Chapter 16

The Heat Capacity of a Solid

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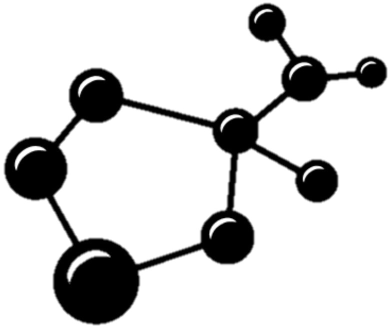
16.1 Introduction



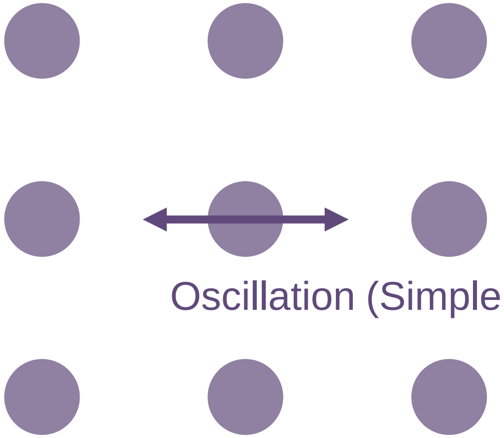
Ideal gas (intermolecular interactions)	Random motion
Compressed gases and Liquids	Pseudocrystalline structure
Solid state	Crystalline structure

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

- Einstein’s Solid

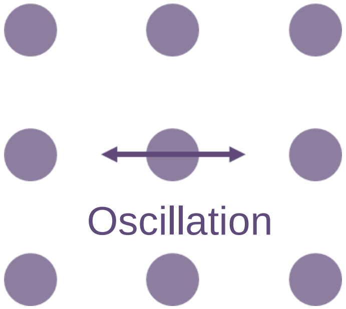
Einstein assumed the solid as the crystal lattice structure of particles connected by oscillators of nature frequency ν_E.

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



Oscillation (Simple harmonic motion)

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



- For each molecule,

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

$$\rightarrow kT \qquad mean\ total\ energy$$

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,

$$\mathrm{U} = 3\mathrm{N}kT = 3n\overline{R}T$$

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

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

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

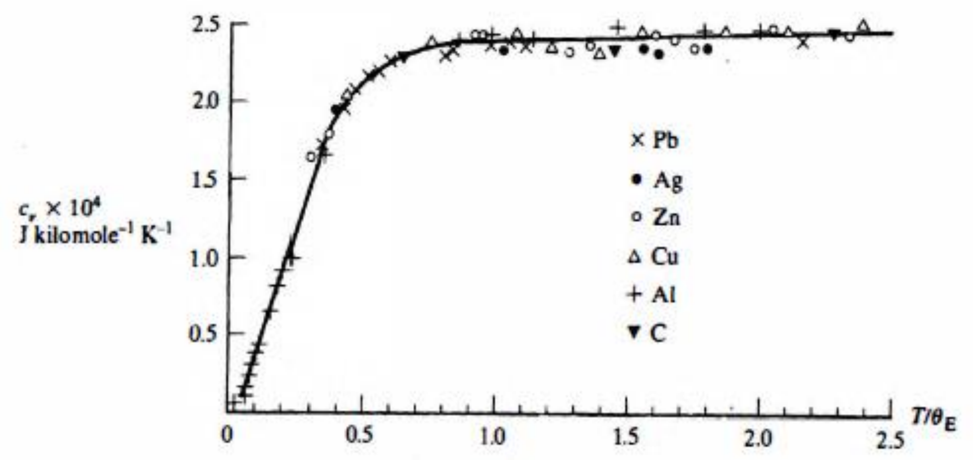


Fig. The specific heat capacity of various solids as a function of T/θ_E.

At high temperatures, C_v is very nearly equal to the classical value $3\overline{R}$, 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

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

- 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

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

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

- The total energy is

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

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

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

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

$$= \frac{\partial}{\partial T} \ln \frac{1}{1 - \exp\left(\frac{-h\nu}{kT}\right)} = \cancel{\left[\boldsymbol{1 - \exp\left(\frac{-h\nu}{kT}\right)}\right]} \frac{\boldsymbol{\exp\left(\frac{-h\nu}{kT}\right) \cdot \frac{h\nu}{kT^2}}}{\boldsymbol{\left[1 - \exp\left(\frac{-h\nu}{kT}\right)\right]^{\cancel{2}}}}$$

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

- The total energy is

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

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

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

- Equation for the vibrational energy of an Einstein solid

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

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

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

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

$$= 3Nk\left(\frac{h\nu}{kT}\right)^2 \frac{\exp\left(\frac{h\nu}{kT}\right)}{\left(\exp\left(\frac{h\nu}{kT}\right) - 1\right)^2}$$

- The Einstein temperature, θ_E is defined as

$$\theta_E = \frac{h\nu_E}{k}$$

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

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

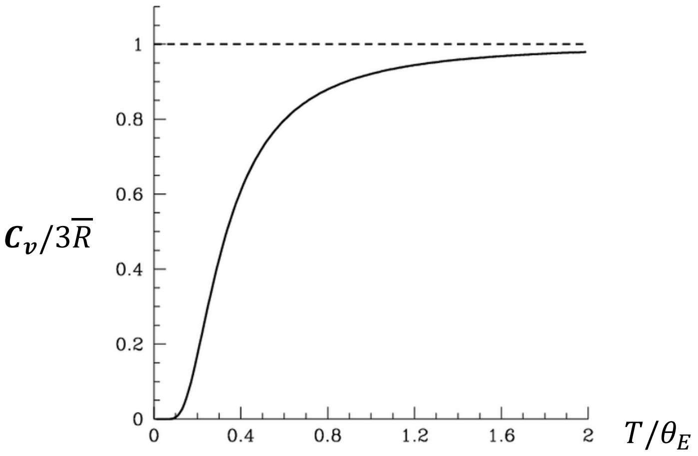


Fig. Specific heat as function of Einstein temperature

- θ_E=?

It is not possible to fine 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**

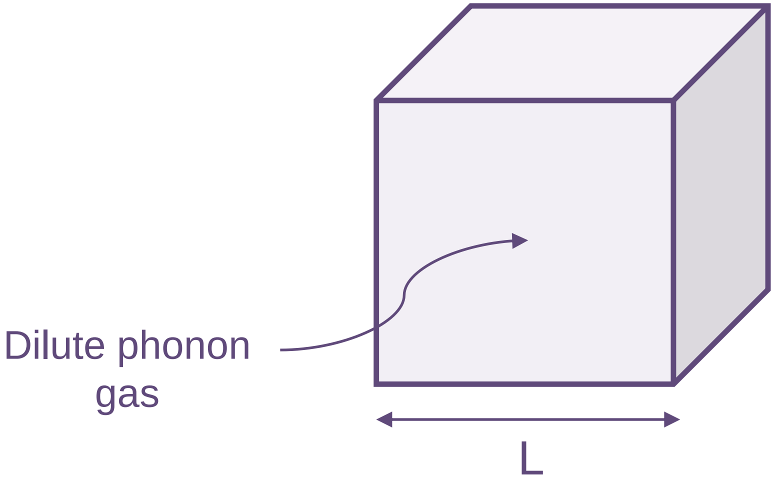
- Born, Von Karman, and Debye

  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

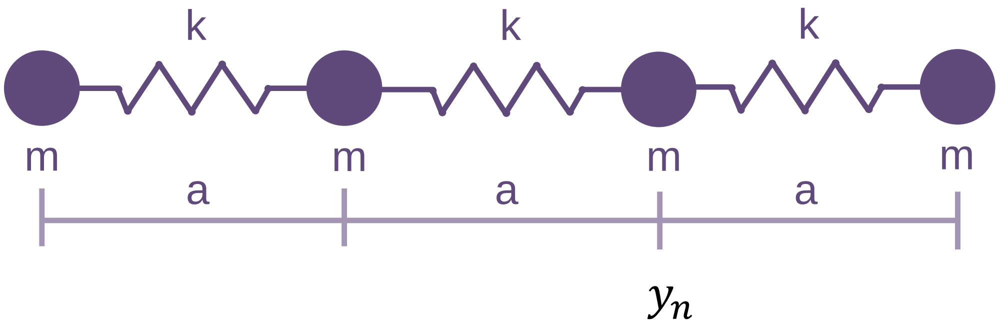
- Debye's solid

  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.



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

- Quantum waves in a one-dimensional box



Equilibrium distance

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

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

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

- Quantum waves in a one-dimensional box

Wave function

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

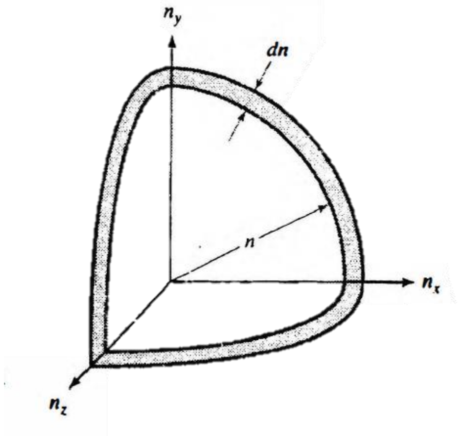
$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{L} \qquad (n = 1,2,3\cdots),$$

Wave velocity

$$c = \lambda\nu$$

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

$$\mathrm{n}^2 = {n_x}^2 + {n_y}^2 + {n_z}^2$$



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, ν_m.

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

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

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

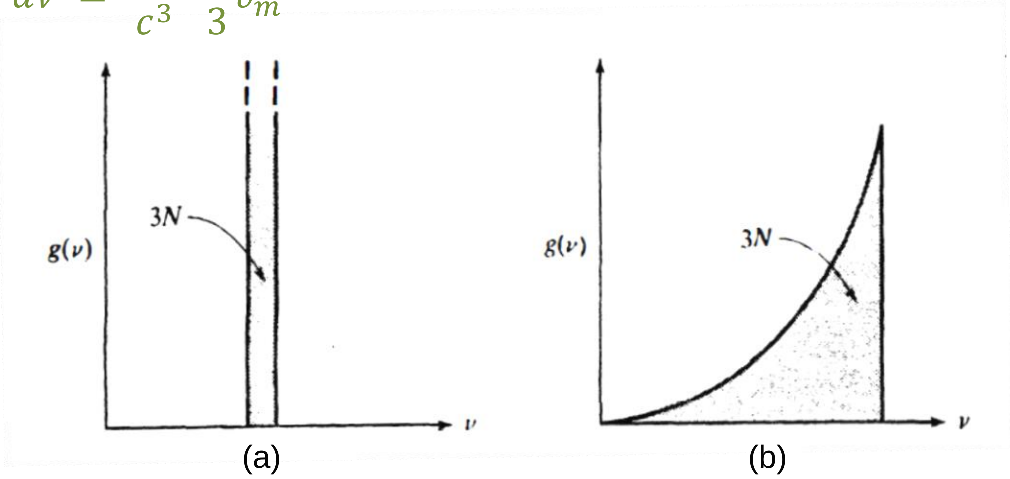


Fig. Frequency spectra of crystal vibrations:

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

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.

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

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

- 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 $\nu + d\nu$

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

# of possible frequencies

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

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

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

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

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

Debye temperature θ_D is defined as

$$\theta_D = \frac{h\nu_m}{k}$$

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

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

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

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

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

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

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 $e^x - 1 \approx x$, $e^x = 1$.

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

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

For low temperatures, $T \ll \theta_D$

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

$$\boldsymbol{C_v = \frac{4\pi^4}{15}\left(\frac{T}{\theta_D}\right)^3 9Nk = \frac{12\pi^4}{5} Nk\left(\frac{T}{\theta_D}\right)^3}$$

Debye's T^3 law