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5.62 Physical Chemistry II
Spring 2008

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Einstein and Debye Solids

Reading: Hill, pp. 98-105, 490-495

The Einstein (quantum) model (all vibrational modes have the same frequency) gave much better agreement with experiment than the Dulong-Petit (classical) model (equipartition). But as T decreases, the Einstein model C_V decreases too fast relative to the experimentally observed (approximately T^{+3} dependence) behavior of C_V . Perhaps it would be more realistic to allow the vibrational frequencies to follow a plausible, computationally convenient, but non-constant probability distribution, $\rho(\nu)$

Debye Treatment

Debye derived an improved model for the thermodynamic properties of solids by assuming that the distribution of normal mode frequencies is equivalent to that for sound waves.

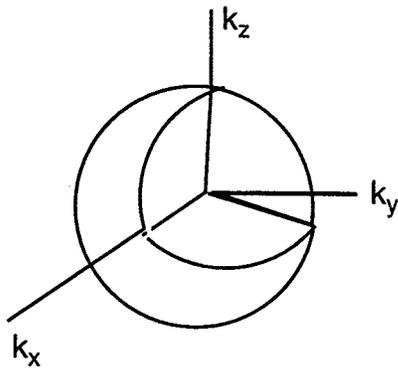
$$C_V = k \sum_{i=1}^{3N-6} \left(\frac{h\nu_i}{kT} \right)^2 \frac{e^{-h\nu_i/kT}}{(1 - e^{-h\nu_i/kT})^2}$$

$$C_V^{Debye} = k \int_0^{\nu_{\max}} d\nu \rho(\nu) \left(\frac{h\nu}{kT} \right)^2 \frac{e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2}$$

↑
density of vibrational frequencies

For sound waves traveling in a three-dimensional solid $\rho(\nu) \propto \nu^2$ [see Nonlecture derivation, below]. One way of seeing this is that $\nu = \frac{c}{2\pi} |\mathbf{k}| = \frac{c}{2\pi} (k_x^2 + k_y^2 + k_z^2)^{1/2}$, where \mathbf{k} is the wave vector such that the wave is described by $e^{i\mathbf{k}\cdot\mathbf{r}}$ and $\lambda = \frac{2\pi}{|\mathbf{k}|}$. The density of states with a given ν is the number of ways of choosing \mathbf{k} with the corresponding magnitude, $|\mathbf{k}|$.

Just as the degeneracy for a given speed state is proportional to c^2 in the kinetic theory of gases (as you'll see later in 5.62), the number of ways of picking \mathbf{k} with magnitude $k = |\mathbf{k}|$ is proportional to k^2 .



$$\text{So } \rho(v) \propto k^2 \propto v^2$$

This figure is supposed to show a spherical shell of radius $|k|$ and thickness dk . The number of \vec{k} states with $|k|$ between $|k|$ and $|k| + dk$ is proportional to the volume of this shell, $4\pi|k|^2 dk$.

Problem: What is the distribution of acoustic frequencies in an elastic solid? We are interested in the $3N$ lowest frequencies.

Solution: Find the harmonic frequencies which satisfy the boundary condition that the displacements are zero at the surface of a crystal of volume V . The wave equation for this problem is very similar to the Schrödinger Equation for a particle in a 3D infinite cubical well.

Consider the initial wave at $t = 0$, with displacements as function of position, x :

$$\Phi_0(x) = \Phi(x, t = 0).$$

At $t \neq 0$, the initial wave has moved in the $+x$ direction by $v_s t$, where v_s is the speed of sound in this medium

$$\Phi(x, t) = \Phi_0(x - v_s t).$$

Making the harmonic approximation:

$$\begin{aligned} \Phi_0(x) &= A \cos\left(\frac{2\pi x}{\lambda}\right) \\ \Phi(x, t) &= A \cos\left[\frac{2\pi(x - v_s t)}{\lambda}\right] \quad \text{where } \frac{v_s}{\lambda} = v \\ &= A \cos\left[\frac{2\pi v x}{v_s} - 2\pi v t\right] \end{aligned}$$

Find the values of v for which $\Phi(x, t) = 0$, where x is at the surface of the crystal of volume, V .

$$\text{Schrödinger Equation: } \nabla^2 \psi(x, y, z) = \frac{-2m\varepsilon}{\hbar^2} \psi(x, y, z).$$

For 3-D infinite cubical box of length a on each edge

$$\frac{2m\varepsilon_{n_x, n_y, n_z}}{\hbar^2} = \frac{\pi^2}{a^2} (n_x^2 + n_y^2 + n_z^2)$$

where $\{\varepsilon_{n_x, n_y, n_z}\}$ satisfy the boundary condition that $\psi(x, y, z) = 0$ on all six surfaces of the cube.

Now use the required values of $\{\varepsilon\}$ to solve for allowed v 's:

$$\begin{aligned} \frac{d^2 \Phi(x, t)}{dx^2} &= \frac{d^2}{dx^2} \left[A \cos \left(\frac{2\pi v x}{v_s} - 2\pi v t \right) \right] \\ &= - \left(\frac{2\pi v}{v_s} \right)^2 \Phi(x, t). \end{aligned}$$

Generalize to 3 dimensions

$$\nabla^2 \Phi(x, y, z, t) = - \left(\frac{2\pi v}{v_s} \right)^2 \Phi(x, y, z, t).$$

Comparing prefactors for Schrödinger equation and wave equation

$$\left(\frac{2\pi v}{v_s} \right)^2 = \frac{\pi^2}{a^2} (n_x^2 + n_y^2 + n_z^2).$$

So now we know how v depends on the number of standing waves in each of the three crystal directions. We want to know the density of vibrational modes as a function of frequency, $\rho(v)$, but it is easier to derive the density of modes as a function of n , $\rho(n)$, where

$$n^2 \equiv (n_x^2 + n_y^2 + n_z^2).$$

This is the equation for a sphere. So the number of modes between n and $n + dn$ is given by the volume of one octant (n_x, n_y, n_z , and n are all positive) of a spherical shell of radius n and thickness dn

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

We want $\rho(v)$

$$\rho(v) = \rho(n) \frac{dn}{dv}$$

To find the value of the Jacobian, $\frac{dn}{dv}$, for the transformation between n and v as the independent variable,

$$\begin{aligned} n &= (n_x^2 + n_y^2 + n_z^2)^{1/2} \\ \frac{2\pi v}{v_s} &= \frac{\pi}{a} n = \frac{\pi}{a} (n_x^2 + n_y^2 + n_z^2)^{1/2} \\ n &= \frac{2av}{v_s} \\ \frac{dn}{dv} &= \frac{2a}{v_s} \\ \rho(v) &= \rho(n) \frac{dn}{dv} = \frac{1}{8} (4\pi n^2) \frac{2a}{v_s} = \frac{4\pi a^3 v^2}{v_s^3} \\ a^3 &= V. \end{aligned}$$

There are 3 polarizations (x, y, or z) for each lattice mode, thus

$$\rho(v) = 3 \frac{4\pi V}{v_s^3} v^2$$

This is the frequency distribution function that goes into the Debye model.

So we have a physically reasonable model for the density of vibrational states as a function of frequency, $\rho(v)$.

But Debye had one more trick up his sleeve before inputting $\rho(v)$ to a statistical mechanical calculation of macroscopic thermodynamic properties.

There cannot be an infinite number of modes; only $3N-6 \approx 3N$. So Debye cut off the mode distribution arbitrarily at v_{\max} to give the correct number of modes.

$\rho(v) = Av^2$ where A is determined by Debye's cutoff at v_{\max}

$$3N = \int_0^{v_{\max}} \rho(v) dv = A \int_0^{v_{\max}} v^2 dv = \frac{Av_{\max}^3}{3} \Rightarrow A = \frac{9N}{v_{\max}^3} \Rightarrow \rho(v) = \frac{9N}{v_{\max}^3} v^2$$

NOTE: We still don't know what v_{\max} is, only that the mode distribution is normalized to this parameter.

Now calculate some bulk properties:

$$C_v = k \int_0^\infty \frac{(h\nu / kT)^2 e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2} \rho(\nu) d\nu$$

$$C_V^{Debye} = k \int_0^{\nu_{\max}} \frac{9N}{v_{\max}^3} v^2 \left(\frac{h\nu}{kT} \right)^2 \frac{e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2} d\nu$$

$$\text{Debye Temp.} \equiv \theta_D \equiv \frac{h\nu_{\max}}{k} \quad x = \frac{h\nu}{kT} \quad d\nu = \frac{kT}{h} dx$$

Change of variable from ν to x

$$\begin{aligned} C_V^{Debye} &= k \int_0^{\theta_D/T} \frac{9N}{v_{\max}^3} x^2 \left(\frac{kT}{h} \right)^2 x^2 \frac{e^{-x}}{(1 - e^{-x})^2} \left(\frac{kT}{h} \right) dx \\ &= 9Nk \left(\frac{kT}{h\nu_{\max}} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^{-x}}{(1 - e^{-x})^2} dx \\ &= 9Nk \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \xrightarrow{y=\theta_D/T} \frac{9Nk}{y^3} \int_0^y \frac{x^4 e^x}{(e^x - 1)^2} dx \end{aligned}$$

not a generally tabulated function

Integrate by parts

$$u = x^4$$

$$v = \frac{-1}{(e^x - 1)}$$

$$du = 4x^3 dx \quad dv = \frac{e^x}{(e^x - 1)^2} dx$$

$$\begin{aligned} C_V^{debye} &= \frac{9Nk}{y^3} \left[\frac{-x^4}{e^x - 1} \Big|_0^y + \int_0^y \frac{4x^3 dx}{e^x - 1} \right] = 3Nk \cdot \frac{3}{y^3} \left[4 \int_0^y \frac{x^3 dx}{e^x - 1} - \frac{y^4}{e^y - 1} \right] \\ &= 3Nk \cdot \left[4 \cdot \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx - \frac{3y}{e^y - 1} \right] \end{aligned}$$

$$C_V^{Debye} = 3Nk \cdot \left[4D(y) - \frac{3y}{e^y - 1} \right]$$

Debye Einstein
Function Function

Check *high* and *low* temperature limits of C_V^{Debye} :

high T limit

$$\begin{aligned} \frac{C_V^{Debye}}{3Nk} &= \frac{12}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx - \frac{3y}{e^y - 1} & x &= \frac{h\nu}{kT} & y &= \frac{\theta_D}{T} = \frac{h\nu_{max}}{kT} \\ &\approx \frac{12}{y^3} \int_0^y \frac{x^3}{(1+x+\dots-1)} dx - \frac{3y}{(1+y+\dots-1)} & T &\gg \theta_D \Rightarrow x, y \rightarrow 0 \\ &= \frac{12}{y^3} \int_0^y x^2 dx - 3 = \frac{12}{y^3} \cdot \frac{y^3}{3} - 3 = 4 - 3 = 1 \end{aligned}$$

$\therefore C_V^{Debye} \longrightarrow 3Nk$ for $T \gg \theta_D$
(agrees with classical and Einstein treatments)

low T limit

$$\begin{aligned} \frac{C_V^{Debye}}{3Nk} &= \frac{12}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx - \frac{3y}{e^y - 1} & T \rightarrow 0 &\Rightarrow x, y \rightarrow \infty \\ &\approx \frac{12}{y^3} \int_0^\infty \frac{x^3}{e^x - 1} dx - 0 \\ &= \frac{12}{y^3} \left(\frac{\pi^4}{15} \right) \end{aligned}$$

$$\therefore C_V^{Debye} = 3Nk \cdot \frac{4}{5} \pi^4 \left(\frac{T}{\theta_D} \right)^3 \text{ for } T \rightarrow 0$$

low T limit

(Note the correct T^3 behavior that agrees with experiment)

Note: The Debye T^3 heat capacity law is in excellent agreement with actual data at all temperatures!

OTHER THERMODYNAMIC FUNCTIONS CALCULATED IN DEBYE MODEL

$$\begin{aligned}
 (U - E_0)_{vib} &= kT \sum_{i=1}^{3N-6} \frac{h\nu / kT}{e^{h\nu/kT} - 1} \\
 &= kT \sum_{i=1}^{3N-6} \frac{(h\nu / kT) e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} \\
 &= kT \int_0^{\infty} \frac{(h\nu / kT) e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} \rho(\nu) d\nu
 \end{aligned}$$

$$\rho(\nu) = \frac{9N}{v_{\max}^3} \nu^2$$

$$(U - E_0)_{vib} = kT \int_0^{v_{\max}} \frac{9N}{v_{\max}^3} \nu^2 \frac{(h\nu / kT) e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} d\nu \quad x = h\nu / kT, \theta_D = \frac{h\nu_{\max}}{k}$$

$$= 3NkT \cdot \frac{3}{v_{\max}^3} \int_0^{\theta_D/T} \frac{x^3 \left(\frac{kT}{h}\right)^3 e^{-x}}{1 - e^{-x}} dx$$

$$= 3NkT \cdot 3 \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3 e^{-x}}{1 - e^{-x}} dx$$

$$= 3NkT \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx = 3NkT \cdot D(y)$$

$$y = \frac{\theta_D}{T}$$

$$D(y) = 3y^{-3} \int_0^y \frac{x^3}{e^x - 1} dx$$

$$(A - E_0)_{vib} = kT \sum_{i=1}^{3N-6} \ln(1 - e^{-h\nu_i/kT}) = kT \int_0^{v_{\max}} \rho(\nu) \ln(1 - e^{-h\nu/kT}) d\nu$$

$$= \frac{9NkT}{v_{\max}^3} \int_0^{v_{\max}} \nu^2 \ln(1 - e^{-h\nu/kT}) d\nu$$

$$= 3NkT \cdot \frac{3}{v_{\max}^3} \int_0^{\theta_D/T} x^2 \left(\frac{kT}{h}\right)^3 \ln(1 - e^{-x}) dx$$

$$= 3NkT \cdot \frac{3}{y^3} \int_0^y x^2 \ln(1 - e^{-x}) dx$$

$$= 3NkT \cdot \frac{3}{y^3} \left[\frac{x^3}{3} \ln(1 - e^{-x}) \Big|_0^y - \int_0^y \frac{x^3}{3} \frac{dx}{e^x - 1} \right]$$

Integrate by parts:

$$u = \ln(1 - e^{-x}) \quad v = \frac{x^3}{3}$$

$$du = \frac{e^{-x}}{1 - e^{-x}} dx = \frac{dx}{e^x - 1} \quad dv = x^2 dx$$

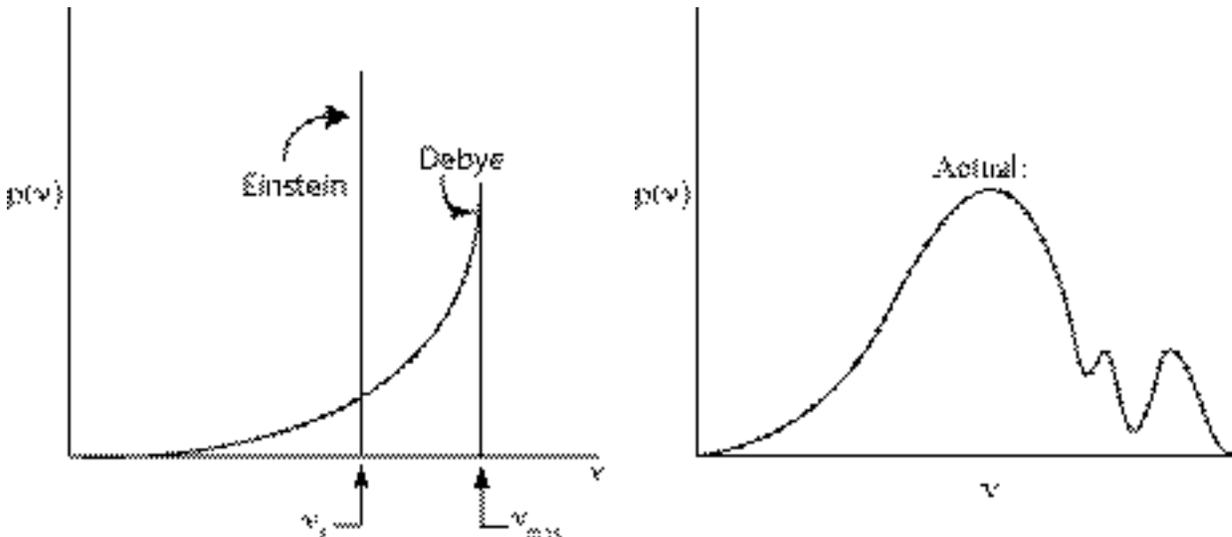
$$= 3NkT \left[\ln(1 - e^{-y}) - \frac{1}{3} \frac{3}{y^3} \int_0^y \frac{x^3 dx}{e^x - 1} \right] = 3NkT \left[\ln(1 - e^{-y}) - \frac{1}{3} D(y) \right]$$

$$S_{vib} = \frac{(U - A)_{vib}}{T} = \frac{(U - E_0)_{vib} - (A - E_0)_{vib}}{T}$$

$$= 3Nk \left[D(y) - \ln(1 - e^{-y}) + \frac{1}{3} D(y) \right]$$

$$= 3Nk \left[\frac{4}{3} D(y) - \ln(1 - e^{-y}) \right]$$

NOTE: The Debye model does not fit the phonon mode distribution of actual solids terribly well, but C_v is not too sensitive to these differences. It works well for insulating crystals but fails badly for metals. **What is special about metals?** Also, fails near melting point of solid because the harmonic approximation fails. Why? Large displacements are necessarily anharmonic.



In the actual $\rho(\nu)$, what are the resonances at high ν ?