Chapter 16

The Heat Capacity
of a Solid

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16.1 Introduction

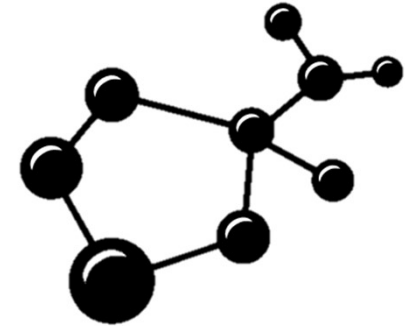Ideal gas (intermolecular interactions)   Random motion

Compressed gases and Liquids   Pseudocrystalline structure

Solid state   Crystalline structure

- Einstein's Solid

    Einstein assumed the solid as the crystal lattice structure of

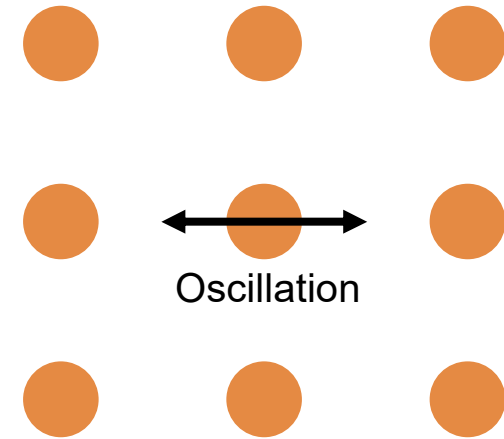   particles connected by oscillators of nature frequency ν_E.

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

Oscillation (Simple harmonic motion)
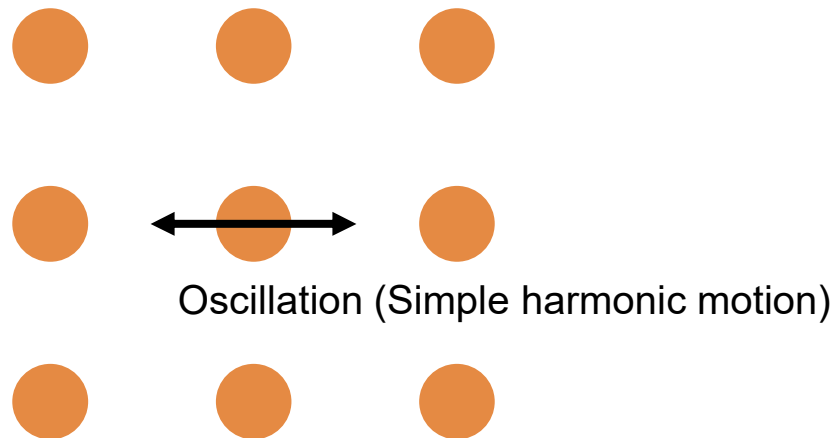
16.2 Einstein's Theory of the Heat Capacity of a Solid

- For each molecule,

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

Oscillation

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,

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

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

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v = 3\overline{R} \qquad \text{Dulong-Petit Relation}$$
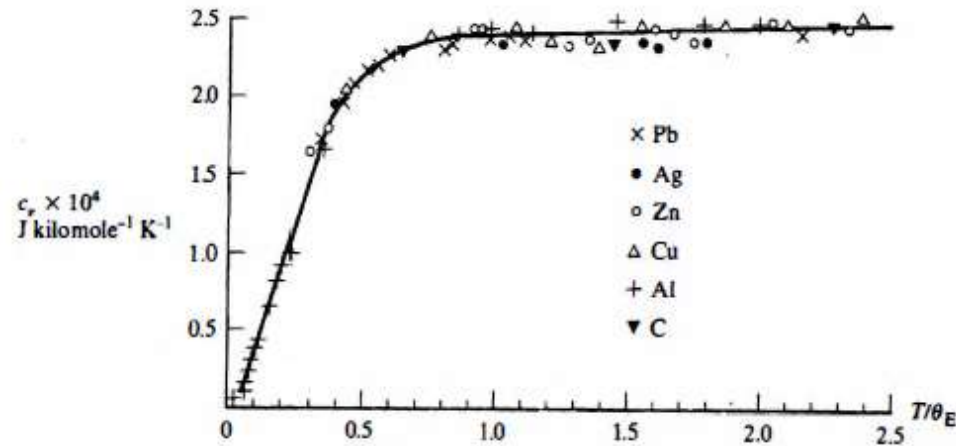
Fig. The specific heat capacity of various solids as a function of T/θ$_E$.

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

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

- At low temperatures, energy level of simple harmonic oscillator

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

- The partition function

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

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

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

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

- The total energy is

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

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

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

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

- Equation for the vibrational energy of an Einstein solid

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

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

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

- The Einstein temperature, θ_E is defined as $\quad \theta_E = \frac{h\nu_E}{k}$

- For 1 kmole,

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

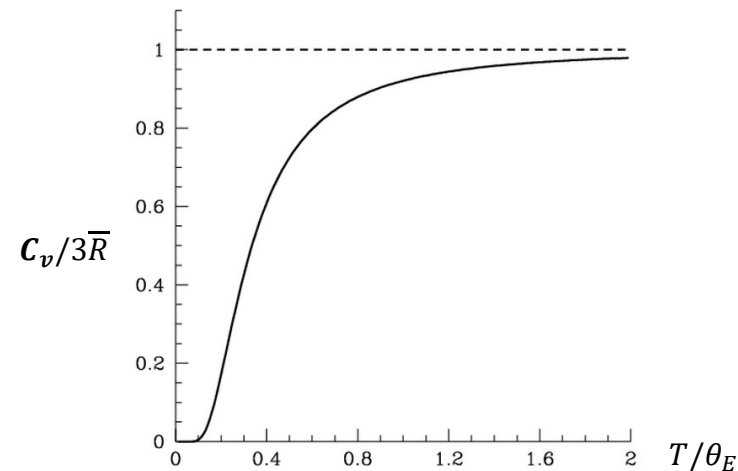# 16.2 Einstein's Theory of the Heat Capacity of a Solid

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 -> $C_{v,exp.} > C_{v,theory}$

  3. When T -> 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,** ν , $2\nu, \cdots , \nu_{max}$

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.

Dilute phonon gas

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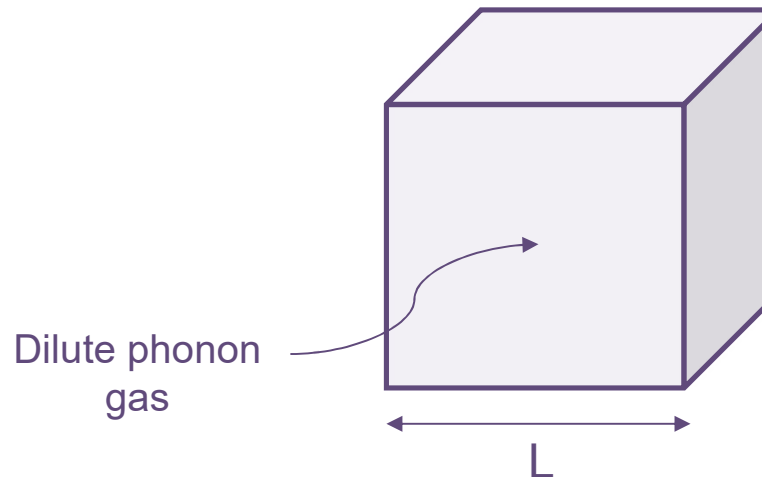
16.3 Debye's Theory of the Heat Capacity of a Solid

- 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.
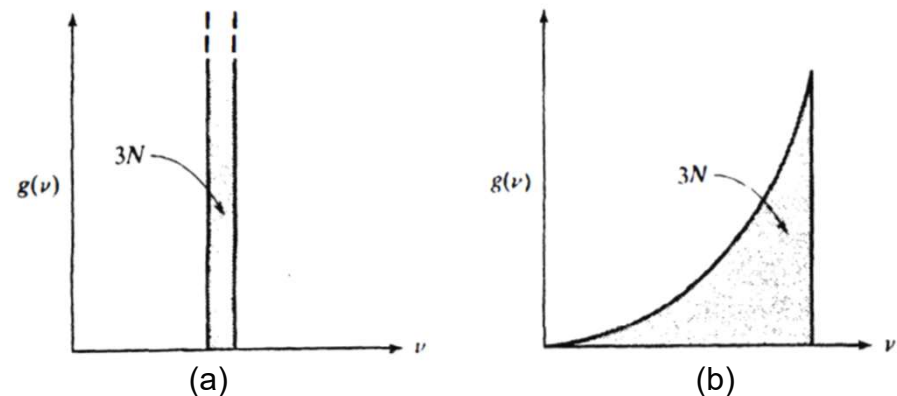
Fig. Frequency spectra of crystal vibrations:
(a) Einstein model; (b) Debye model.

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.

$$f(\epsilon_i) \equiv \frac{N_i}{g_i} = \frac{1}{e^{(\epsilon_i - \cancel{\mu})/kT} - 1}$$
$$\,_0$$

In this expression, the chemical potential μ 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.

- Quantum waves in a one-dimensional box

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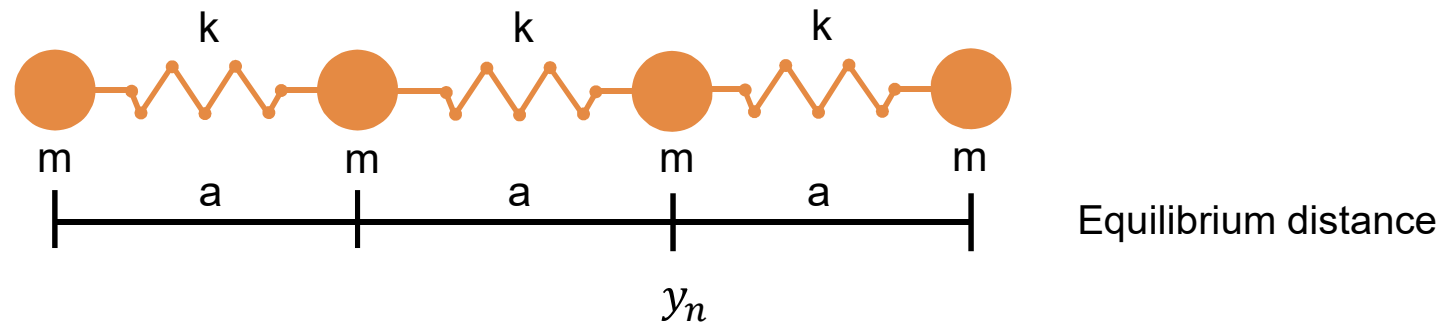
$$m \frac{d^2 y_n}{dx^2} = k(y_{n+1} - y_n) - k(y_n - y_{n-1})$$

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

- Quantum waves in a one-dimensional box

  Wave function

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

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

  Wave velocity

  $$c = \lambda v$$

  $$n = \frac{2L}{\lambda} = \frac{2L}{c}v = \frac{2V^{1/3}}{c}v \qquad (V = L^3)$$
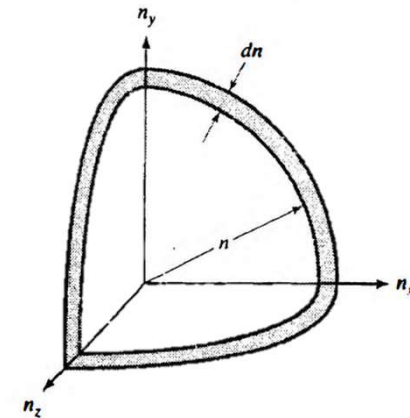
  $$n^2 = n_x{}^2 + n_y{}^2 + n_z{}^2$$

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

- Density of frequency distribution

$g(v)dv$: *the number of possible frequencies in the range v to v + dv*

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

$$= \frac{\pi}{2}\frac{4V^{2/3}}{c^2}v^2\frac{2V^{1/3}}{c}dv = \frac{4\pi V}{c^3}v^2 dv$$

Because there are 3N oscillators, there must be upper limit of

frequency, v_m.

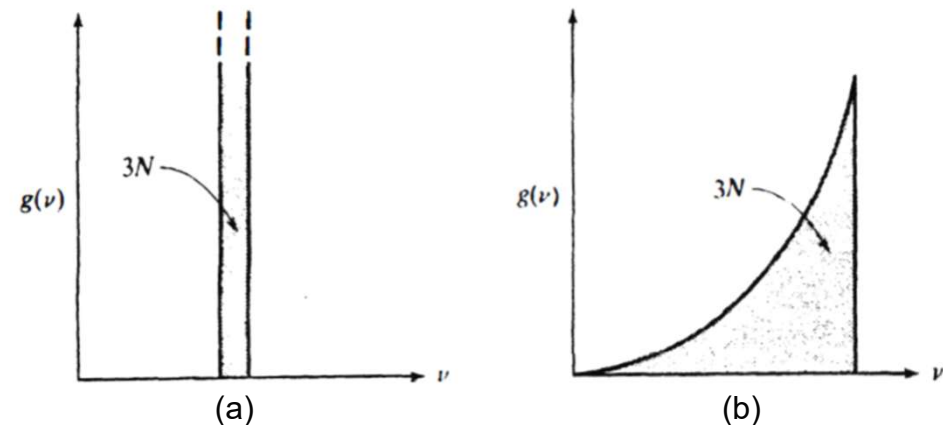$$3N = \int_0^{v_m}g(v)dv = \int_0^{v_m}\frac{4\pi V}{c^3}v^2 dv = \frac{4\pi V}{c^3}\frac{1}{3}v_m^3$$

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

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

Fig. Frequency spectra of crystal vibrations:
(a) Einstein model; (b) Debye model.

(a)

(b)

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

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

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

- 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

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

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

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

Debye temperature θ_D is defined as $\quad \boldsymbol{\theta_D} \equiv \dfrac{\boldsymbol{h v_m}}{\boldsymbol{k}}$

$$U - U_0 = \frac{9N}{v_m{}^3} \int_0^{v_m} \frac{h v^3 dv}{e^{hv/kT} - 1}$$

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

$$= \frac{9N}{v_m{}^3} \int_0^{v_m} \frac{\dfrac{hv}{kT^2} e^{hv/kT}}{(e^{hv/kT} - 1)^2} h v^3 dv$$

$$= \frac{9N h^2}{v_m{}^3} \frac{1}{kT^2} \int_0^{v_m} \frac{v^4 e^{hv/kT}}{(e^{hv/kT} - 1)^2} dv$$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ *Let* $x = \dfrac{hv}{kT},\quad x_m = \dfrac{h v_m}{kT} = \dfrac{\theta_D}{T}$

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

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

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

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

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

For low temperatures, $T \ll \theta_D$

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

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