Lecture 14 — 28 October 2008

# Review Heat Capacity of Solids

## Experimental Facts

1) Molar heat capacity is $3R \sim 24.9\ J\,K^{-1}$
2) Some exceptions: Diamond $C_V = 6.1\ J\,K^{-1}$
3) As $T \to 0$ $C_V \to 0$, required by the 3rd Law of Thermodynamics
4) For vibrations $C_V \to T^3$ as $T \to 0$ (not explained by Dulong + Petit Rules
5) $C_V$ of KE of ~~ions~~ conduction electrons $C_V \to T$ have to treat the electrons quantum mechanically to explain.

## Calculating Heat Capacity

1) 3N degrees of freedom → 3N simple harmonic oscillators
2) Quantized energy of one oscillator $E_n = (n + 1/2)\hbar\omega$
3) Take one oscillator as the system, the rest as the heat bath.
4) Derived $\bar{E} = \dfrac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$
5) Classical limit $\hbar \to 0$ $\bar{E} \to kT$ $\bar{E} \to 3N\bar{E} = 3NkT$
6) In classical limit $C_V = \left(\dfrac{\partial \bar{E}}{\partial T}\right)_V = 3Nk$ the Dulong-Petit rule
7) Average vibrational energy of the solid

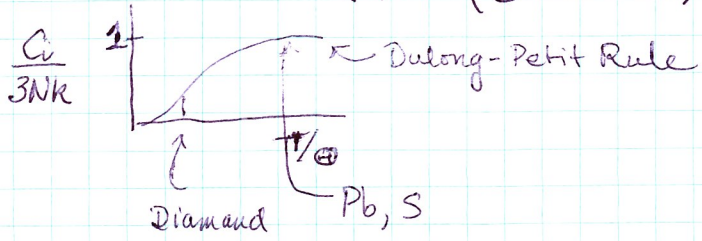
$$\bar{E} = \sum_{\alpha=1}^{3N} \frac{\hbar\omega_\alpha}{\left(e^{\hbar\omega_\alpha/kT} - 1\right)}$$

8) $$C_V = -\left(\frac{\partial \bar{E}}{\partial T}\right)_V = k\sum_{\alpha=1}^{3N} \left(\frac{k\omega_\alpha}{kT}\right)^2 \frac{e^{k\omega_\alpha/kT}}{\left(e^{\hbar\omega_\alpha/kT} - 1\right)^2}$$

9) $\omega_\alpha$ - depends on intermolecular forces
10) Atmospheric pressure gives different $C_p$
Exact expression in Maxdl (Compressibility, etc.)
11) Einstein's model treated all the $\omega_\alpha$'s the same

$$\Theta_E = \frac{\hbar\omega_E}{k}$$ dimension of temperature

$$C_V = 3Nk\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{\left(e^{\Theta_E/T} - 1\right)^2}$$ $k$ in $J\,K^{-1}$




Pb, S $\sim 24.9\ J\,K^{-1}$

$\Theta_E \gg$ Room Temperature
1300K
for diamond $\Theta_E \to C_V \sim 6.1\ J\,K^{-1}$

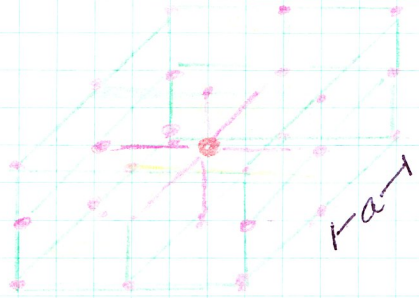
But Einstein's Model doesn't explain $C_V \propto T^3$ at low temperatures
Debye's Model Does! ...

NOTE BOOK

# Calculating $\omega_E$ DeBye Model

You can get $\omega_E$ from the elastic properties of solids

Definition of Young's Modulus $Y = \frac{\text{Stress}}{\text{Strain}}$




Treat the lattice as cubic.
Each atom ~~shares~~ is shared by 8 cubes.

$\text{Strain} = \frac{\varepsilon}{a}$ $\varepsilon$ = displacement, $a$ = interatomic distance

$\text{Stress} = \frac{m\omega_E^2 \varepsilon}{a^2}$ $m$ = mass per atom

$$Y = \frac{\varepsilon/a}{m\omega_E^2 \varepsilon/a^2} = \frac{a}{m\omega_E^2}$$

$$\omega_E = \sqrt{\frac{a}{mY}}$$

$\Theta_E = \frac{\hbar\omega_E}{k}$ can get from fitting experimental data

$\rho = \frac{m}{a^3}$ = density $M = mN_0$ $\omega_E = \frac{N_0^{1/3} Y^{1/2}}{\rho^{1/6} M^{1/3}}$

Diamond is very hard/stiff so $\omega_E$ is quite large thats why Einstein temperature is quite large

## DeBye Model

The DeBye model is successful low temperatures. It works best for small normal mode frequencies when $KT \ll$ small. Treat the solid as a homogeneous media. Neglect angular frequencies. We can treat the oscillations as elastic waves and use the wave equation:

$$\frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2} - \nabla^2\psi = 0$$

$\psi$ = displacement of an atom in the solid

$v$ ← phase velocity of the wave

The wave equation predicts either a standing or traveling wave.

Can separate $\psi = f(t)\,\phi(x,y,z)$

where $f(t) = A\cos\omega t + B\sin\omega t$

NOTE BOOK

# Lecture 14 continued... Density of States of waves in Lattice (DeBye model)

$$\frac{\partial^2 \psi}{\partial t^2} = -\omega^2 \psi$$

for standing waves

$$-\frac{\omega^2}{v^2}\psi - \nabla^2 \psi = 0$$

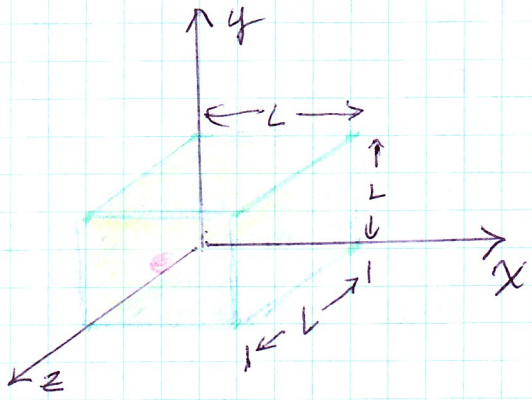
$$\left(\nabla^2 + \frac{\omega^2}{v^2}\right)\psi = 0$$

$$\nabla^2 \phi f(t) + \frac{\omega^2}{v^2} f(t) \phi = 0$$

the time independent part

$$\frac{\omega}{v} = k$$

$$\nabla^2 \phi + k^2 \phi = 0$$




Cube in cartesian coordinates the variables will be Separable

$$\psi = X(x)\,Y(y)\,Z(z)$$

Substitute to get

$$\frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} = -k^2$$

only depends on x; only depends on y; only depends on z

$$\rightarrow \frac{X''}{X} = -k_1^2 \quad \frac{Y''}{Y} = -k_2^2 \quad \frac{Z''}{Z} = -k_3^2$$

$$k_1^2 + k_2^2 + k_3^2 = +k^2$$

The solution is

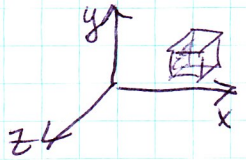
$$X = A_1 \cos(k_1 x) + B_1 \sin(k_1 x)$$
$$Y = A_2 \cos(k_2 x) + B_2 \sin(k_2 x)$$
$$Z = A_3 \cos(k_3 x) + B_3 \sin(k_3 x)$$

Subject to the boundary conditions

$$X(0) = X(L) = 0 \quad \therefore k_1 x = n_1 \pi \rightarrow k_1 = \frac{n_1 \pi}{L} \quad n_1 = 0, 1, 2, 3, \ldots$$

The normal modes for the elastic waves of a solid

$$n_1 = \frac{k_1 L}{\pi} \quad n_2 = \frac{k_2 L}{\pi} \quad n_3 = \frac{k_3 L}{\pi}$$



It is a cubic lattice and all allowed modes $n_1, n_2, n_3$ will lie of the cubic lattice. Every point on the lattice corresponds to a normal mode

There is only 1 mode per unit cell
the others are shared

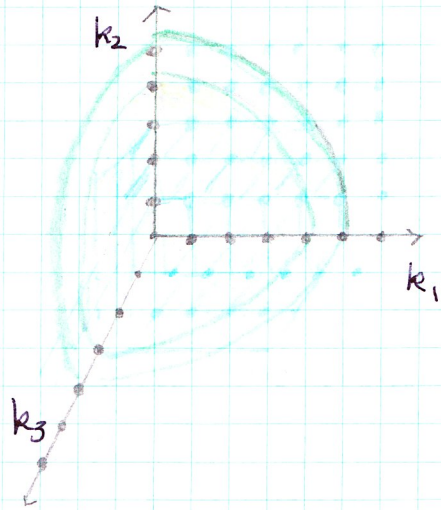
Volume of unit cell in k space $\left(\frac{L}{\pi}\right)^3$ since $k_1 = \left(\frac{\pi}{L}\right) n_1$ etc.

For most of the modes $n_1, n_2, n_3$ are quite large

There is one allowed mode per unit cell.
What is the number of allowed unit vectors in a spherical shell?

First, just consider one octant
because $n_1 > 0$ $n_2 > 0$ $n_3 > 0$
Want the volume of a spherical shell in that positive octant

$$V = \frac{1}{8}\left(4\pi k^2 dk\right)$$




The number of normal modes whose magnitude of $\vec{k}$ vector ~~fides~~ is between $\vec{k}$ and $\vec{k} + d\vec{k}$

$$\text{number of modes} = \frac{\frac{1}{8}\left(4\pi k^2 dk\right)}{\left(\pi/L\right)^3}$$

$dn = \frac{L^3 k^2}{2\pi^2} dk$ is the number of modes whose magnitude $|\vec{k}|$ is between $|\vec{k}|$ and $|\vec{k} + d\vec{k}|$

$|\vec{k}| = \frac{\omega}{v}$ when $\omega = vk$ $d\omega = v\,dk$ $\frac{d\omega}{dk} = v_g$ no dispersion

$$dn = \frac{V}{2\pi^2}\left(\frac{\omega}{v}\right)^2 \left(\frac{dk}{d\omega}\right) d\omega = \frac{V}{2\pi}\frac{\omega^2 d\omega}{v^3}$$

One more complication: There are two independent transverse modes for every $\vec{k}$ vector, and one longitudinal mode. The expression is more complicated because the velocity is different for transverse and longitudinal components.

$$dn = \frac{V}{2\pi^2}\omega^2 d\omega\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)$$

Since there's no dispersion, then can treat as an average velocity $\frac{3}{\bar{v}^3}$

$$\boxed{dn = \frac{V}{2\pi^2}\omega^2 d\omega \frac{3}{\bar{v}^3}}$$

for light, $v_t = c$ in vacuum.

NOTE BOOK