

7.E. Heat Capacity of a Debye Solid

Vibrations in a continuum are acoustic (sound) waves satisfying the wave equations

$$\begin{aligned} \left(\frac{1}{v_l^2} \frac{\partial^2}{\partial t^2} - \nabla^2 \right) \psi_l &= 0 && \text{[Longitudinal waves.]} \\ \left(\frac{1}{v_t^2} \frac{\partial^2}{\partial t^2} - \nabla^2 \right) \psi_t &= 0 && \text{[Transverse waves.]} \end{aligned} \quad (7.61a)$$

where v_l & v_t are the phase velocities.

With the periodic boundary conditions imposed, we can take the Fourier transform of the (7.61a) and get

$$\begin{aligned} \left(\frac{1}{v_l^2} \omega^2 - k^2 \right) \phi_l &= 0 \\ \left(\frac{1}{v_t^2} \omega^2 - k^2 \right) \phi_t &= 0 \end{aligned} \quad (7.61b)$$

The solutions to (7.61b) are called **normal modes** of the vibrations.

$$\begin{aligned} \omega &= v_l k = \omega_l(\mathbf{k}) && \psi_l = \psi_l \hat{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r} - i\omega_l t} \\ \omega &= v_t k = \omega_t(\mathbf{k}) && \psi_{t1} = \psi_t \hat{\mathbf{e}} e^{i\mathbf{k} \cdot \mathbf{r} - i\omega_t t} && \hat{\mathbf{e}} \cdot \hat{\mathbf{k}} = 0 \\ &&& \psi_{t2} = \psi_t \hat{\mathbf{k}} \times \hat{\mathbf{e}} e^{i\mathbf{k} \cdot \mathbf{r} - i\omega_t t} \end{aligned} \quad (7.61c)$$

where $\hat{\mathbf{e}}$ denotes unit vectors. For a cubic solid of sides L ,

$$\begin{aligned} \mathbf{k} &= \frac{2\pi}{L} \mathbf{n} \\ &= \frac{2\pi}{L} (n_x, n_y, n_z) && n_j = 0, \pm 1, \pm 2, \dots && j = x, y, z \end{aligned} \quad (7.61d)$$

Combining (7.61c & d) gives

$$[\omega_\alpha(\mathbf{k})]^2 = v_\alpha^2 k^2 = v_\alpha^2 \left(\frac{2\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) \quad (7.61)$$

Caution: Reichl used the standing wave boundary conditions.

If we mimic the Einstein solid and quantize these normal modes, we get the **Debye solid**. Treating each normal mode as a harmonic oscillator, we get

$$\hat{H} = \sum_{\mathbf{k}} \sum_{\alpha=l, t1, t2} \hbar \omega_\alpha(\mathbf{k}) \left(\hat{n}_\alpha(\mathbf{k}) + \frac{1}{2} \right) \quad (7.62)$$

where $\hat{n}_\alpha(\mathbf{k})$ is the number operator for the normal mode $\omega_\alpha(\mathbf{k})$ so that

$$\hat{n}_\alpha(\mathbf{k}) | n_\alpha(\mathbf{k}) \rangle = n_\alpha(\mathbf{k}) | n_\alpha(\mathbf{k}) \rangle \quad n_\alpha(\mathbf{k}) = 0, 1, 2, \dots \quad (7.62a)$$

Since there are no coupling between the normal modes, the partition function is easily evaluated.

$$\begin{aligned} Z(T) &= \text{Tr} \left\{ \exp \left[-\beta \sum_{\mathbf{k}} \sum_{\alpha=l, t1, t2} \hbar \omega_\alpha(\mathbf{k}) \left(\hat{n}_\alpha(\mathbf{k}) + \frac{1}{2} \right) \right] \right\} \\ &= \prod_{\mathbf{k}} \prod_{\alpha=l, t1, t2} \left\{ \sum_{n_\alpha(\mathbf{k})=0}^{\infty} \exp \left[-\beta \hbar \omega_\alpha(\mathbf{k}) \left(n_\alpha(\mathbf{k}) + \frac{1}{2} \right) \right] \right\} \\ &= \prod_{\mathbf{k}} \prod_{\alpha=l, t1, t2} \frac{\exp \left[-\frac{\beta}{2} \hbar \omega_\alpha(\mathbf{k}) \right]}{1 - \exp \left[-\beta \hbar \omega_\alpha(\mathbf{k}) \right]} \end{aligned}$$

$$= \prod_{\mathbf{k}} \prod_{\alpha=l, t1, t2} \frac{1}{2 \sinh\left[\frac{\beta}{2} \hbar \omega_{\alpha}(\mathbf{k})\right]} \quad (7.65)$$

where

$$\frac{1}{2 \sinh\left[-\frac{\beta}{2} \hbar \omega_{\alpha}(\mathbf{k})\right]} = \text{partition function for mode } \omega_{\alpha}(\mathbf{k}).$$

Thus

$$\begin{aligned} U = \langle H \rangle &= -\frac{\partial}{\partial \beta} \ln Z(T) && \text{[See Answer (b) of Ex.7.4]} \\ &= \sum_{\mathbf{k}} \sum_{\alpha=l, t1, t2} \frac{\partial}{\partial \beta} \ln \left\{ \sinh\left[\frac{\beta}{2} \hbar \omega_{\alpha}(\mathbf{k})\right] \right\} \\ &= \sum_{\mathbf{k}} \sum_{\alpha=l, t1, t2} \frac{\cosh\left[\frac{\beta}{2} \hbar \omega_{\alpha}(\mathbf{k})\right]}{\sinh\left[\frac{\beta}{2} \hbar \omega_{\alpha}(\mathbf{k})\right]} \left[\frac{1}{2} \hbar \omega_{\alpha}(\mathbf{k}) \right] \\ &= \sum_{\mathbf{k}} \sum_{\alpha=l, t1, t2} \frac{\exp\left[\frac{\beta}{2} \hbar \omega_{\alpha}(\mathbf{k})\right] + \exp\left[-\frac{\beta}{2} \hbar \omega_{\alpha}(\mathbf{k})\right]}{\exp\left[\frac{\beta}{2} \hbar \omega_{\alpha}(\mathbf{k})\right] - \exp\left[-\frac{\beta}{2} \hbar \omega_{\alpha}(\mathbf{k})\right]} \left[\frac{1}{2} \hbar \omega_{\alpha}(\mathbf{k}) \right] \\ &= \sum_{\mathbf{k}} \sum_{\alpha=l, t1, t2} \frac{\exp\left[\beta \hbar \omega_{\alpha}(\mathbf{k})\right] + 1}{\exp\left[\beta \hbar \omega_{\alpha}(\mathbf{k})\right] - 1} \left[\frac{1}{2} \hbar \omega_{\alpha}(\mathbf{k}) \right] \\ &= \sum_{\mathbf{k}} \sum_{\alpha=l, t1, t2} \left[1 + \frac{2}{\exp\left[\beta \hbar \omega_{\alpha}(\mathbf{k})\right] - 1} \right] \left[\frac{1}{2} \hbar \omega_{\alpha}(\mathbf{k}) \right] \\ &= \sum_{\mathbf{k}} \sum_{\alpha=l, t1, t2} \left\{ \frac{1}{2} \hbar \omega_{\alpha}(\mathbf{k}) + \frac{\hbar \omega_{\alpha}(\mathbf{k})}{\exp\left[\beta \hbar \omega_{\alpha}(\mathbf{k})\right] - 1} \right\} \end{aligned} \quad (7.64)$$

Taking the average of (7.62) gives

$$\langle H \rangle = \sum_{\mathbf{k}} \sum_{\alpha=l, t1, t2} \hbar \omega_{\alpha}(\mathbf{k}) \left[\langle n_{\alpha}(\mathbf{k}) \rangle + \frac{1}{2} \right] \quad (7.64a)$$

Comparing (7.64 & a) gives

$$\langle n_{\alpha}(\mathbf{k}) \rangle = \frac{1}{\exp\left[\beta \hbar \omega_{\alpha}(\mathbf{k})\right] - 1} \quad (7.65)$$

= average number of quanta in mode $\omega_{\alpha}(\mathbf{k})$.

(7.65) is known as **Planck's formula**.

For $L \gg 1$, we have

$$\sum_{\mathbf{k}} \approx \left(\frac{L}{2\pi}\right)^3 \int d^3 k = \frac{V}{(2\pi)^3} \int d^3 k \quad V = L^3 = \text{volume of solid}$$

(7.64) then becomes

$$\langle H \rangle = \sum_{\alpha=l, t1, t2} \frac{V}{(2\pi)^3} \int d^3 k \hbar \omega_{\alpha}(\mathbf{k}) \left\{ \frac{1}{\exp\left[\beta \hbar \omega_{\alpha}(\mathbf{k})\right] - 1} + \frac{1}{2} \right\} \quad (7.65a)$$

Using

$$d\omega = \nabla_{\mathbf{k}} \omega \cdot d\mathbf{k} = |\nabla_{\mathbf{k}} \omega| dk_{\perp}$$

where dk_{\perp} is the distance between the surfaces of constant ω & $\omega + d\omega$, we have

$$\begin{aligned} \int d^3 k &= \int dk_{\perp} \int_{\omega} d^2 k & \int_{\omega} d^2 k &= \text{surface of constant } \omega \\ &= \int \frac{d\omega}{|\nabla_{\mathbf{k}} \omega|} \int_{\omega} d^2 k \end{aligned}$$

For the mode

$$\omega_{\alpha}(\mathbf{k}) = v_{\alpha} \mathbf{k}$$

we have

$$|\nabla_{\mathbf{k}} \omega| = v_{\alpha} \quad \int_{\omega} d^2 k = 4\pi \left(\frac{\omega_{\alpha}(\mathbf{k})}{v_{\alpha}} \right)^2$$

$$\rightarrow \int d^3 k = \frac{4\pi}{v_{\alpha}^3} \int d\omega_{\alpha} \omega_{\alpha}^2$$

For an arbitrary function $f[\omega_{\alpha}(\mathbf{k})]$,

$$\begin{aligned} \sum_{\mathbf{k}} \sum_{\alpha=l,t1,t2} f[\omega_{\alpha}(\mathbf{k})] &= \sum_{\alpha=l,t1,t2} \frac{V}{(2\pi)^3} \int d^3 k f[\omega_{\alpha}(\mathbf{k})] \\ &= \sum_{\alpha=l,t1,t2} \frac{V}{(2\pi)^3} \frac{4\pi}{v_{\alpha}^3} \int d\omega_{\alpha} \omega_{\alpha}^2 f[\omega_{\alpha}(\mathbf{k})] \\ &= \frac{V}{2\pi^2} \left(\sum_{\alpha=l,t1,t2} \frac{1}{v_{\alpha}^3} \right) \int d\omega \omega^2 f(\omega) \\ &= \frac{V}{2\pi^2 \tilde{v}^3} \int d\omega \omega^2 f(\omega) \end{aligned} \quad (7.65b)$$

where

$$\frac{1}{\tilde{v}^3} = \sum_{\alpha=l,t1,t2} \frac{1}{v_{\alpha}^3} = \frac{2}{v_t^3} + \frac{1}{v_l^3} \quad (7.65c)$$

Introducing the density of states $g(\omega)$ by

$$\sum_{\mathbf{k}} \sum_{\alpha=l,t1,t2} f[\omega_{\alpha}(\mathbf{k})] = \int d\omega g(\omega) f(\omega) \quad (7.65d)$$

we get

$$g(\omega) = \frac{V}{2\pi^2 \tilde{v}^3} \omega^2 \quad (7.70a)$$

For a solid with N atoms, the total number of normal modes is $3N - 6$, where we have subtracted 3 translational and 3 rotational modes. Hence,

$$\begin{aligned} \sum_{\mathbf{k}} \sum_{\alpha=l,t1,t2} 1 &= \int d\omega g(\omega) = 3N - 6 \\ &\approx 3N \quad \text{for } N \gg 1 \end{aligned}$$

We therefore introduce the Debye frequency ω_D such that

$$\begin{aligned} \int_0^{\omega_D} d\omega g(\omega) &= 3N \\ &= \frac{V}{2\pi^2 \tilde{v}^3} \int_0^{\omega_D} d\omega \omega^2 \\ &= \frac{V}{6\pi^2 \tilde{v}^3} \omega_D^3 \end{aligned} \quad (7.68)$$

$$\rightarrow \omega_D^3 = \frac{18 N \pi^2 \tilde{v}^3}{V} \quad (7.69)$$

so that (7.70a) becomes

$$g(\omega) = \frac{V}{2 \pi^2} \frac{18 N \pi^2}{V \omega_D^3} \omega^2 = \frac{9 N}{\omega_D^3} \omega^2 \quad (7.70)$$

Using (7.65d) on (7.65a) gives

$$U = \int_0^{\omega_D} d\omega g(\omega) \hbar \omega \left(\frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right) \quad (7.71)$$

$$= \frac{9 N}{\omega_D^3} \int_0^{\omega_D} d\omega \hbar \omega^3 \left(\frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right)$$

$$= \frac{9}{8} N \hbar \omega_D + \frac{9 N}{\omega_D^3} \int_0^{\omega_D} d\omega \frac{\hbar \omega^3}{e^{\beta \hbar \omega} - 1} \quad (7.72)$$

The heat capacity is

$$C_N = \left(\frac{\partial U}{\partial T} \right)_N = \frac{9 N}{\omega_D^3} \int_0^{\omega_D} d\omega \frac{-\hbar \omega^3 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \left(-\frac{\hbar \omega}{k_B T^2} \right)$$

$$= \frac{9 N}{\omega_D^3} \int_0^{\omega_D} d\omega \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \left(\frac{\hbar^2 \omega^4}{k_B T^2} \right)$$

$$= \frac{9 N k_B}{\omega_D^3} \frac{1}{\hbar^2 \beta^2} \int_0^{\omega_D} d\omega \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} (\beta \hbar \omega)^4$$

$$= \frac{9 N k_B}{(\beta \hbar \omega_D)^3} \int_0^{x_D} dx \frac{e^x}{(e^x - 1)^2} x^4 \quad (7.73)$$

where

$$x = \beta \hbar \omega = \frac{\hbar \omega}{k_B T} \quad x_D = \beta \hbar \omega_D = \frac{\hbar \omega_D}{k_B T} = \frac{T_D}{T} \quad T_D = \frac{\hbar \omega_D}{k_B} \quad (7.73a)$$

Thus,

$$C_N = \frac{9 N k_B}{T_D^3} T^3 \int_0^{T_D/T} dx \frac{e^x}{(e^x - 1)^2} x^4 \quad (7.73b)$$

$$= \frac{9 n R}{T_D^3} T^3 \int_0^{T_D/T} dx \frac{e^x}{(e^x - 1)^2} x^4$$

so that the molar heat capacity is

$$c_N = \frac{C_N}{n} = \frac{9 R}{T_D^3} T^3 \int_0^{T_D/T} dx \frac{e^x}{(e^x - 1)^2} x^4 \quad (7.73c)$$

At high temperatures,

$$T \gg T_D \rightarrow x_D \ll 1$$

(7.73c) becomes

$$c_N \approx \frac{9 R}{T_D^3} T^3 \int_0^{T_D/T} dx \frac{1+x+\dots}{x^2+\dots} x^4$$

$$\approx \frac{9 R}{T_D^3} T^3 \int_0^{T_D/T} dx x^2$$

$$= \frac{9 R}{T_D^3} T^3 \frac{1}{3} \left(\frac{T_D}{T} \right)^3$$

$$= 3 R \quad (7.73d)$$

From the equipartition theorem, each oscillator has an average energy $\langle h \rangle = k_B T$ since there are 2 quadratic terms in the Hamiltonian. For $3 N$ normal modes,

$$U = 3 N k_B T = 3 n R T \quad \rightarrow \quad C_N = 3 n R$$

in agreement with (7.73d).

At low temperatures, $T \ll T_D$, (7.73) becomes

$$\begin{aligned} C_N &\approx \frac{9 N k_B}{(\beta \hbar \omega_D)^3} \int_0^\infty dx \frac{e^x}{(e^x - 1)^2} x^4 \\ &= \frac{9 N k_B T^3}{T_D^3} \int_0^\infty dx \frac{e^x}{(e^x - 1)^2} x^4 \end{aligned} \quad (7.74a)$$

Now,

$$\begin{aligned} I &= \int_0^\infty dx \frac{e^x}{(e^x - 1)^2} x^4 \\ &= \int_0^\infty dx x^4 e^{-x} (1 - e^{-x})^{-2} \\ &= \sum_{n=0}^\infty (n+1) \int_0^\infty dx x^4 e^{-x} e^{-nx} \\ &= \sum_{n=0}^\infty \frac{1}{(1+n)^4} \int_0^\infty dy y^4 e^{-y} \quad [y = (n+1)x] \\ &= \Gamma(5) \sum_{n=0}^\infty \frac{1}{(1+n)^4} \quad [\Gamma = \text{Gamma function.}] \\ &= 4! \sum_{n=1}^\infty \frac{1}{n^4} = 24 \zeta(4) \quad [\zeta = \text{Riemann-zeta function.}] \\ &= 24 \frac{\pi^4}{90} \end{aligned}$$

Hence, (7.74a) becomes

$$C_N \approx \frac{12 \pi^4 N k_B}{5 (\beta \hbar \omega_D)^3} = \frac{12 \pi^4 N k_B}{5 T_D^3} T^3 \quad (7.74)$$

which agrees with the T^3 -law observed in experiments.

Consider now the heat capacity of the Einstein solid [see (8) of Ex.7.1 in §7.B]

$$\begin{aligned} C_N &= 3 N \frac{(\hbar \omega)^2}{k_B T^2} \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2} \\ &\xrightarrow{T \rightarrow \infty} 3 N \frac{(\hbar \omega)^2}{k_B T^2} \frac{1 - \beta \hbar \omega + \dots}{(\beta \hbar \omega)^2 + \dots} \\ &\approx 3 N k_B \quad \forall \omega \end{aligned} \quad (7.74b)$$

For low temperatures, $e^{-\beta \hbar \omega} \ll 1$ and (7.74b) becomes

$$C_N \xrightarrow{T \rightarrow 0} 3 N \frac{(\hbar \omega)^2}{k_B T^2} e^{-\beta \hbar \omega}$$

which violates the T^3 law.

Thus, the Debye model is superior to the Einstein model.

In a comparison between the Einstein and Debye solids, we may use any Einstein frequency ω_E that is the same order of magnitude of the Debye frequency ω_D . Fig.7.2 shows the case $\omega_E = \omega_D$.

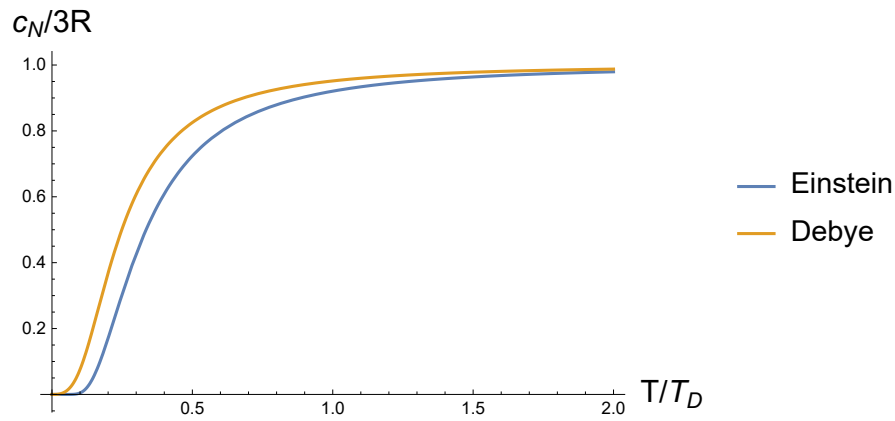


Fig.7.2. Molar heat capacities of the Einstein and Debye solids of the same characteristic frequencies.

Code

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In[*]:= (* CN for Einstein solid *)
ei[T_] :=  $\frac{1}{T^2} \frac{e^{-1/T}}{(1 - e^{-1/T})^2}$ 

In[*]:= (* CN for Debye solid *)
cn[T_] := 3 T3 NIntegrate[ $\frac{e^x x^4}{(e^x - 1)^2}$ , {x, 0, 1/T}]

In[*]:= Plot[{ei[T], cn[T]}, {T, 0, 2},
  PlotRange → All,
  AxesLabel → {"T/TD", "CN/3R"},
  PlotLegends → {"Einstein", "Debye"}
]

```