

**Chapter 14**

**The Classical Statistical  
Treatment of an Ideal Gas**

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# 14.1 Thermodynamic Properties from the Partition Function

$$S = \frac{U}{T} + Nk(\ln Z - \ln N + 1) \quad \text{for Maxwell-Boltzmann Distribution}$$

$\sum g_j e^{-\epsilon_j/kT}$        $6 \times 10^{23}$  molecules       $S = k \ln W$

Partition function

Helmholtz function  $F = U - TS = -NkT(\ln Z - \ln N + 1)$

cf.  $dF = -SdT - PdV + \mu dN$

$$\mu = \left( \frac{dF}{dN} \right)_{T,V} \quad \mu = -kT(\ln Z - \ln N)$$

# 14.1 Thermodynamic Properties from the Partition Function

## (1) Internal energy

$$U = \sum N_j \varepsilon_j = \sum g_j \frac{N}{Z} e^{-\varepsilon_j/kT} \varepsilon_j$$

Partition function  $Z = \sum g_j e^{-\varepsilon_j/kT}$

$$\left. \frac{\partial Z}{\partial T} \right)_V = \sum g_j \frac{\varepsilon_j}{kT^2} e^{-\varepsilon_j/kT}$$

$\varepsilon_j$  fixed 

$$\therefore U = \frac{N}{Z} kT^2 \left. \frac{\partial Z}{\partial T} \right)_V = NkT^2 \left. \frac{\partial \ln Z}{\partial T} \right)_V$$

# 14.1 Thermodynamic Properties from the Partition Function

## (2) Gibbs function

$$G = \mu N = -NkT(\ln Z - \ln N)$$

## (3) Enthalpy

$$H = G + TS$$

$$= -NkT(\ln Z - \ln N) + T \left[ \frac{U}{T} + Nk(\ln Z - \ln N + 1) \right]$$

$$= U + NkT$$

$$= NkT \left[ 1 + T \left( \frac{\partial \ln Z}{\partial T} \right)_V \right]$$

# 14.1 Thermodynamic Properties from the Partition Function

## (4) Pressure

$$P = - \left( \frac{dF}{dV} \right)_{T,N} = NkT \left( \frac{\partial \ln Z}{\partial V} \right)_T$$

cf.  $dF = -SdT - PdV + \mu dN$

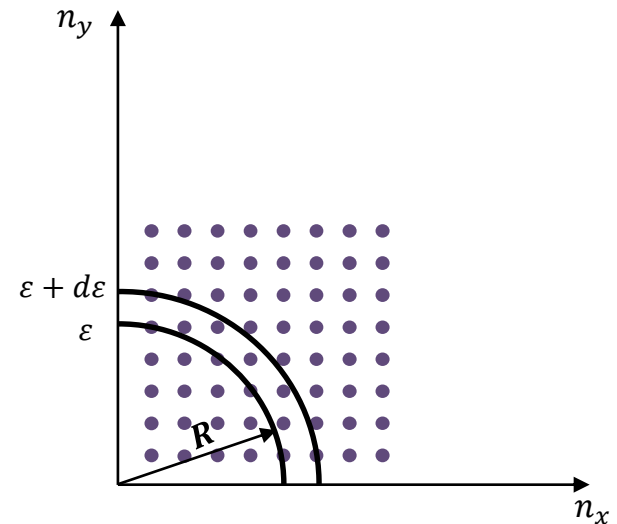
# 14.2 Partition Function for a Gas

- Partition function

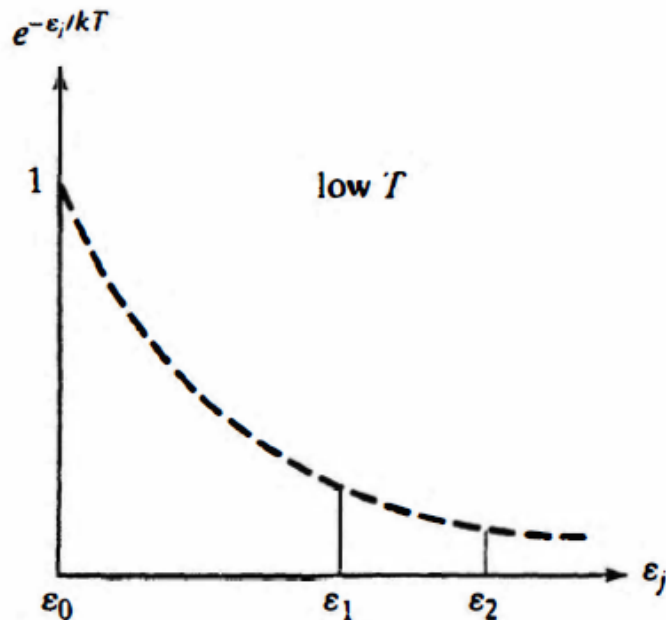
$$\begin{aligned}
 Z &= \sum g_j e^{-\varepsilon_j/kT} \\
 &= \int g(\varepsilon) e^{-\varepsilon/kT} d\varepsilon = \int_0^\infty \frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon \\
 &= \frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \int_0^\infty \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon \\
 Z &= V \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \frac{kT}{2} \sqrt{\pi kT}
 \end{aligned}$$

cf.  $g(\varepsilon)d\varepsilon$  : number of quantum state  $\varepsilon < \varepsilon + d\varepsilon$

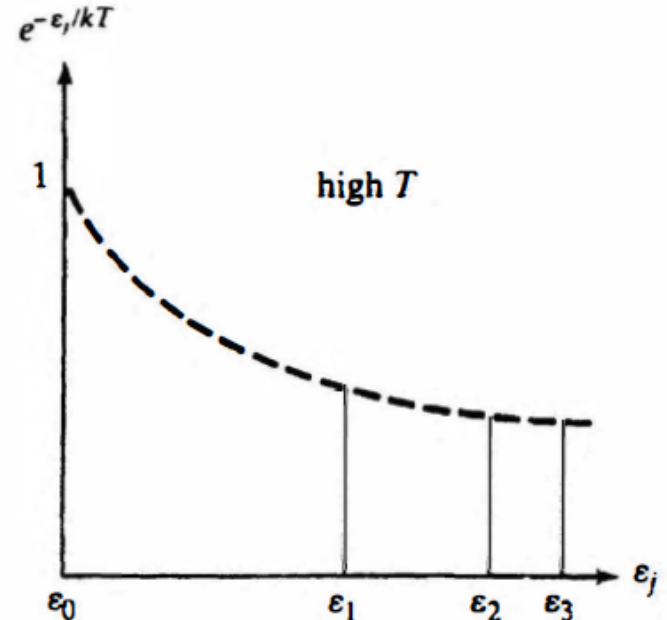
$$g(\varepsilon)d\varepsilon = \frac{\pi}{6} V \left( \frac{2^{9/2} m^{3/2}}{h^3} \right) \frac{3}{2} \varepsilon^{1/2} d\varepsilon = \frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \varepsilon^{1/2} d\varepsilon$$



## 14.2 Partition Function for a Gas



(a)



(b)

Successive terms of the partition function sum for (a) low temperature; and (b) high temperature. The energy level spacings are comparatively large for a small volume.

## 14.3 Properties of a Monatomic Ideal Gas

The partition function depends on both volume and temperature

$$\ln Z = \frac{3}{2} \ln T + \ln V + \frac{3}{2} \ln \left( \frac{2\pi mk}{h^2} \right)$$

$$\left( \frac{\partial \ln Z}{\partial V} \right)_T = \frac{1}{V} \quad \left( \frac{\partial \ln Z}{\partial T} \right)_V = \frac{3}{2} \cdot \frac{1}{T}$$

$$P = - \left( \frac{\partial F}{\partial V} \right)_T = NkT \left( \frac{\partial \ln Z}{\partial V} \right)_T = \frac{NkT}{V} \quad \longrightarrow \quad PV = NkT$$

$$U = NkT^2 \left( \frac{\partial \ln Z}{\partial T} \right)_V = NkT^2 \frac{3}{2T} \quad \longrightarrow \quad U = \frac{3}{2} NkT$$



# 14.3 Properties of a Monatomic Ideal Gas

The calculation of entropy

$$S = \frac{U}{T} + Nk(\ln Z - \ln N + 1)$$

$$= \frac{U}{T} + Nk \left( \frac{3}{2} \ln T + \ln V + \frac{3}{2} \ln \left( \frac{2\pi mk}{h^2} \right) - \ln N + 1 \right)$$

$$= \frac{5}{2} Nk + Nk \ln \left[ \frac{V(2\pi mkT)^{3/2}}{Nh^3} \right] \quad \text{Sackur-Tetrode Equation}$$

# 14.3 Properties of a Monatomic Ideal Gas

Statistical approach

$$s = S/n, \quad Nk = n\bar{R} \quad c_v = \frac{3}{2}R$$

$$s = c_v \ln T + R \ln v + s_0$$

Classical approach

$$Tds = du + Pdv$$

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

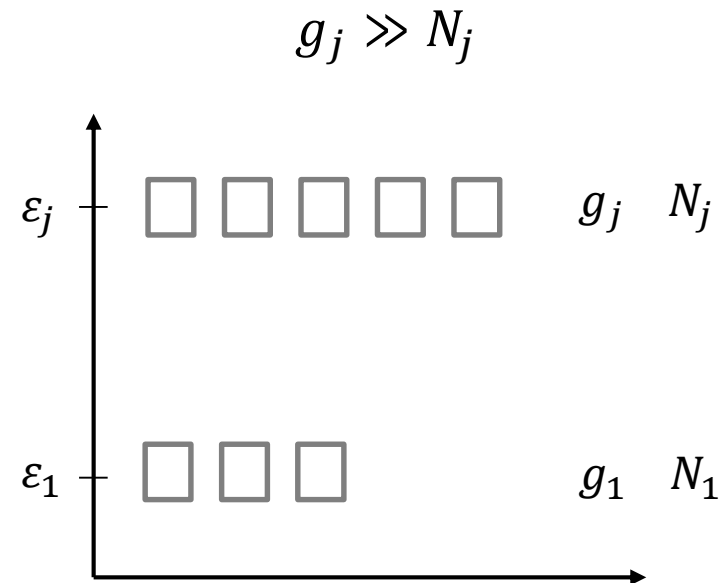
# 14.4 Applicability of MB Distribution

Maxwell-Boltzmann distribution: valid under dilute gas

$$Z = V n_Q = V \left( \frac{2\pi m k T}{h^2} \right)^{3/2}$$

Maxwell-Boltzmann distribution

$$\frac{N_j}{g_j} = \frac{N}{Z} e^{-\varepsilon_j/kT} = \left( \frac{N}{V} \right) \frac{1}{n_Q} e^{-\varepsilon_j/kT}$$



## 14.4 Applicability of MB Distribution

For Helium,

$$m = 6.65 \times 10^{-27} \text{ kg}$$

$$T = 273 \text{ K}$$

$$k = 1.381 \times 10^{-23} \text{ J/K}$$

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$\longrightarrow n_Q = 7 \times 10^{30} \text{ m}^{-3}$$

$$\begin{array}{l} \text{Number of particles} \\ \text{per unit volume} \end{array} \quad \frac{N}{V} = \frac{6 \times 10^{26}}{22.4 \text{ m}^3} \approx 3 \times 10^{25} \text{ m}^{-3}$$

$$\frac{N_j}{g_j} = \frac{N}{Z} e^{-\varepsilon_j/kT} = \left(\frac{N}{V}\right) \frac{1}{n_Q} e^{-\varepsilon_j/kT} \sim 4 \times 10^{-6}$$

# 14.5 Distribution of Molecular Speed

$$f(\varepsilon) = \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{N}{Z} e^{-\varepsilon_j/kT} \quad \text{Maxwell-Boltzmann distribution}$$

$N(\varepsilon)d\varepsilon$  : # of particles  $\varepsilon < \varepsilon + d\varepsilon$

For an ideal gas,

$$Z = V \left( \frac{2\pi mkT}{h^2} \right)^{3/2}$$

The density of states is given by

$$g(\varepsilon) = \frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \varepsilon^{1/2}$$

# 14.5 Distribution of Molecular Speed

$$\begin{aligned} N(\varepsilon)d\varepsilon &= \frac{Ne^{-\varepsilon/kT}}{V \left(\frac{2\pi mkT}{h^2}\right)^{3/2}} \cdot \frac{4\sqrt{2}\pi V}{h^3} m^{3/2} \varepsilon^{1/2} d\varepsilon \\ &= \frac{2\pi N}{(\pi kT)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon \end{aligned}$$

$\varepsilon$  is the single particle kinetic energy. Thus

$$\varepsilon = \frac{1}{2}mv^2, \quad d\varepsilon = mv dv$$

$$\varepsilon^{1/2} d\varepsilon = \frac{(mv^2)^{1/2}}{\sqrt{2}} mv dv = \frac{1}{\sqrt{2}} m^{3/2} v^2 dv$$

# 14.5 Distribution of Molecular Speed

$N(v)dv$  : # of particles  $v < v < v + dv$

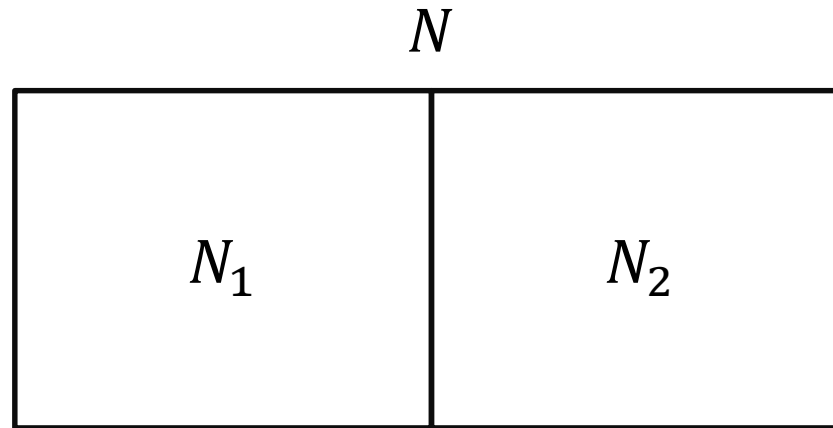
$$\begin{aligned} N(v)dv &= \frac{2\pi N}{(\pi kT)^{3/2}} \cdot \frac{1}{\sqrt{2}} m^{3/2} v^2 dv \cdot e^{-mv^2/2kT} \\ &= 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv \end{aligned}$$

cf. from kinetic theory,

$$dN_v = \underbrace{(N\alpha^3 e^{-\beta^2 v^2})}_{\rho} \times \underbrace{(4\pi v^2 dv)}_V = 4\pi N\alpha^3 v^2 e^{-\beta^2 v^2} dv$$

$$dN_v = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv$$

# 14.7 Entropy Change of Mixing



$$\Delta S = -n\bar{R}(x_1 \ln x_1 + x_2 \ln x_2)$$

- **Effect of mixing**

$$\Delta W = \frac{N!}{N_1! N_2!} = \frac{N!}{(x_1 N)! (x_2 N)!}$$



# 14.7 Entropy Change of Mixing

$$\Delta S = k \ln W = k[\ln N! - \ln(x_1 N)! - \ln(x_2 N)!]$$

$$\begin{aligned}\frac{\Delta S}{k} &= N \ln N - N - \{x_1 N \ln(x_1 N) - x_1 N\} - \{x_2 N \ln(x_2 N) - x_2 N\} \\ &= -N(x_1 \ln x_1 + x_2 \ln x_2)\end{aligned}$$

**Chapter 15**

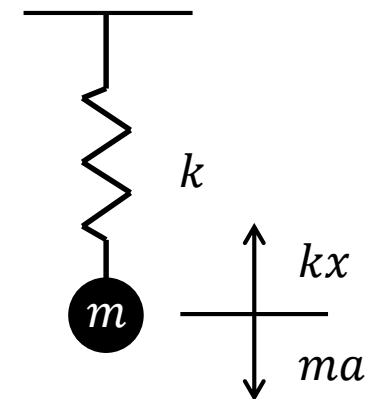
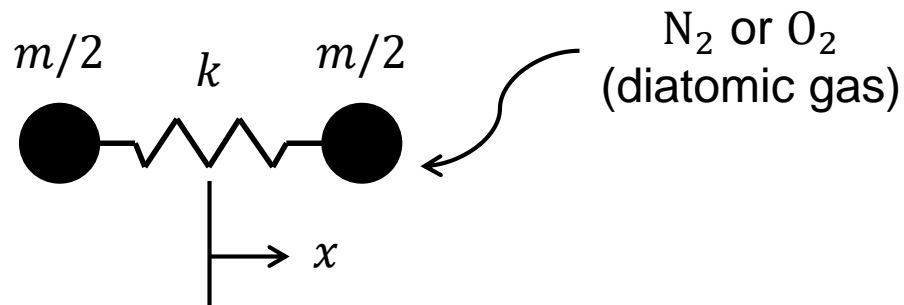
**The Heat Capacity of  
a Diatomic Gas**

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# 15.1 Introduction

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



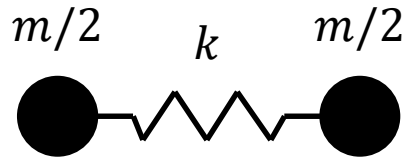
$$m\ddot{x} + kx = 0$$

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

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

# 15.1 Introduction

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



$$\epsilon_{kinetic} = \frac{1}{2} m v^2$$

$$\epsilon_{potential} = \frac{1}{2} k x^2$$

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

※ Potential energy

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

# 15.1 Introduction

※ Schrödinger equation for vibrational mode

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

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

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

# 15.1 Introduction

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

$$\alpha = \frac{2\varepsilon}{h\nu}$$

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

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

# 15.1 Introduction

- Hermite polynomial

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

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

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

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

energy levels are nondegenerate  
one energy level = one solution

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

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

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

# 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

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

$$= e^{-\theta/2T} + e^{-3\theta/2T} + e^{-5\theta/2T} + \dots = \frac{e^{-\theta/2T}}{1 - e^{-\theta/T}} \quad \text{Characteristic temperature } \left(\theta = \frac{h\nu}{k}\right)$$

- The Boltzmann distribution

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

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

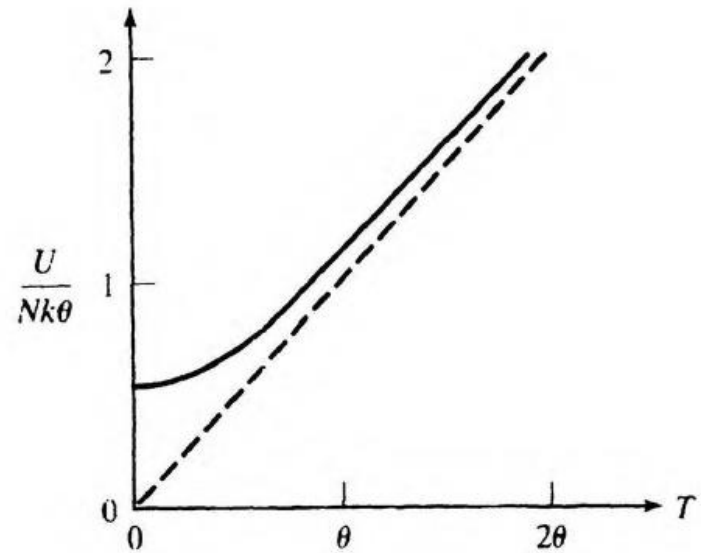
$$= e^{-\frac{j\theta}{T}} \left(1 - e^{-\frac{\theta}{T}}\right)$$



## 15.2 The Quantized Linear Oscillator

- Internal energy

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



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

# 15.3 Vibrational Modes of Diatomic Molecules

- Heat capacity

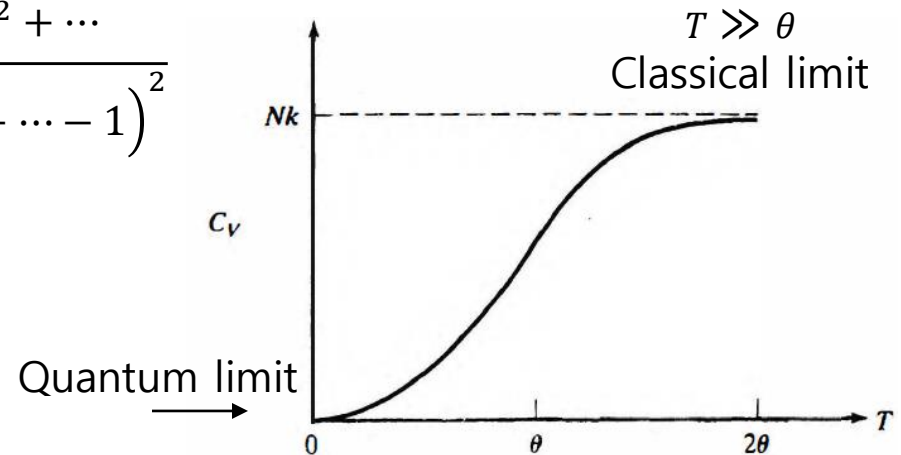
$$C_V = \left( \frac{\partial U}{\partial T} \right)_v = Nk\theta \frac{-e^{\theta/T}(-\theta/T^2)}{(e^{\theta/T} - 1)^2} = Nk \left( \frac{\theta}{T} \right)^2 \frac{e^{\theta/T}}{(e^{\theta/T} - 1)^2}$$

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

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

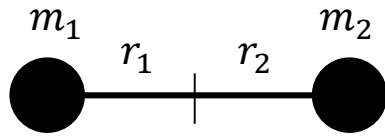
at low temperature  $\theta/T \gg 1$ ,

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



**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

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

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

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

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

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

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

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

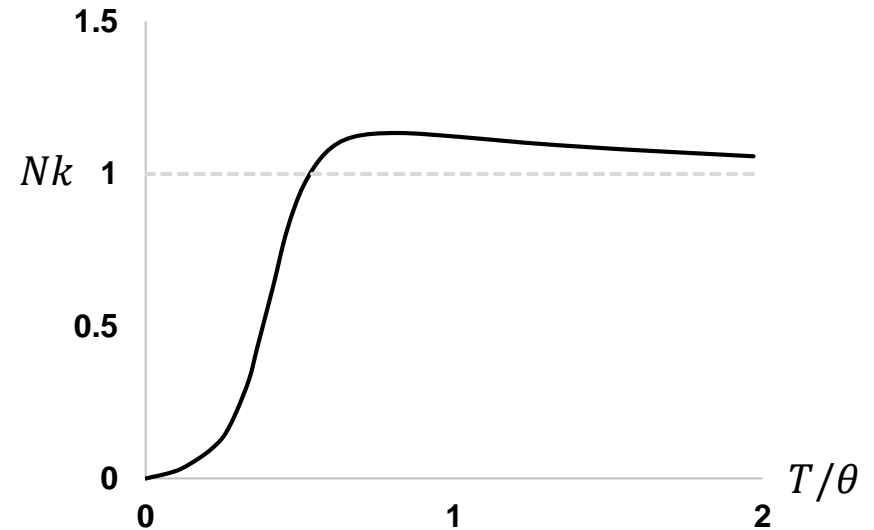
- Heat capacity of rotational energy

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

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

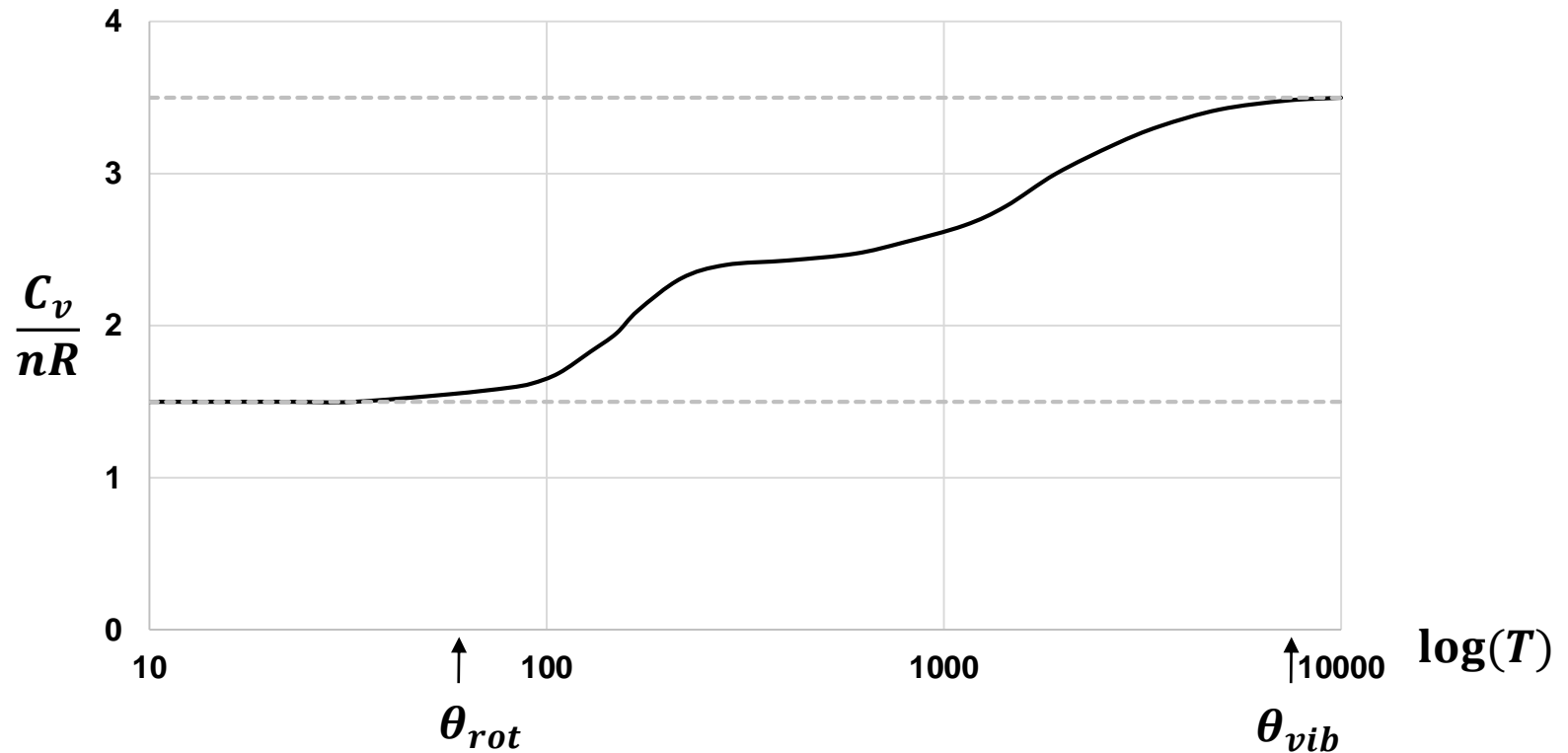


Figure Values of  $C_v/nR$  for hydrogen as a function of temperature