_j}{N} &= e^{-\frac{\varepsilon_j}{kT}} e^{\frac{\theta}{2T}} \left(1 - e^{-\frac{\theta}{T}}\right) && \left(\text{cf. } \frac{N_j}{g_j} = \frac{N}{Z} e^{-\frac{\varepsilon_j}{kT}}\right) \\ &= e^{-\frac{1}{kT}\left(j+\frac{1}{2}\right)h\nu} e^{\frac{\theta}{2T}} \left(1 - e^{-\frac{\theta}{T}}\right) \\ &= e^{-\frac{j\theta}{T}} \left(1 - e^{-\frac{\theta}{T}}\right) \end{aligned}$$

## 15.2 The Quantized Linear Oscillator

- Internal energy

$$\begin{aligned}U &= NkT^2 \left( \frac{\partial \ln Z}{\partial T} \right)_v \\&= NkT^2 \frac{\partial}{\partial T} \left[ -\frac{\theta}{2T} - \ln(1 - e^{-\frac{\theta}{T}}) \right] \\&= NkT^2 \left[ \frac{\theta}{2T^2} - \frac{-e^{-\frac{\theta}{T}}}{1 - e^{-\frac{\theta}{T}}} \frac{\theta}{T^2} \right] \\&= Nk\theta \left[ \frac{1}{2} + \frac{1}{e^{\theta/T} - 1} \right] \\&\approx Nk\theta \left( \frac{1}{2} + \frac{T}{\theta} \right) \\&\approx NkT \quad \text{if } \frac{T}{\theta} \gg 1 \\&\approx Nk\theta/2 \quad \text{if } \frac{T}{\theta} \ll 1\end{aligned}$$



**Figure** Variation with temperature of the internal energy of an assembly of linear oscillators



## 15.3 Vibrational Modes of Diatomic Molecules

- Heat capacity

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

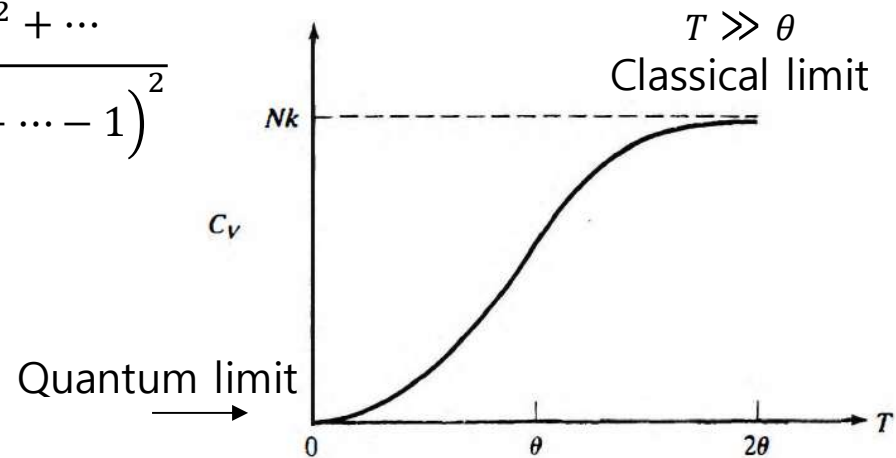
at high temperature  $\theta/T \ll 1$ ,

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

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

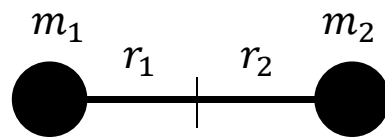
at low temperature  $\theta/T \gg 1$ ,

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



**Figure** Variation with temperature of heat capacity of an assembly of linear oscillators

# 15.4 Rotational Modes of Diatomic Molecules



**Rigid Rotator**

$$m_1 r_1 = m_2 r_2$$

$$r = r_1 + r_2$$

**Moment of inertia**

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

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

Reduced mass

※ Spherical polar coordinates

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

- The quantized energy levels

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

- Degeneracy

$$g_l = 2l + 1$$

## 15.4 Rotational Modes of Diatomic Molecules

- Partition function of rotational energy

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

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

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

In contrast, when  $T \ll \theta_{rot}$ , it becomes

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

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

Rotational characteristic temperature  $\sim 10$  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  $T \ll \theta_{rot}$ ,

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

## 15.4 Rotational Modes of Diatomic Molecules

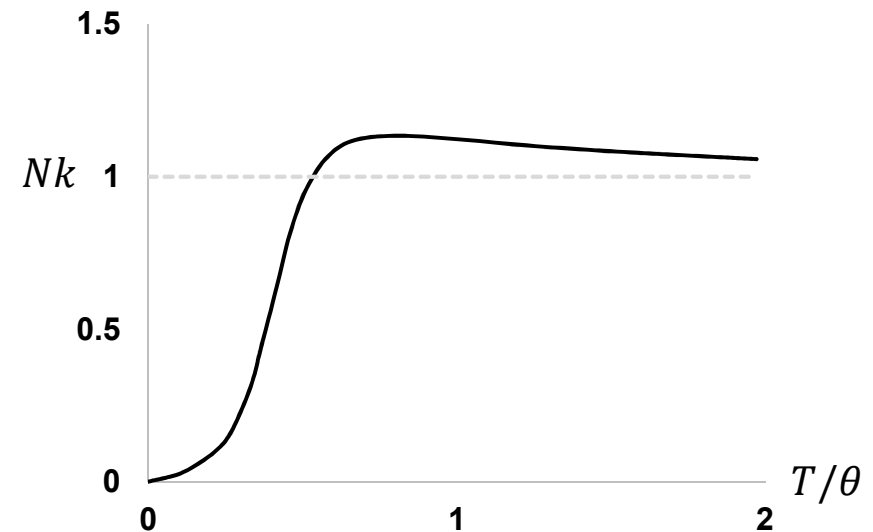
- Heat capacity of rotational energy

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

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

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

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v = 12Nk \left( \frac{\theta_{rot}}{T} \right)^2 e^{-2\theta_{rot}/T}$$



**Figure** Variation with temperature of heat capacity of an assembly of rigid rotators

# 15.6 The Total Heat Capacity

- Total heat capacity

$$C_v = C_{v,tr} + C_{v,rot} + C_{v,vib} = \frac{3}{2}Nk + Nk + Nk \left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{\theta_{vib}/T}}{(e^{\theta_{vib}/T} - 1)^2}$$

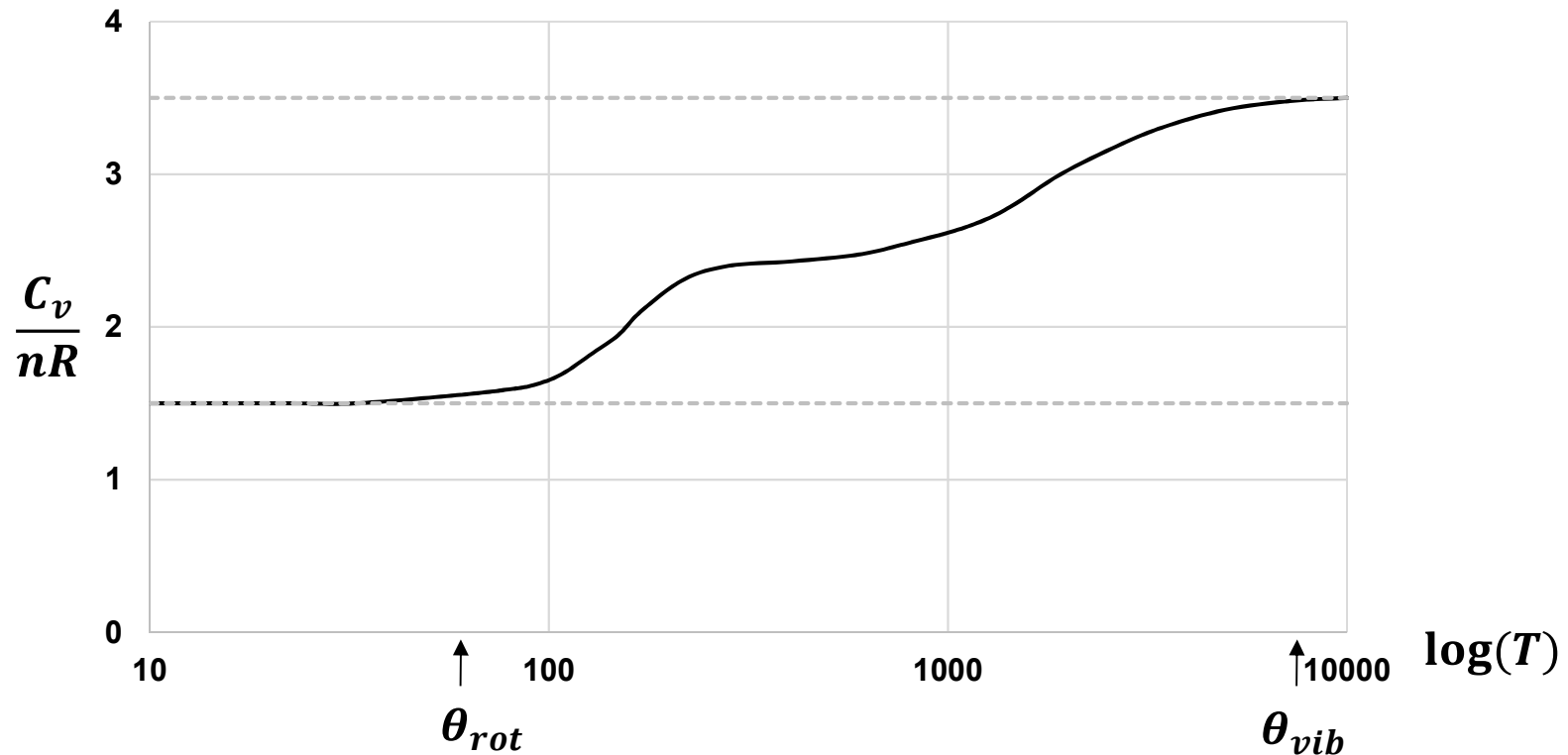


Figure Values of  $C_v/nR$  for hydrogen as a function of temperature