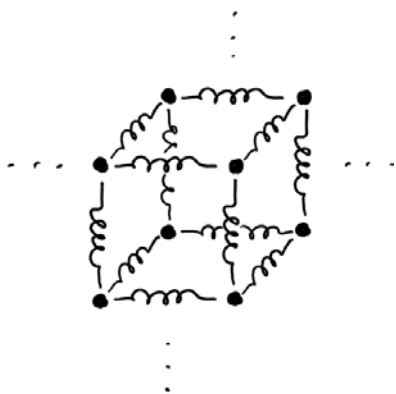## Lecture 14 – Debye model

LAST TIME: Statistical mechanics of EM waves in a cavity

TODAY: Statistical mechanics of <u>elastic</u> waves in a solid

A solid crystal is a collection of $N$ atoms arranged in a periodic lattice of volume $V = L_x L_y L_z$.

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

We've already seen treatments of oscillator systems: classical (equipartition theorem), quantum (Einstein model)

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**Question 1: Write down an expression for the heat capacity at constant volume $C_V$ of a system with $N$ 3-D harmonic oscillators in the classical regime (high $T$)**

In classical regime, we use equipartition theorem

We have $N$ atoms, in 3-D, and 2 quadratic degrees of freedom for each (K.E. and P.E. for $i$-th oscillator: $\varepsilon_i = \dfrac{p_i^2}{2m} + \dfrac{1}{2}\kappa x_i^2$ ), therefore

$$U_{tot} = N \cdot 3 \cdot 2 \cdot \frac{1}{2} k_B T = 3Nk_B T \quad \text{and} \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B$$

This is called the <u>Dulong-Petit</u> law. Matches experimental data, but only when $T$ is large

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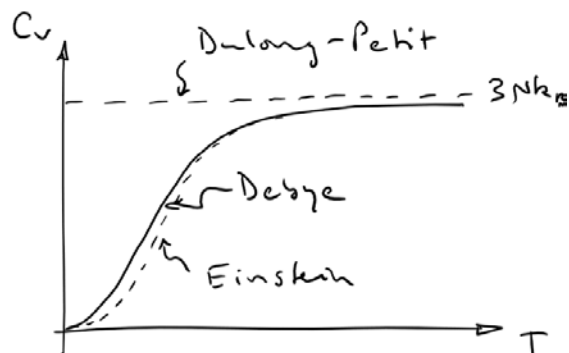At lower $T$, classical picture breaks down and quantum mechanical treatment is necessary: Energy of oscillator is quantized

$$\varepsilon_s = \hbar\omega\left(s + \frac{1}{2}\right) \quad \text{with } s = 0,1,2\cdots$$

Elastic wave is quantized. Quanta of wave energy are called <u>phonons</u>, in analogy with photons.

In the Einstein model, we found for a single 1-D oscillator:

$$U_1 = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

where the $\frac{1}{2}\hbar\omega$ was dropped.

$C_v$

Dulong-Petit

$3Nk_B$

Debye

Einstein

T

For total system, all $N$ oscillators (and directions in 3-D) are identical and independent so

$$U_{tot} = 3N\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \quad \text{and}$$

$$C_V = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}$$

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**Question 2: Write down an expression for the heat capacity at constant volume $C_V$ for the Einstein model a) at high temperatures, and b) low temperatures.**

a) At high temperatures $k_BT \gg \hbar\omega$,

$$U_{tot} \approx 3N\frac{\hbar\omega}{1 + \beta\hbar\omega - 1} = 3Nk_BT \quad \text{so} \quad C_V = 3Nk_B$$
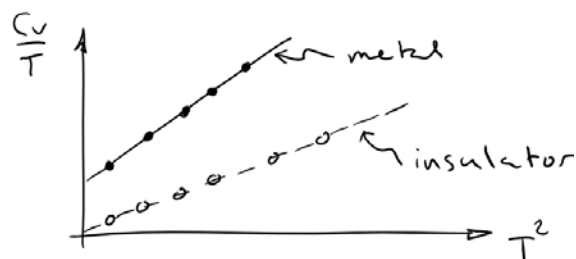
which matches classical Dulong-Petit law.

b) At low temperatures $k_BT \ll \hbar\omega$,

$$U_{tot} \approx 3N\hbar\omega e^{-\hbar\omega/k_BT} \quad \text{so} \quad C_V = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 e^{-\hbar\omega/k_BT}$$

predicts $C_V \sim e^{-\hbar\omega/k_BT}$ as $T \to 0$.

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However, that is not observed experimentally at low $T$:

$\dfrac{C_V}{T}$

metal

insulator

$T^2$

For an insulator: $C_V = AT^3$

For a metal: $C_V = \gamma T + AT^3$

↑ ↑

electrons   phonons

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

The problem with Einstein model is that it assumes the oscillators are independent and identical (i.e. $\hbar\omega$ is the same for all oscillators). Both of these are incorrect.

KEY CONCEPT: Debye model
Gets correct $T^3$ dependence. (For electronic contribution to $C_V$ in metals, we will need more tools before we can derive the $T$ dependence in Lect. 17).

Vibrational modes of a solid:
- Atoms do not vibrate independently – if one moves, its neighbors also move
- Consider 1-D chain of $N_x$ identical atoms with mass $m$ coupled with springs of stiffness $\kappa$



$\longrightarrow$ X   with $i = 1,2 \cdots N_x$

equilibrium lattice spacing
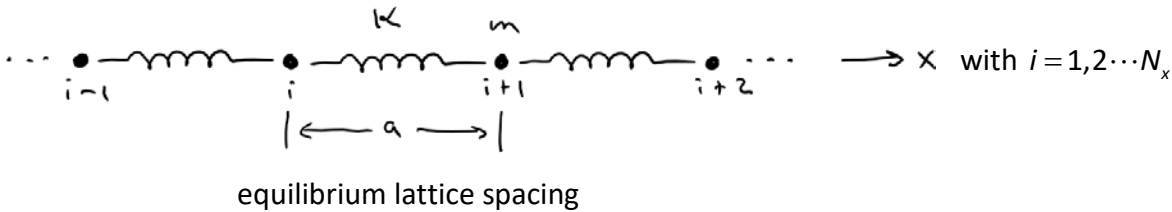
Now displace atom $i$. $r_i$, $r_{i+1}$ ... are positions of atoms. The force on atom $i$ is:
$$F_i = \kappa(r_{i+1} - r_i - a) - \kappa(r_i - r_{i-1} - a)$$
$$m\frac{d^2 r_i}{dt^2} = \kappa(r_{i+1} - 2r_i + r_{i-1})$$

Look at $r_{i+1} - 2r_i + r_{i-1}$. This is a discrete version of second derivative:
$$\frac{df}{dx} = \lim_{a \to 0} \frac{f(x+a) - f(x)}{a}$$
$$\frac{d^2 f}{dx^2} = \lim_{a \to 0} \frac{[f(x+a) - f(x)] - [f(x) - f(x-a)]}{a^2} = \lim_{a \to 0} \frac{f(x+a) - 2f(x) + f(x-a)}{a^2}$$

So,
$$\frac{r_{i+1} - 2r_i + r_{i-1}}{a^2} \approx \frac{d^2 r}{dx^2}$$

provided $a$ is "small" (we'll see what "small" means below). In this limit,
$$\frac{d^2 r}{dx^2} = \frac{m}{\kappa a^2}\frac{d^2 r}{dt^2} = \frac{1}{c_s^2}\frac{d^2 r}{dt^2}$$

which is just the wave equation.

Lattice vibrations behave like waves (sound waves) propagating at speed $c_s$ (speed of sound). Solution has the same form as an EM wave:
$$r(x,t) \sim e^{ikx - i\omega t} \text{ with } \omega = c_s k$$

This approximation is valid as long as $\lambda = 2\pi/k \gg a$ ("long" wavelength), i.e. when $k \ll 2\pi/a$

The Debye model assumes this approximation is always valid
- For arbitrary $k$, the solution is more involved

- In general, for real solid, this approximation will always be valid for sufficiently long wavelength $\lambda$ (or small $k$ and $\omega$) oscillations

In 3-D atoms move $\perp$ or $\parallel$ to wave. Three polarizations: 2 transverse ($\perp$), 1 longitudinal ($\parallel$). (Note difference between elastic and EM wave: longitudinal polarization not allowed for EM wave.)

Longitudinal                                    Transverse
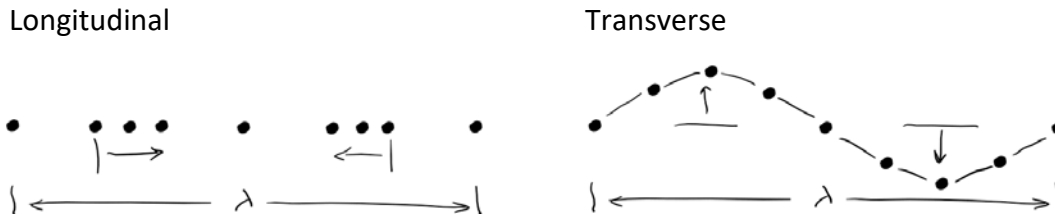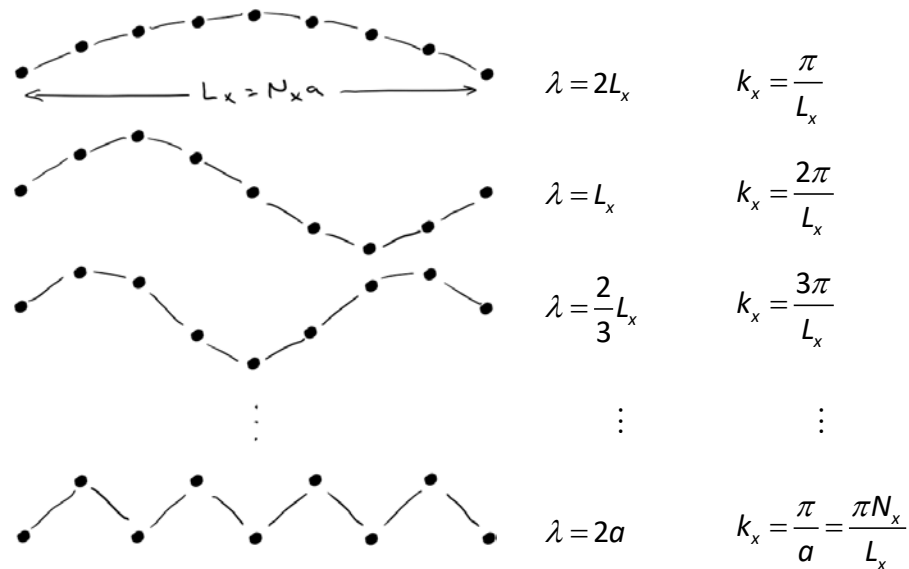


Note: In general $c_s$ may be different for different polarizations. We'll assume they are the same for simplicity.

Counting vibrational modes:
Just like EM waves in cavity, boundary conditions restrict $\lambda$ (or $k$) of vibrational waves.
Like EM waves, $k$ is quantized, with <u>one important difference</u>:

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



$\lambda = 2L_x \qquad k_x = \dfrac{\pi}{L_x}$

$\lambda = L_x \qquad k_x = \dfrac{2\pi}{L_x}$

$\lambda = \dfrac{2}{3}L_x \qquad k_x = \dfrac{3\pi}{L_x}$

$\vdots \qquad\qquad \vdots \qquad\qquad \vdots$

$\lambda = 2a \qquad k_x = \dfrac{\pi}{a} = \dfrac{\pi N_x}{L_x}$

$\lambda$ cannot be less than $2a$ because of finite spacing between atoms.

$$k_x = n_x \frac{\pi}{L_x}, \text{ with } n_x = 1, 2, 3 \cdots N_x$$

$\uparrow$
number of atoms along $x$

Same for $k_y$, $k_z$.

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

$$\text{Total \# of modes} = 3N_x N_y N_z = 3N$$

↑ ↑

3 polarizations    number of atoms

Note similarities / differences with EM waves: quantization is the same but $\{n_x, n_y, n_z\}$ can go to ∞, i.e. $\lambda$ can be arbitrarily short, so number of modes is ∞! (This led to ultraviolet catastrophe in classical description of Raleigh-Jeans law).

<u>Photon gas</u>

$\omega = ck$ always

Polarizations:

  2 transverse

$k_{x,y,z} = n_{x,y,z} \dfrac{\pi}{L_{x,y,z}}, \quad n_{x,y,z} = 1,2,3\cdots\infty$

Sum over modes:

$2 \displaystyle\sum_{n_x, n_y, n_z} \rightarrow \infty$

<u>Phonon gas</u>

$\omega \approx c_s k$ for $k \rightarrow 0$

Polarizations:

  2 transverse
  1 longitudinal

$k_{x,y,z} = n_{x,y,z} \dfrac{\pi}{L_{x,y,z}}, \quad n_{x,y,z} = 1,2,3\cdots N_{x,y,z}$

Sum over modes:

$3 \displaystyle\sum_{n_x, n_y, n_z} = 3N$

Going back to quantum harmonic oscillator energies:

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

where $n$ is shorthand for $\{n_x, n_y, n_z\}$ and represents each mode.

Once again we replace sum with integral using density of states: $\displaystyle\sum_n \rightarrow \int d\omega D(\omega)$

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**Question 3: Write down an expression for $D(\omega)$ of the phonons in the Debye model**

$$\begin{matrix}\text{\# of modes with frequency} \\ \text{between } \omega \text{ and } \omega + d\omega\end{matrix} \approx \text{\# polarizations} \times \frac{\text{vol. of shell in } k\text{-space with } k = \omega/c_s}{\text{vol. in } k\text{-space per state}}$$

$$D(\omega)d\omega \approx 3\frac{4\pi k^2 dk/8}{\pi^3/V} = \frac{3V}{2\pi^2}k^2 dk = \frac{3V}{2\pi^2}\frac{\omega^2 d\omega}{c_s^3}$$
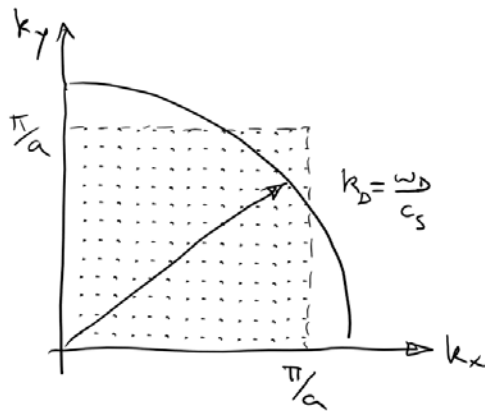
↑

Accounts for 3 polarization state of each mode

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Same as for photon gas except for a factor of 3/2 due to difference in # of polarizations.

<div align="center">Wait, what is the upper limit?</div>

<div align="center">↓</div>

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

Problem is that unlike photon gas, integration occurs over finite volume in $k$-space – in this simple case, a cube of side $\pi/a$ (this will depend on crystal lattice).



Integrating over $k$-space volume must give the correct number of modes $3N$.

Debye came up with a trick – instead of integrating over exact volume in $k$-space (here a cube), integrate over a sphere with the same volume. Having the same volume ensures the correct number of modes.

Sphere must have the right radius to match volumes. Define Debye frequency $\omega_D$ to satisfy this condition:

$$3N = 3\frac{\frac{4}{3}\pi k_D^3/8}{\pi^3/V} = \frac{V}{2\pi^2}k_D^3 = \frac{V}{2\pi^2}\left(\frac{\omega_D}{c_s}\right)^3 \quad \text{i.e.}\quad \omega_D = \left(6\pi^2\frac{N}{V}\right)^{1/3}c_s$$

So,

$$U_{tot} = \int_0^{\omega_D} d\omega\, D(\omega)\frac{\hbar\omega}{e^{\beta\hbar\omega}-1} = \frac{3V\hbar}{2\pi^2 c_s^3}\int_0^{\omega_D} d\omega\,\frac{\omega^3}{e^{\beta\hbar\omega}-1}$$

Let $x = \hbar\omega/k_B T$

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

Compared to the expression for a photon gas, the integral is not simply a numerical constant, but a function of temperature $T$ because the upper limit depends on $T$

Define the Debye temperature $\Theta_D \equiv \hbar\omega_D/k_B$ (note that $x_D = \Theta_D/T$ then).

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

Two regimes:

Low-temperature limit $T \ll \Theta_D$ (or $k_B T \ll \hbar\omega_D$):

In this limit $x_D \gg 1$, so

$$U_{tot} \approx \frac{3V\hbar}{2\pi^2 c_s^3}\left(\frac{k_B T}{\hbar}\right)^4 \underbrace{\int_0^\infty dx\, \frac{x^3}{e^x - 1}}_{\pi^4/15} = 9Nk_B T\left(\frac{T}{\Theta_D}\right)^3 \frac{\pi^4}{15} = \frac{3\pi^4}{5}Nk_B T\left(\frac{T}{\Theta_D}\right)^3$$

(The integrand is the Planck radiation law, which decays rapidly with *x* past its peak at 2.82. For $x_D \gg 1$, it's a good approximation to make the upper limit of integration ∞.) It follows that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \approx \frac{12\pi^4}{5}Nk_B\left(\frac{T}{\Theta_D}\right)^3$$

High-temperature limit $T \gg \Theta_D$ (or $k_B T \gg \hbar\omega_D$):

Debye's trick ensures that $C_V \approx 3Nk_B$ (you will prove this in PS #7), matching the classical Dulong-Petit result.

So, the Debye model gets high-*T* ($T \gg \Theta_D$) and low-*T* ($T \ll \Theta_D$) limits right, but intermediate regime $T \approx \Theta_D$ is not quite correct. There $\omega = c_s k$ is no longer a valid approximation and the integral over *k*-space must be done over the correct volume. These will depend on details of the crystal structure and vibrational modes. This is beyond the scope of this course.