

Chapter 16

The Heat Capacity of a Solid

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16.1 Introduction

Ideal gas (intermolecular interactions)

Compressed gases and Liquids

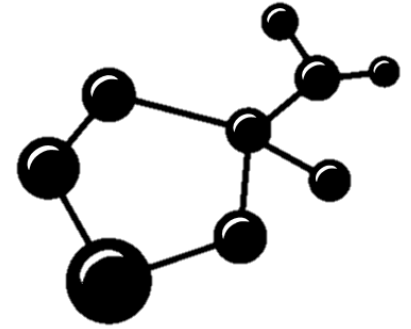
Solid state



Random motion

Pseudocrystalline structure

Crystalline structure

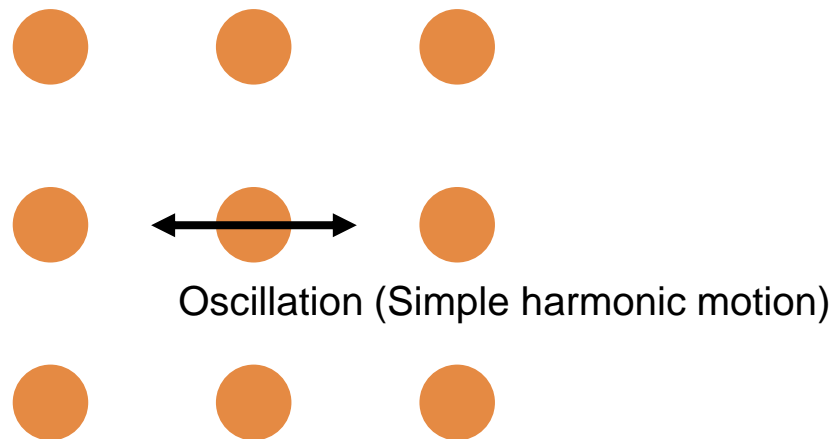


16.2 Einstein's Theory of the heat capacity of a solid

- Einstein's Solid

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

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

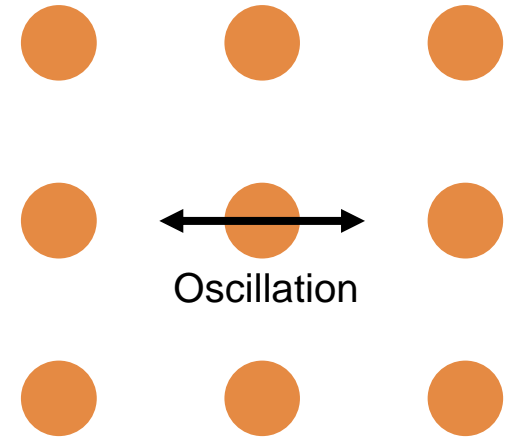


16.2 Einstein's Theory of the heat capacity of a solid

- For each molecule,

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

$\rightarrow kT$ mean total energy



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

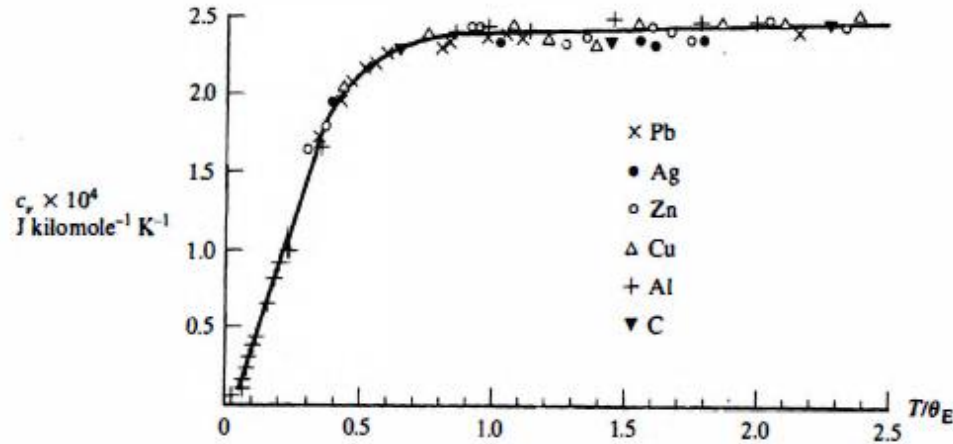


Fig. The specific heat capacity of various solids as a function of T/θ_E .

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

$$\begin{aligned}
 E &= 3N \frac{\sum \left(n + \frac{1}{2}\right) h\nu \cdot \exp \left[-\left(n + \frac{1}{2}\right) h\nu/kT\right]}{Z} \\
 &= 3N \frac{\sum \left(nh\nu + \frac{1}{2}h\nu\right) \cdot \left[\exp\left(\frac{-nh\nu}{kT}\right) \exp\left(\frac{-h\nu}{2kT}\right)\right]}{\exp\left(\frac{-h\nu}{2kT}\right) \sum \exp\left(\frac{-nh\nu}{kT}\right)} \\
 &= 3N \frac{1}{2} h\nu + 3N \frac{\sum nh\nu \cdot \exp\left(\frac{-nh\nu}{kT}\right)}{\sum \exp\left(\frac{-nh\nu}{kT}\right)} = kT^2 \frac{\partial}{\partial T} \ln \sum \exp\left(\frac{-nh\nu}{kT}\right) = \frac{h\nu \cdot \exp\left(\frac{-h\nu}{kT}\right)}{1 - \exp\left(\frac{-h\nu}{kT}\right)}
 \end{aligned}$$

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

- 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 $Nk = \bar{R}$,

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

- The Einstein temperature, θ_E is defined as

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

16.2 Einstein's Theory of the heat capacity of a solid

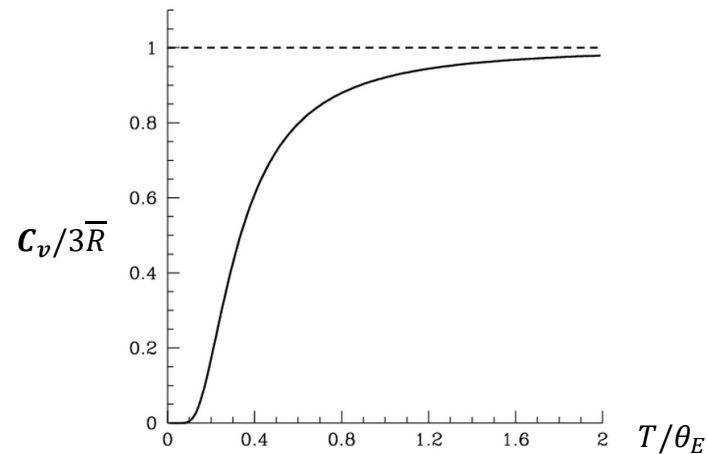


Fig. Specific heat as function of Einstein temperature

- $\theta_E = ?$

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

1. Proper θ_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 ν**

- Nernst and Lindemann

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

- Born, Von Karman, and Debye

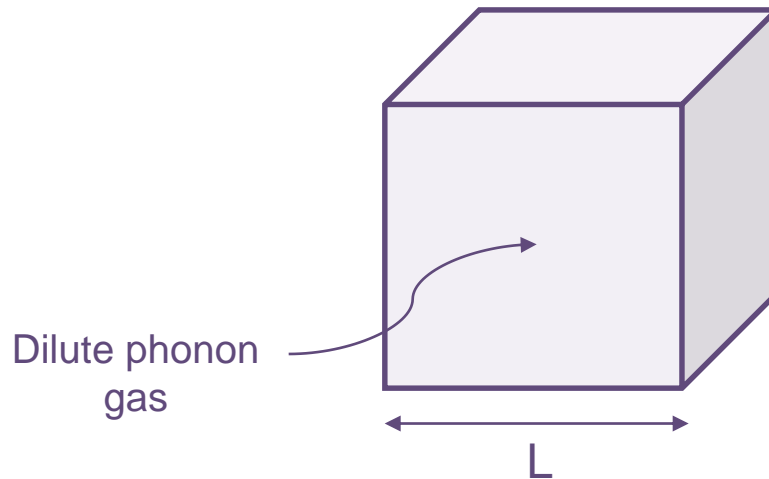
They considered that the thermal vibrations of the individual molecules could be replaced by a set of stationary elastic waves having a **continuous range of frequencies up to a certain maximum value, $\nu, 2\nu, \dots, \nu_{max}$**

16.3 Debye's theory of the heat capacity of a solid

- Debye's solid

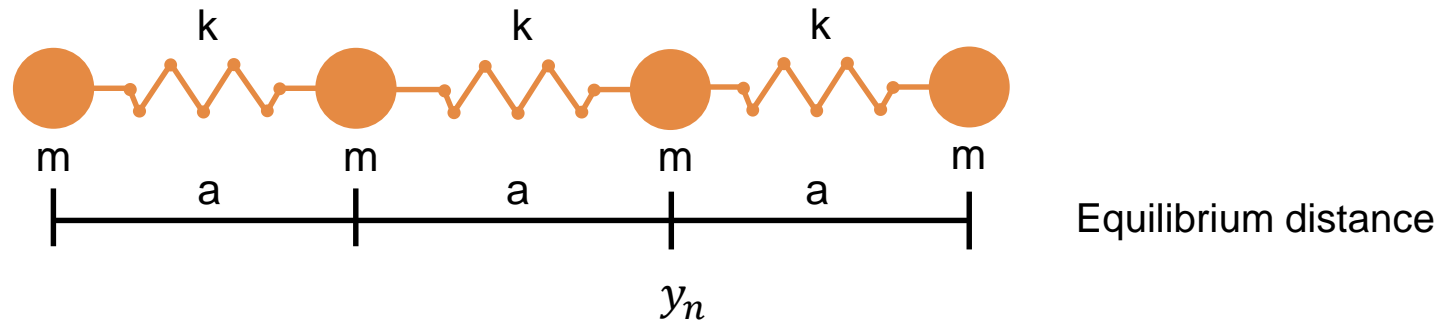
Debye assumed solid as a continuous elastic solid composed of particles called phonon with stationary elastic sound waves.

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



16.3 Debye's theory of the heat capacity of a solid

- 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

$$c = \lambda\nu$$

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

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

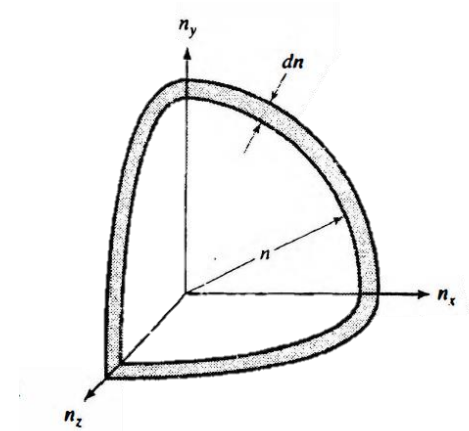


Fig. A shell of thickness dn of an octant of a sphere of radius n

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 ν 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, ν_m .

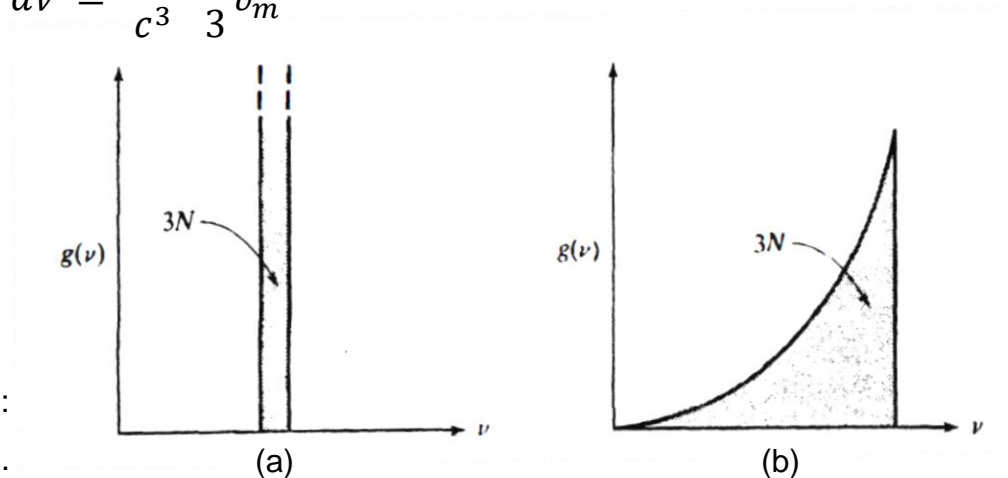
$$3N = \int_0^{\nu_m} g(\nu)d\nu = \int_0^{\nu_m} \frac{4\pi V}{c^3} \nu^2 d\nu = \frac{4\pi V}{c^3} \frac{1}{3} \nu_m^3$$

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

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

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.

$$\frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{(\varepsilon-\mu)/kT} - 1} \quad \mu = 0 = \left. \frac{\partial F}{\partial N} \right)_{T,V}$$

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

- 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 ν to $\nu + d\nu$

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

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

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

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

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

$$= \frac{9Nh^2}{\nu_m^3} \frac{1}{kT^2} \int_0^{\nu_m} \frac{\nu^4 e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} d\nu \quad \text{Let } x = \frac{h\nu}{kT}, \quad x_m = \frac{h\nu_m}{kT} = \frac{\theta_D}{T}$$

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

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, $T \ll \theta_D$

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

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