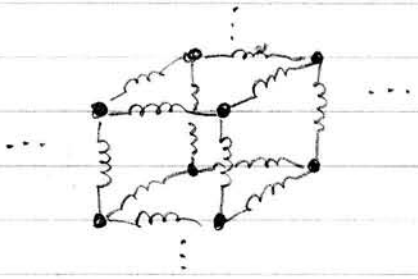
Lecture 10

A solid crystal is a collection of N atoms on a periodic lattice



Treat system as N, 3-D harmonic oscillators. Vibrations of atoms produce elastic waves that propagate through solid

In classical regime, use equipartition theorem

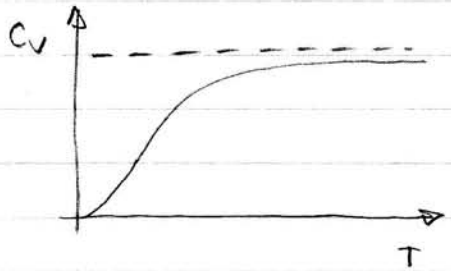
$E_n = \frac{p_n^2}{2m} + \frac{1}{2}Kx_n^2$ energy of n-th oscillator

$U_{tot} = N \cdot 3 \cdot 2 \, \frac{1}{2} k_B T = 3N k_B T$

(3-D, 2 degrees of freedom (K.E. + P.E.))

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B}$$ Dulong-Petit law

This matches data, but only when T is large



For lower T, quantum mechanical treatment is necessary:

$E_n = \hbar\omega_n\left(s_n + \frac{1}{2}\right)$ $s_n = 0, 1, 2 \cdots$ n-th oscillator

Elastic wave is quantized. Quantum of elastic wave energy is called a phonon

We have a model for quantum oscillators - Einstein model
Recall that for 1-D oscillator we found:

$$U_{osc} = \langle E_n \rangle = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \qquad \text{(ignoring zero-pt energy)}$$

Einstein model - all oscillators are identical, independent

$$\therefore \; U_{tot} = 3N \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \qquad C_V = 3N \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

(3N: 3-D # of oscillators)

For $k_B T \gg \hbar\omega$ (classical regime):

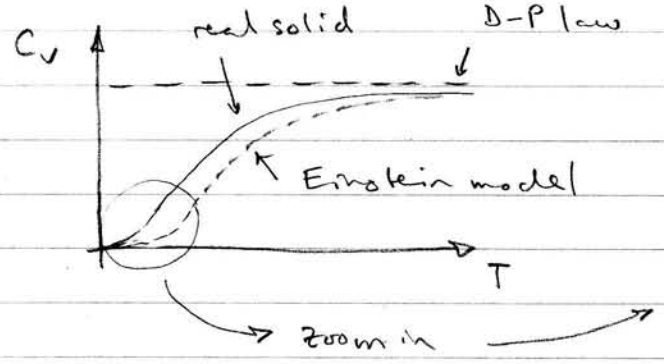
$$U_{tot} = 3N \frac{\hbar\omega}{1 + \beta\hbar\omega \cdots - 1} = 3N k_B T \qquad C_V = 3N k_B \quad \checkmark$$

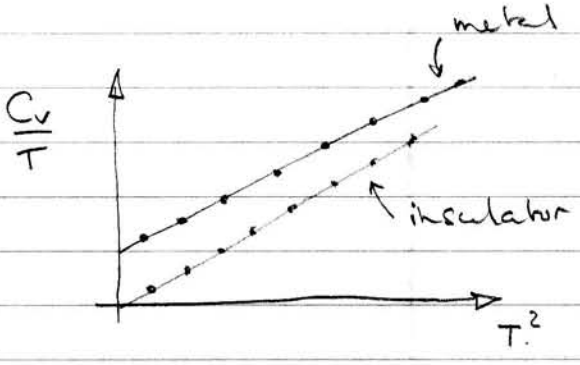
For $k_B T \ll \hbar\omega$

$$U_{tot} = 3N \hbar\omega e^{-\hbar\omega/k_B T} \qquad C_V = 3N k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 e^{-\hbar\omega/k_B T}$$

Predicts $C_V \sim e^{-\hbar\omega/k_B T}$ as $T \to 0$

However:





For an insulator: $\frac{C_V}{T} = bT^2 \quad \therefore \; C_V \sim T^3$

For a metal: $\frac{C_V}{T} = a + bT^2 \qquad C_V = aT + bT^3$

(a: due to electrons; bT^2: due to phonons)

Vibrational contribution to C_v at low T varies as T^3 not as $e^{-\hbar\omega/k_BT}$, i.e. slower than exponential

Must treat vibrations more accurately

The problem with Einstein model is that it assumes that
- the oscillators are independent
- they are identical (i.e. $\hbar\omega$ the same for all oscillators)

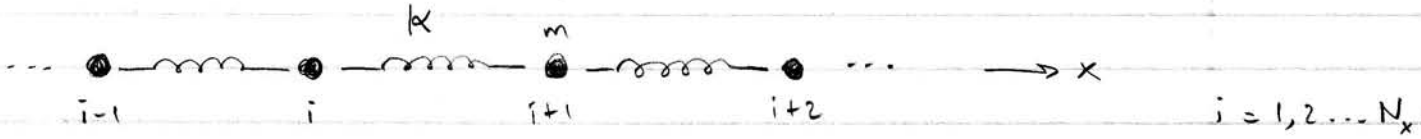
Both of these are incorrect

Debye model gets T^3 dependence

(for electronic contribution to C_v in metals, we will need some more tools before we can derive it)

Vibrational modes of a solid

- Atoms don't vibrate independently of each other
  If one moves its neighbors move too
- Consider 1-D chain of N_x identical atoms with mass m coupled with springs with stiffness K



$\leftarrow a \rightarrow$

equilibrium lattice spacing

Now displace atom i. r_i, r_{i+1} ... are positions of atoms

Force on atom $i = F_i = K(r_{i+1} - r_i - a) - K(r_i - r_{i-1} - a)$

$$m\frac{d^2r_i}{dt^2} = K(r_{i+1} - 2r_i + r_{i-1})$$

Look at: $r_{i+1} - 2r_i + r_{i-1}$

Looks like discrete version of second derivative

$$\frac{df}{dx} = \lim_{a\to 0} \frac{f(x+a) - f(x)}{a} \qquad \text{so,}$$

$$\frac{d^2f}{dx^2} = \lim_{a\to 0} \frac{[f(x+a) - f(x)] - [f(x) - f(x-a)]}{a^2} = \lim_{a\to 0} \frac{f(x+a) - 2f(x) + f(x-a)}{a^2}$$

$$\therefore \quad \frac{r_{i+1} - 2r_i + r_{i-1}}{a^2} \approx \frac{\partial^2 r}{\partial x^2} \qquad \text{provided } a \text{ is "small"}$$

$$\text{So:} \quad \frac{\partial^2 r}{\partial x^2} = \frac{m}{\kappa a^2} \frac{\partial^2 r}{\partial t^2} = \frac{1}{c_s^2} \frac{\partial^2 r}{\partial t^2}$$

This is a wave eq'n with speed $c_s = \sqrt{\kappa/m}\, a$

Vibrations act like waves (sound waves) that propagate at speed c_s (speed of sound)

$r(x,t) \sim \sin(kx - \omega t)$ $\qquad \boxed{\omega = c_s k}$ same form as EM wave

This approximation is valid as long as $\lambda = \frac{2\pi}{k} \gg a$ ("long" λ)

i.e. when $k \ll \frac{2\pi}{a}$

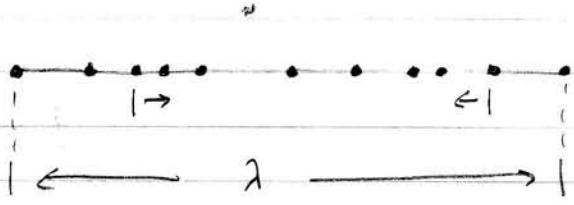
Debye model assumes this approximation is valid

For arbitrary k, solution is more involved

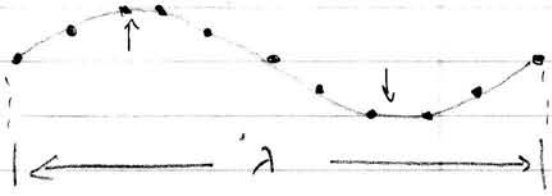
In general, for real solid, approximation $\omega = c_s k$ will always be valid for sufficiently long λ (or small k)

In 3-D, atoms can move ∥ to wave or ⊥ to it
3 polarizations: 2 transverse (⊥), 1 longitudinal (∥)

Longitudinal



Transverse



(Note this is unlike EM wave which can only be transverse)

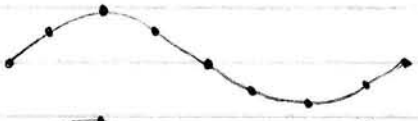
In general c_s may be different for different polarizations
We'll assume they are the same for simplicity

Counting vibrational modes

Just like EM waves in cavity, boundary conditions impose restrictions on λ (and k) of vibrational waves
Like EM waves k is quantized, with one important difference

Look at a transverse wave in 1-D chain with $L_x = N_x a$

$\lambda = 2L_x$ $\quad k_x = \frac{\pi}{L_x}$



$= L_x$ $\quad = \frac{2\pi}{L_x}$

$= \frac{2}{3}L_x$ $\quad = \frac{3\pi}{L_x}$

⋮ ⋮ ⋮

$= 2a$ $\quad = \frac{\pi}{a} = N_x \frac{\pi}{L_x}$

λ cannot be less than $2a$ because of finite spacing between atoms

$\therefore \quad k_x = \frac{n_x \pi}{L_x} \qquad n_x = 1, 2, 3 \cdots N_x$

N_x: # of atoms along x

Same for k_y, k_z

Each triplet $\{n_x, n_y, n_z\}$ defines a single mode (given polarization)

Total # of modes $= 3 N_x N_y N_z = 3N$

3: 3 polarizations; N: total # of atoms in crystal

Note similarity / difference with EM wave: quantization is the same but n_x, n_y, n_z can go to ∞ (i.e. λ can be arbitrarily short) so # of modes is ∞! (This led to UV catastrophe in classical regime)

Photon gas	Phonon gas
$\omega = ck$ always	$\omega = c_s k$ for $k \to 0$
polarization: 2 transverse	polarization: 2 transverse, 1 longitudinal
$k_x = \frac{n_x \pi}{L_x} \quad n_x = 1, 2 \cdots \infty$	$k_x = \frac{n_x \pi}{L_x} \quad n_x = 1, 2, \cdots N_x$
Total # modes: $2 \sum_{k_x k_y k_z} \to \infty$	Total # modes: $3 \sum_{k_x k_y k_z} = 3N$

$$\omega_n = c_s k_n \qquad k_n = \pi \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)^{1/2}$$

Going back to quantum harmonic oscillator energies

$$U_{tot} = \sum_{n=1}^{3N} \frac{\hbar\omega_n}{e^{\beta\hbar\omega_n} - 1}$$

n represents each mode

Replace sum with integral $\sum_{n=1}^{3N} \longrightarrow \int d\omega$

modes with energy ω, $\omega + d\omega$:

$$N(\omega)\,d\omega = 3 \cdot \frac{V}{\pi^3} V_{shell} = \frac{3V}{(2\pi)^3} 4\pi k^2 dk$$

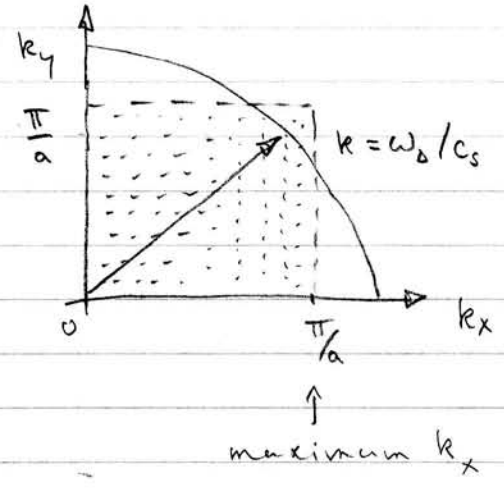
$$= \frac{3}{2}\frac{V}{\pi^2}\frac{\omega^2 d\omega}{c_s^3}$$

(compare to photon gas)

$$\Rightarrow U_{tot} = \int_0^{(?)} \frac{N(\omega)\,\hbar\omega\,d\omega}{e^{\beta\hbar\omega} - 1}$$

Wait, what is the upper limit?

Problem is that unlike photon gas, integration occurs over finite volume in k-space.



Debye used a trick

$$\int_0^{\omega_D} N(\omega)\,d\omega = 3N$$

Integrating must give correct # of modes
Replace finite volume in k-space (here a cube of side $\frac{\pi}{a}$) with a sphere with the same volume

Define ω_D Debye frequency to satisfy that condition

$$3N = \int_0^{\omega_D} N(\omega)\,d\omega = \frac{3V}{2\pi^2}\int_0^{\omega_D}\frac{\omega^2 d\omega}{c_s^3} = \frac{V}{2\pi^2}\left(\frac{\omega_D}{c_s}\right)^3$$

$$\therefore \omega_D = \left(\frac{3N}{V}\, 2\pi^2 c_s^3\right)^{1/3}$$

So $$U_{tot} = \frac{3V\hbar}{2\pi^2 c_s^3} \int_0^{\omega_D} \frac{\omega^3 d\omega}{e^{\beta\hbar\omega} - 1} \qquad \text{let } x \equiv \frac{\hbar\omega}{k_B T}$$

$$= \frac{3V\hbar}{2\pi^2 c_s^3} \left(\frac{k_B T}{\hbar}\right)^4 \underbrace{\int_0^{x_D} \frac{x^3 dx}{e^x - 1}}_{\text{function of } T} \qquad x_D \equiv \frac{\hbar\omega_D}{k_B T} \equiv \frac{\Theta_D}{T}$$

Debye temperature $\Theta_D \equiv \frac{\hbar}{k_B} c_s \left(6\pi^2 \frac{N}{V}\right)^{1/3}$

We're interested in low T limit i.e. $k_B T \ll \hbar\omega_D$ (or $T \ll \Theta_D$)

so $x_D = \frac{\Theta_D}{T} \gg 1$

$$\therefore U_{tot} \approx \frac{3V\hbar}{2\pi^2 c_s^3} \left(\frac{k_B T}{\hbar}\right)^4 \underbrace{\int_0^{\infty} \frac{x^3 dx}{e^x - 1}}_{\frac{\pi^4}{15}} \sim T^4$$

$$\therefore C_V = \left(\frac{\partial U}{\partial T}\right)_V \approx \frac{2\pi^2 V}{5} \left(\frac{k_B T}{\hbar c_s}\right)^3 k_B = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3 \sim T^3$$

Debye T^3 Law

Debye model gets both high-T ($T \gg \Theta_D$) and low-T ($T \ll \Theta_D$) correct, intermediate regime not quite right

There, $\omega = c_s k$ is no longer a valid approximation and integral over k-space must be done over correct volume. These will depend on details of crystal structure and vibrational modes and fall beyond the scope of this course (take Phys. 460 – "condensed matter physics")