

## Chapter 16

# The Heat Capacity of a Solid

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# 16.1 Introduction

Ideal gas (intermolecular interactions)

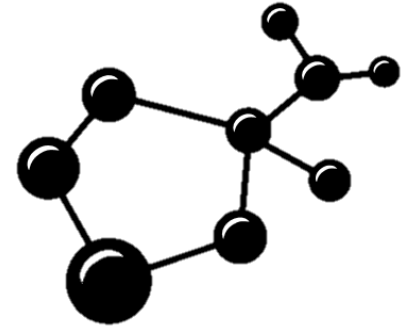
Compressed gases and Liquids

Solid state

Random motion

Pseudocrystalline structure

Crystalline structure

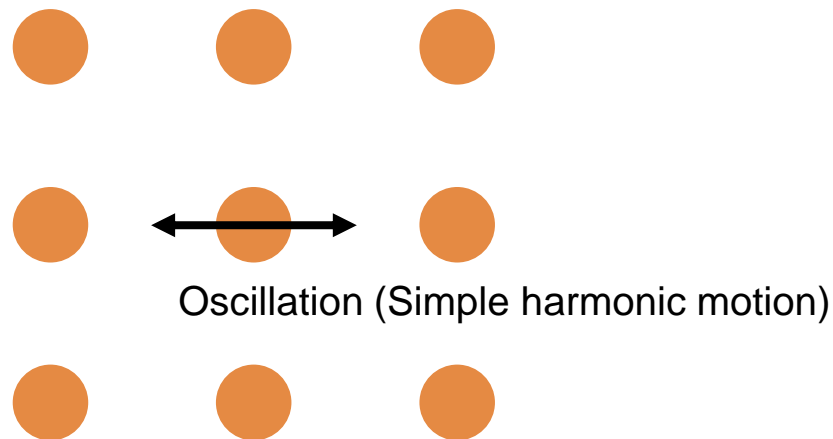


# 16.2 Einstein's Theory of the Heat Capacity of a Solid

- Einstein's Solid

Einstein assumed the solid as the crystal lattice structure of particles connected by oscillators of nature frequency  $\nu_E$ .

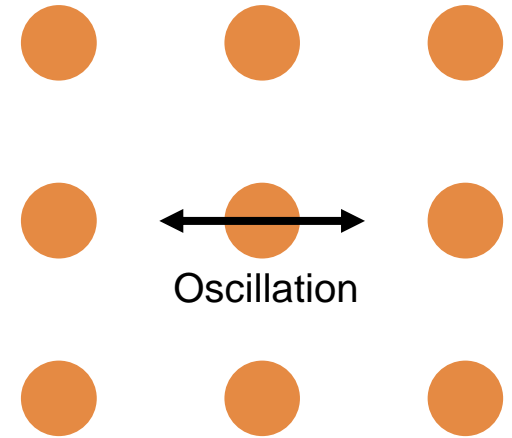
Therefore, there are  $3N$  oscillators for a solid with  $N$  particles.



# 16.2 Einstein's Theory of the Heat Capacity of a Solid

- For each molecule,

$$x - dir. \begin{cases} \frac{1}{2}kT & \text{for kinetic energy} \\ \frac{1}{2}kT & \text{for potential energy} \\ \rightarrow kT & \text{mean total energy} \end{cases}$$



Since the molecules of a solid are free to oscillate in three dimensions, a mean energy  $3kT$  is assigned to each molecule.

- At moderate  $T$ ,

$$U = 3NkT = 3n\bar{R}T$$

$$u = \frac{U}{n} = 3\bar{R}T \quad \text{Internal energy per mole}$$

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v = 3\bar{R} \quad \text{Dulong-Petit Relation}$$

# 16.2 Einstein's Theory of the Heat Capacity of a Solid

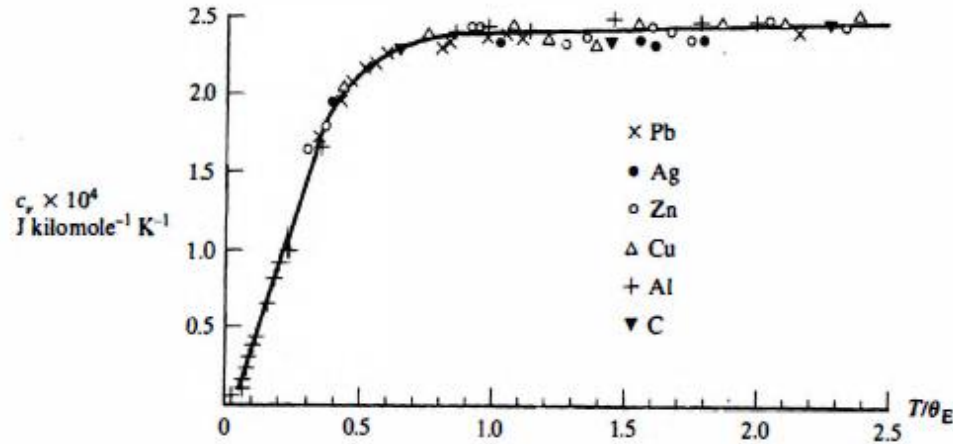


Fig. The specific heat capacity of various solids as a function of  $T/\theta_E$ .

At high temperatures,  $C_v$  is very nearly equal to the classical value  $3\bar{R}$ , but it decreases to zero at 0 K.

At low temperatures, Einstein suggested that quantum theory should be applied to this problem.

## 16.2 Einstein's Theory of the Heat Capacity of a Solid

- At low temperatures, energy level of simple harmonic oscillator

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

- The partition function

$$Z = \sum \exp \left[ - \left(n + \frac{1}{2}\right) h\nu / kT \right] = \frac{\exp(-\frac{h\nu}{2kT})}{1 - \exp(-\frac{h\nu}{kT})}$$

$$\frac{N_n}{N} = \frac{\exp(-\frac{\varepsilon_n}{kT})}{Z} = \frac{\exp \left[ - \frac{\left(n + \frac{1}{2}\right) h\nu}{kT} \right]}{Z}$$

- For  $3N$  simple harmonic independent oscillators, the total energy is

$$E = 3N \sum \left( \frac{N_n}{N} \varepsilon_n \right) = 3N \frac{\sum \left(n + \frac{1}{2}\right) h\nu \cdot \exp \left[ - \left(n + \frac{1}{2}\right) h\nu / kT \right]}{Z}$$

# 16.2 Einstein's Theory of the Heat Capacity of a Solid

- The total energy is

$$E = 3N \frac{\sum \left( n + \frac{1}{2} \right) h\nu \cdot \exp \left[ - \left( n + \frac{1}{2} \right) h\nu / kT \right]}{Z}$$

$$= 3N \frac{\sum \left( nh\nu + \frac{1}{2} h\nu \right) \cdot \left[ \exp \left( \frac{-nh\nu}{kT} \right) \exp \left( \frac{-h\nu}{2kT} \right) \right]}{\exp \left( \frac{-h\nu}{2kT} \right) \sum \exp \left( \frac{-nh\nu}{kT} \right)}$$

$$= 3N \frac{1}{2} h\nu + 3N \frac{\sum nh\nu \cdot \exp \left( \frac{-nh\nu}{kT} \right)}{\sum \exp \left( \frac{-nh\nu}{kT} \right)} = kT^2 \frac{\partial}{\partial T} \ln \sum \exp \left( \frac{-nh\nu}{kT} \right) = \frac{h\nu \cdot \exp \left( \frac{-h\nu}{kT} \right)}{1 - \exp \left( \frac{-h\nu}{kT} \right)}$$

$$* \frac{\partial}{\partial T} \ln \sum \exp \left( \frac{-nh\nu}{kT} \right) = \frac{\partial}{\partial T} \ln \left[ 1 + \exp \left( \frac{-h\nu}{kT} \right) + \exp \left( \frac{-2h\nu}{kT} \right) + \dots \right] \approx \frac{\partial}{\partial T} \ln \frac{1}{1 - \exp \left( \frac{-h\nu}{kT} \right)} = \frac{\exp \left( \frac{-h\nu}{kT} \right) \cdot \frac{h\nu}{kT^2}}{1 - \exp \left( \frac{-h\nu}{kT} \right)}$$

- Equation for the vibrational energy of an Einstein solid

$$\therefore E = \frac{3N}{2} h\nu + \frac{3Nh\nu \cdot \exp \left( \frac{-h\nu}{kT} \right)}{1 - \exp \left( \frac{-h\nu}{kT} \right)}$$

## 16.2 Einstein's Theory of the Heat Capacity of a Solid

- With  $Nk = n\bar{R}$ ,

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = 3N\bar{R} \frac{-\exp\left(\frac{h\nu}{kT}\right) \frac{-h\nu}{kT^2}}{\left(\exp\left(\frac{h\nu}{kT}\right) - 1\right)^2} = 3Nk \left(\frac{h\nu}{kT}\right)^2 \frac{\exp\left(\frac{h\nu}{kT}\right)}{\left(\exp\left(\frac{h\nu}{kT}\right) - 1\right)^2}$$

- The Einstein temperature,  $\theta_E$  is defined as  $\theta_E = \frac{h\nu_E}{k}$
- For 1 kmole,

$$C_v = 3\bar{R} \left(\frac{\theta_E}{T}\right)^2 \frac{\exp\left(\frac{\theta_E}{T}\right)}{\left(\exp\left(\frac{\theta_E}{T}\right) - 1\right)^2}$$



# 16.2 Einstein's Theory of the Heat Capacity of a Solid

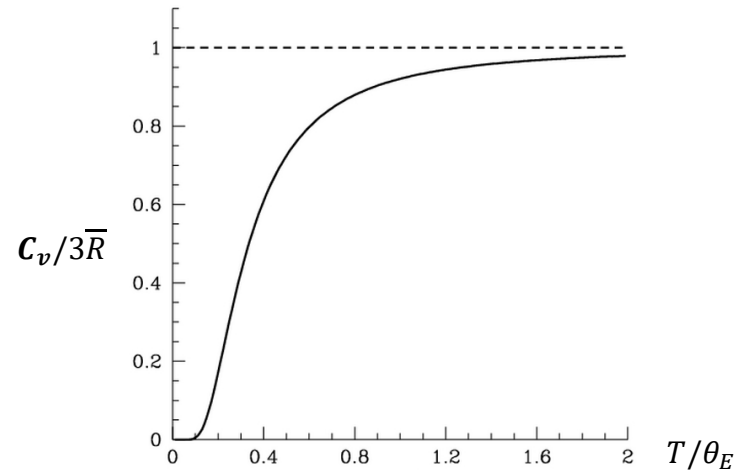


Fig. Specific heat as function of Einstein temperature

- $\theta_E = ?$

It is not possible to find a value of  $\theta_E$  which gives a good agreement with experiments at both high and low temperatures.

1. Proper  $\theta_E$  gives a good agreement at high temperatures,
2. At low temperatures  $\rightarrow C_{v,exp.} > C_{v,theory}$
3. When  $T \rightarrow 0$ , comparison with experiment is not satisfactory.

# 16.2 Einstein's Theory of the Heat Capacity of a Solid

- Einstein

Einstein theory assumes that all the molecules oscillate with the **same frequency  $\nu$**

- Nernst and Lindemann

Nernst and Lindemann assume that the molecules of a solid could oscillate at **two frequencies,  $\nu$  and  $2\nu$**

- Born, Von Karman, and Debye

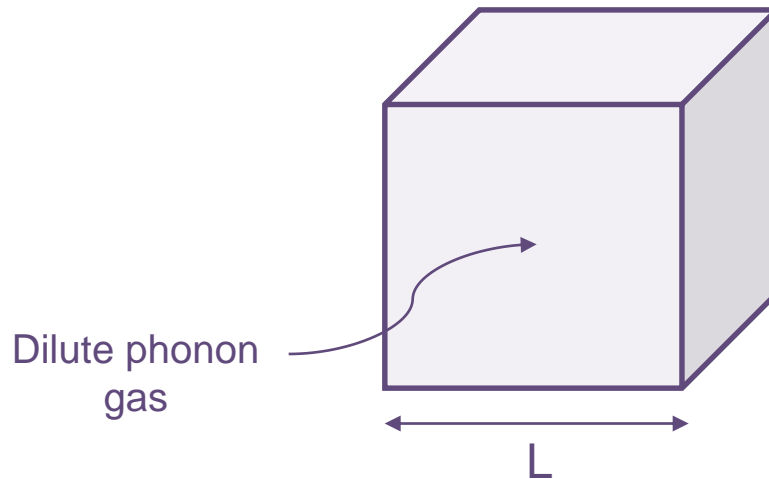
They considered that the thermal vibrations of the individual molecules could be replaced by a set of stationary elastic waves having a **continuous range of frequencies up to a certain maximum value,  $\nu$ ,  $2\nu, \dots, \nu_{max}$**

# 16.3 Debye's Theory of the Heat Capacity of a Solid

- Debye's solid

Debye assumed solid as a continuous elastic solid composed of particles called phonon with stationary elastic sound waves.

Therefore a solid of Debye's theory is viewed as phonon gas.



# 16.3 Debye's Theory of the Heat Capacity of a Solid

- Phonon

The Debye theory of solids, where the bosons are the excitations of vibrational modes known as phonons

The principal difference between Einstein's description and Debye's model is in the assumption about the frequency spectrum of the lattice vibration, shown graphically in Fig.

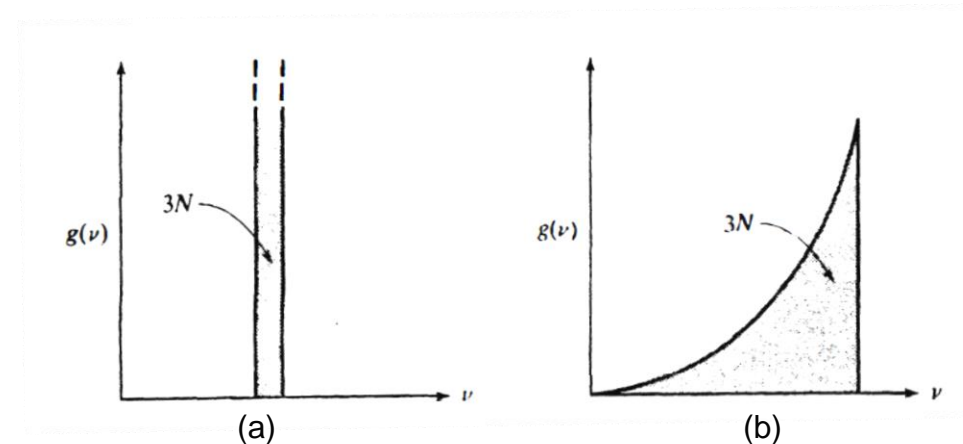


Fig. Frequency spectra of crystal vibrations:

(a) Einstein model; (b) Debye model.

## 16.3 Debye's Theory of the Heat Capacity of a Solid

There is no restriction on the number of phonons per energy level.

Thus, phonons are bosons.

The occupation number must be given by the Bose-Einstein distribution.

$$f(\epsilon_i) \equiv \frac{N_i}{g_i} = \frac{1}{e^{(\epsilon_i - \cancel{\mu})/kT} - 1}$$

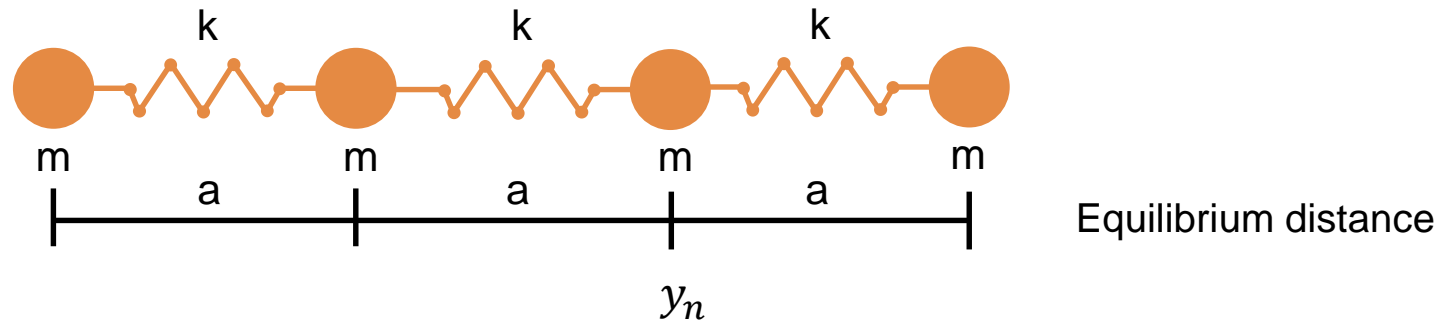
~~μ~~  
0

In this expression, the chemical potential  $\mu$  must be set equal to zero.

Because the total number  $N$  of phonons is not an independent variable but rather is determined by the volume and temperature of the particular crystal being considered.

# 16.3 Debye's Theory of the Heat Capacity of a Solid

- Quantum waves in a one-dimensional box



$$m \frac{d^2 y_n}{dx^2} = k(y_{n+1} - y_n) - k(y_n - y_{n-1})$$

$$y_n = A \cos 2\pi \left( vt - \frac{na}{\lambda} \right) \quad (v: \text{frequency}, \lambda: \text{wave length})$$

# 16.3 Debye's Theory of the Heat Capacity of a Solid

- Quantum waves in a one-dimensional box

Wave function

$$\psi = A \sin kx \quad \psi(0) = \psi(L) = 0$$

$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{L} \quad (n = 1, 2, 3 \dots),$$

Wave velocity

$$c = \lambda\nu$$

$$n = \frac{2L}{\lambda} = \frac{2L}{c} \nu = \frac{2V^{1/3}}{c} \nu \quad (V = L^3)$$

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

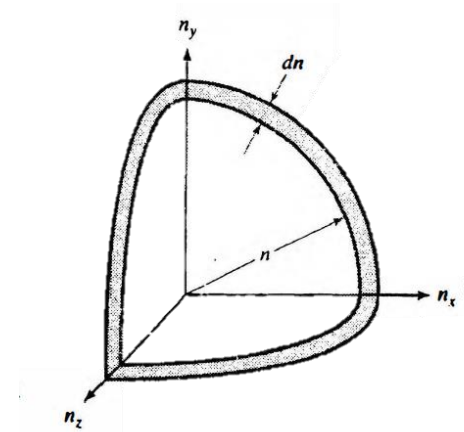


Fig. A shell of thickness  $dn$  of an octant of a sphere of radius  $n$

# 16.3 Debye's Theory of the Heat Capacity of a Solid

- Density of frequency distribution

$g(\nu)d\nu$  : the number of possible frequencies in the range  $\nu$  to  $\nu + d\nu$

$$g(\nu)d\nu = \frac{1}{8} 4\pi n^2 dn = \frac{\pi}{2} n^2 dn$$

$$= \frac{\pi}{2} \frac{4V^{2/3}}{c^2} \nu^2 \frac{2V^{1/3}}{c} d\nu = \frac{4\pi V}{c^3} \nu^2 d\nu$$

Because there are  $3N$  oscillators, there must be upper limit of frequency,  $\nu_m$ .

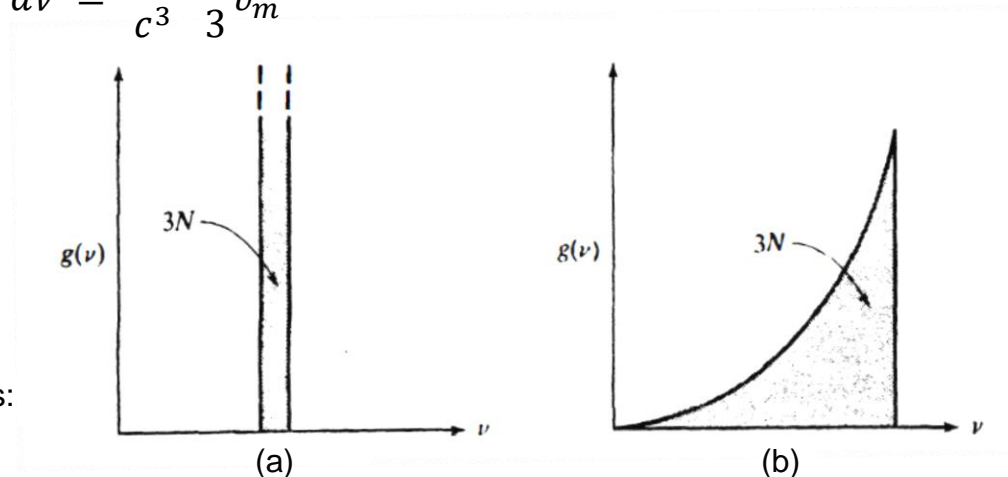
$$3N = \int_0^{\nu_m} g(\nu)d\nu = \int_0^{\nu_m} \frac{4\pi V}{c^3} \nu^2 d\nu = \frac{4\pi V}{c^3} \frac{1}{3} \nu_m^3$$

$$\nu_m \propto \left(\frac{N}{V}\right)^{1/3}$$

$$\left(\frac{N}{V} : \frac{1}{\text{average interatomic spacing}}\right)$$

Fig. Frequency spectra of crystal vibrations:

(a) Einstein model; (b) Debye model.





# 16.3 Debye's Theory of the Heat Capacity of a Solid

- No restriction on the number of phonons per energy level. Thus phonons are bosons. So that phonon gas follows Bose-Einstein statistics.

$$\frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{(\varepsilon-\mu)/kT} - 1} \quad \mu = 0, \quad \varepsilon = h\nu$$

$$N(\nu)d\nu = \frac{g(\nu)d\nu}{e^{h\nu/kT} - 1} = \begin{cases} \frac{9N}{\nu_m^3} \frac{\nu^2 d\nu}{e^{h\nu/kT} - 1} & \nu \leq \nu_m \\ 0 & \nu > \nu_m \end{cases}$$

- The total energy

$$U = \int_0^{\nu_m} \left( \frac{1}{2}h\nu + \frac{h\nu}{e^{h\nu/kT} - 1} \right) g(\nu) d\nu$$

# of photons  $\nu$  to  $\nu + d\nu$

$$= \int_0^{\nu_m} \boxed{h\nu N(\nu) d\nu} + \int_0^{\nu_m} \frac{1}{2} \boxed{h\nu g(\nu) d\nu}$$

# of possible frequencies

$$U_0 = \int_0^{\nu_m} \frac{1}{2} h\nu \frac{4\pi V}{c^3} \nu^2 d\nu = \frac{2\pi Vh}{c^3} \int_0^{\nu_m} \nu^3 d\nu$$

$$= \frac{\pi Vh}{2c^3} \nu^4 = \frac{9}{8} N h \nu_m$$

$$U - U_0 = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu^3 d\nu}{e^{h\nu/kT} - 1}$$

## 16.3 Debye's Theory of the Heat Capacity of a Solid

Debye temperature  $\theta_D$  is defined as  $\theta_D \equiv \frac{h\nu_m}{k}$

$$U - U_0 = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu^3 d\nu}{e^{h\nu/kT} - 1}$$

$$C_v = \frac{\partial U}{\partial T} = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{d}{dT} \left( \frac{1}{e^{h\nu/kT} - 1} \right) h\nu^3 d\nu$$

$$= \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{\frac{h\nu}{kT^2} e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} h\nu^3 d\nu$$

$$= \frac{9Nh^2}{\nu_m^3} \frac{1}{kT^2} \int_0^{\nu_m} \frac{\nu^4 e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} d\nu$$

$$\text{Let } x = \frac{h\nu}{kT}, \quad x_m = \frac{h\nu_m}{kT} = \frac{\theta_D}{T}$$

$$= 9Nk \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

## 16.3 Debye's Theory of the Heat Capacity of a Solid

$$C_v = 9Nk \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

For high temperatures,  $T \gg \theta_D$  and  $x \ll 1$ . So  $e^x - 1 \approx x$ ,  $e^x = 1$ .

$$\int_0^{\theta_D/T} x^2 dx = \frac{1}{3} \left( \frac{\theta_D}{T} \right)^3$$

$$C_v \approx 9Nk \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{x^2} dx = 9Nk \left( \frac{T}{\theta_D} \right)^3 \frac{1}{3} \left( \frac{\theta_D}{T} \right)^3 = 3Nk$$

For low temperatures,  $T \ll \theta_D$

$$\int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15}$$

$$C_v = \frac{4\pi^4}{15} \left( \frac{T}{\theta_D} \right)^3 9Nk = \frac{12\pi^4}{5} Nk \left( \frac{T}{\theta_D} \right)^3 \quad \text{Debye's } T^3 \text{ law}$$