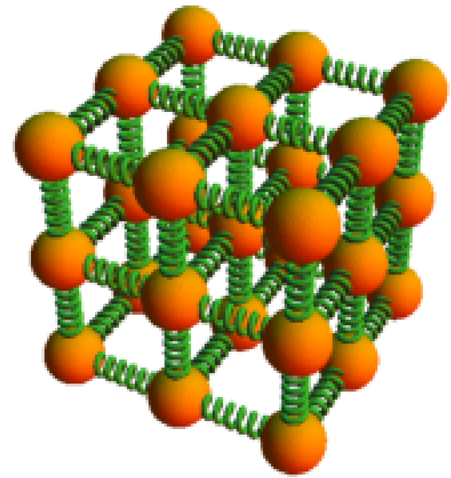
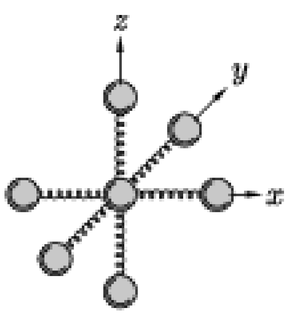
Lecture 24. *Phonons*

- In this lecture, we will focus on lattice vibrations
  - Einstein Model
  - Debye Model
  - Dispersion relation



https://mappingignorance.org/2015/12/17/einstein-and-quantum-solids/

Heat capacity — equipartition result, lecture 19:



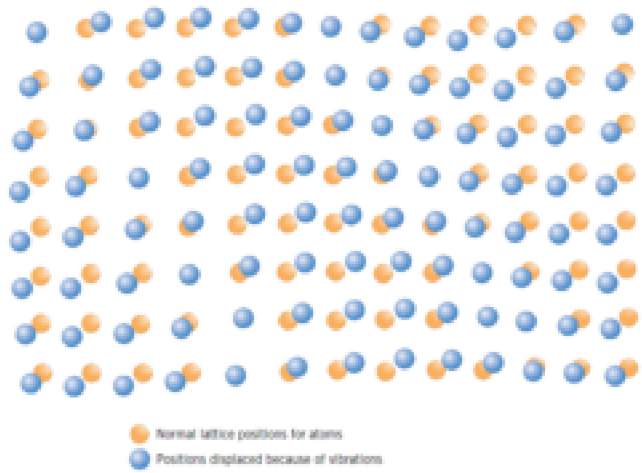
$$\partial\langle E\rangle/\partial T = 3Nk_{\mathrm{B}}$$

For one mole: $C_V = 3R$

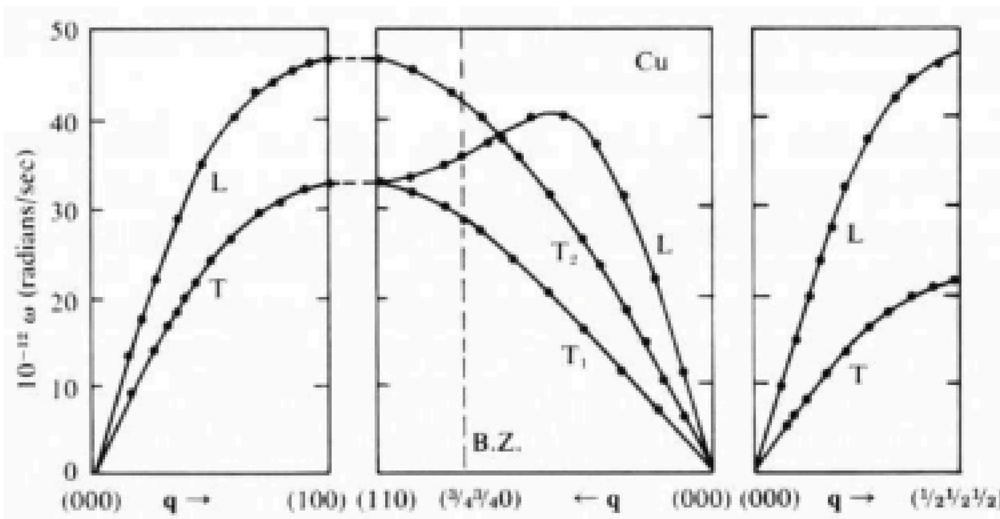
Phonons

- Energy is stored in the lattice vibration
- **Phonons are quantized elementary lattice waves** to describe excitation of vibrations in the lattice.
- Phonons focus on ***normal*** **modes of vibrations: the collection of modes that are independent from one another.**
- They are like simple harmonic oscillators.
- They are described using **dispersion relations.**

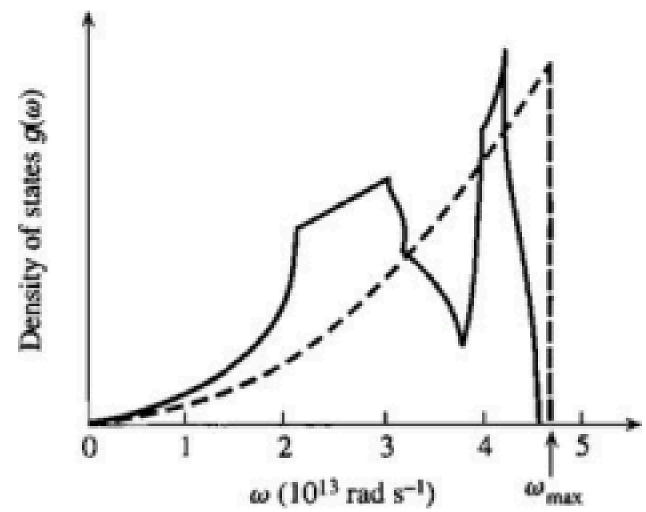
$$\omega \ \ v.s. \ k$$



https://mappingignorance.org/2018/01/18/what-the-heck-is-a-phonon/

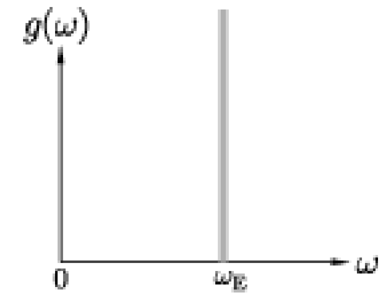


50
40
30
20
10
0
10^{-12} ω (radians/sec)
Cu
L
T
T_2
T_1
B.Z.
(000) q → (100) (110) (¾¾0) ← q (000) (000) q → (½½½)



Density of states g(ω)
0 1 2 3 4 5
ω (10^{13} rad s^{-1})
ω_{max}

Einstein Model

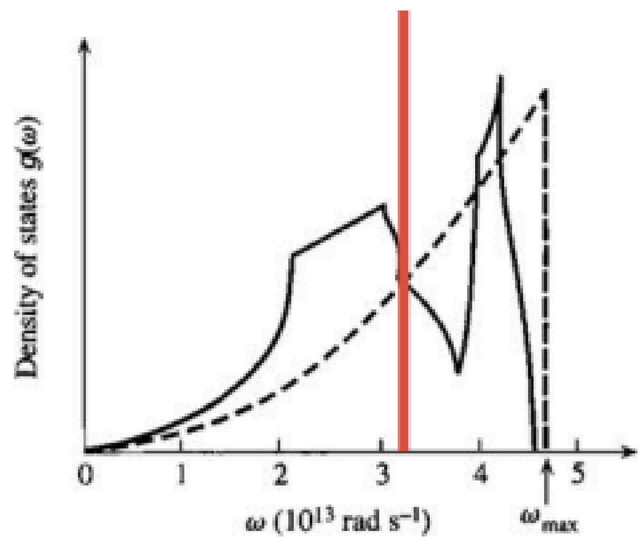


- **Each vibrational mode of the solid have the same frequency ω_E**
- There are $3N$ modes (really $3N-6$*)
- There are independent and do not interact
- The partition function is thus a simple product
- Z_k is the partitions function of a single mode
- Each mode is a simple harmonic oscillator (again!)

$$Z = \prod_{k=1}^{3N} Z_k \qquad \ln Z = \sum_{k=1}^{3N} \ln Z_k$$

$$Z_k = \sum_{n=0}^{\infty} \mathrm{e}^{-(n+\frac{1}{2})\hbar\omega_{\mathrm{E}}\beta} = \frac{\mathrm{e}^{-\frac{1}{2}\hbar\omega_{\mathrm{E}}\beta}}{1-\mathrm{e}^{-\hbar\omega_{\mathrm{E}}\beta}}$$

$$\ln Z = 3N\left[-\frac{1}{2}\hbar\omega_{\mathrm{E}}\beta - \ln(1-\mathrm{e}^{-\hbar\omega_{\mathrm{E}}\beta})\right]$$



Copper

$$\ln Z = 3N\left[-\frac{1}{2}\ \omega_{\mathrm{E}}\beta - \ln(1 - \mathrm{e}^{-\ \omega_{\mathrm{E}}\beta})\right]$$

Internal energy: $U = -\left(\frac{\partial \ln Z}{\partial \beta}\right)$

$$= \frac{3N}{2}\hbar\omega_{\mathrm{E}} + \frac{3N}{1 - \mathrm{e}^{-\hbar\omega_{\mathrm{E}}\beta}}\hbar\omega_{\mathrm{E}}\mathrm{e}^{-\hbar\omega_{\mathrm{E}}\beta}$$

$$= \frac{3N}{2}\hbar\omega_{\mathrm{E}} + \frac{3N\hbar\omega_{\mathrm{E}}}{\mathrm{e}^{\hbar\omega_{\mathrm{E}}\beta} - 1}$$

$$U = 3R\Theta_{\mathrm{E}}\left[\frac{1}{2} + \frac{1}{\mathrm{e}^{\Theta_{\mathrm{E}}/T} - 1}\right]$$

$$\hbar\omega_{\mathrm{E}} = k_{\mathrm{B}}\Theta_{\mathrm{E}}$$

Einstein temperature

*per mole

Limit at hight T

$$U = 3R\Theta_\mathrm{E}\left[\frac{1}{2} + \frac{1}{\mathrm{e}^{\Theta_\mathrm{E}/T} - 1}\right]$$

$$\frac{1}{\mathrm{e}^{\Theta_\mathrm{E}/T} - 1} \to \frac{T}{\Theta_\mathrm{E}}$$

$$U \to 3RT$$

Molar heat capacity of the Einstein solid

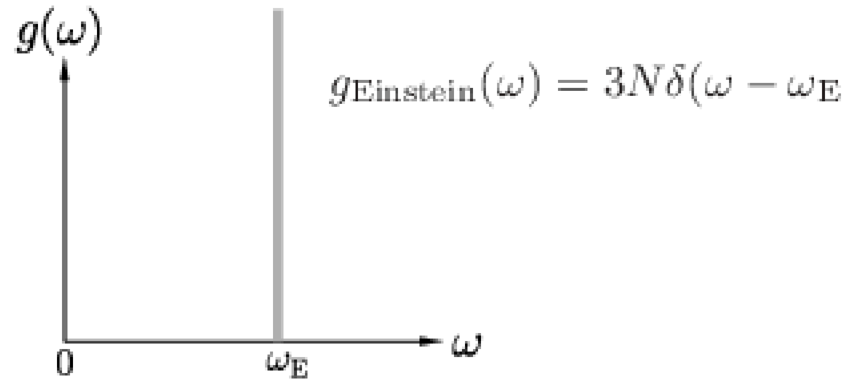
$$C = \left(\frac{\partial U}{\partial T}\right)$$

$$\begin{aligned} C &= 3R\Theta_{\mathrm{E}} \frac{-1}{(\mathrm{e}^{\Theta_{\mathrm{E}}/T} - 1)^2} \mathrm{e}^{\Theta_{\mathrm{E}}/T} \left[-\frac{\Theta_{\mathrm{E}}}{T^2} \right] \\ &= 3R \frac{x^2 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2} \qquad x = \Theta_{\mathrm{E}}/T \end{aligned}$$

$$C \to 3R$$

The Debye Model

- Distribution of frequencies rather than a single one.
- Number of vibrational states between ω and $\omega + d\omega$ is given by $g(\omega)$.
- **Approximation:** all waves travel at the same speed v_s, the speed of sound (q being the wave vector $2\pi/\lambda$)



$$\int g(\omega)\, d\omega = 3N$$

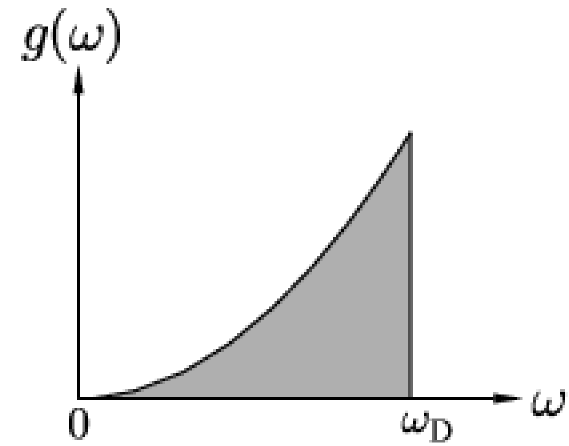
$$\omega = v_s q$$

$$g(q)\mathrm{d}q = \frac{4\pi q^2 \mathrm{d}q}{(2\pi/L)^3} \times 3$$

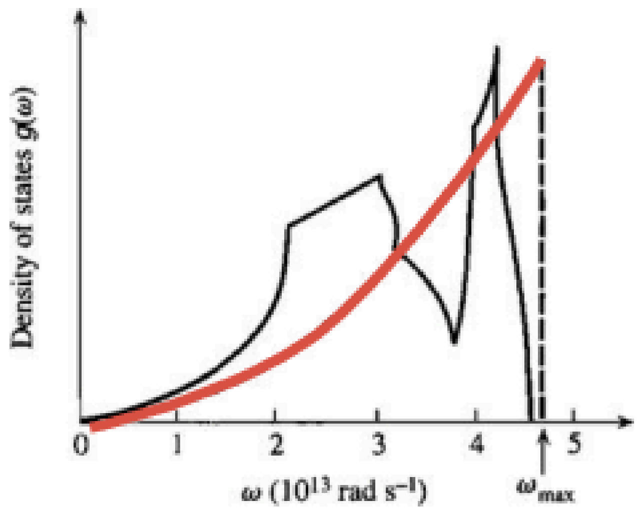
Solid: cube of side length L; factor of three because we have 1 longitudinal and two transverse directions for each q

$$g(q)\,\mathrm{d}q = \frac{3V q^2\,\mathrm{d}q}{2\pi^2};$$

$$g(\omega)\,\mathrm{d}\omega = \frac{3V\omega^2\,\mathrm{d}\omega}{2\pi^2 v_s^3}$$



Debye frequency defined such that: $\int_0^{\omega_D} g(\omega)\,\mathrm{d}\omega = 3N$



Copper

Debye frequency defined such that: $$\int_0^{\omega_\mathrm{D}} g(\omega)\,\mathrm{d}\omega = 3N$$

$$g(\omega)\,\mathrm{d}\omega = \frac{3V\omega^2\,\mathrm{d}\omega}{2\pi^2 v_\mathrm{s}^3}$$

$$\longrightarrow \quad \omega_\mathrm{D} = \left(\frac{6N\pi^2 v_\mathrm{s}^3}{V}\right)^{1/3}$$

Debye temperature: $\Theta_\mathrm{D} = \dfrac{\hbar\omega_\mathrm{D}}{k_\mathrm{B}}$

Examples

Material	Θ_D (K)
Ne	63
Na	150
NaCl	321
Al	394
Si	625
C (diamond)	1860

Internal energy in the Debye model

$$\ln Z = \int_0^{\omega_\mathrm{D}} \mathrm{d}\omega\, g(\omega) \ln\left[\frac{\mathrm{e}^{-\frac{1}{2}\hbar\omega\beta}}{1-\mathrm{e}^{-\hbar\omega\beta}}\right]$$

$$g(\omega)\,\mathrm{d}\omega = \frac{3V\omega^2\,\mathrm{d}\omega}{2\pi^2 v_\mathrm{s}^3}$$

$$\omega_\mathrm{D} = \left(\frac{6N\pi^2 v_\mathrm{s}^3}{V}\right)^{1/3}$$

$$\ln Z = -\int_0^{\omega_\mathrm{D}} \frac{1}{2}\hbar\omega g(\omega)\,\mathrm{d}\omega - \int_0^{\omega_\mathrm{D}} g(\omega)\ln(1-\mathrm{e}^{-\hbar\omega\beta})\,\mathrm{d}\omega$$

$$\ln Z = -\frac{9}{8}N\hbar\omega_\mathrm{D}\beta - \frac{9}{\omega_\mathrm{D}^3}\int_0^{\omega_\mathrm{D}} \omega^2 \ln(1-\mathrm{e}^{-\hbar\omega\beta})\,\mathrm{d}\omega$$

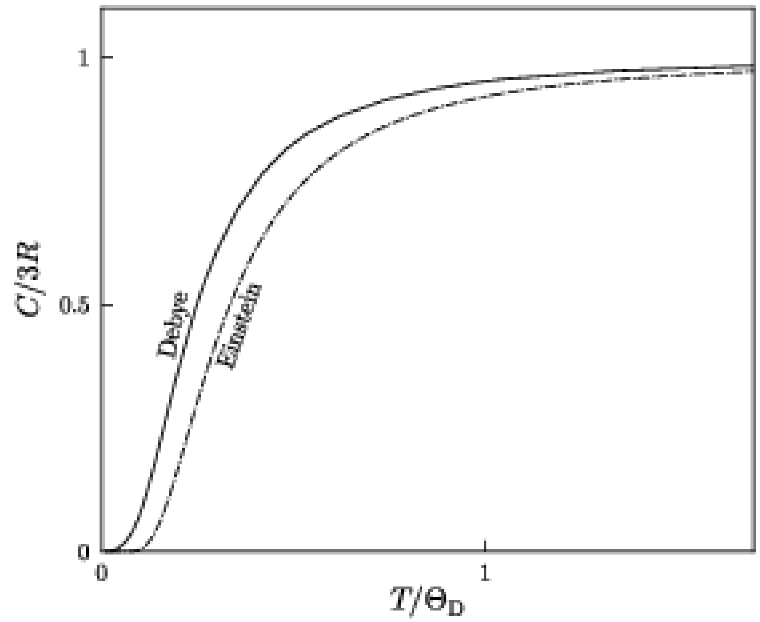
$$U = -\partial \ln Z/\partial\beta \longrightarrow U = \frac{9}{8}N\hbar\omega_\mathrm{D} + \frac{9N\hbar}{\omega_\mathrm{D}^3}\int_0^{\omega_\mathrm{D}} \frac{\omega^3\,\mathrm{d}\omega}{\mathrm{e}^{\hbar\omega\beta}-1}$$

Heat capacity $C = \left(\frac{\partial U}{\partial T}\right)$

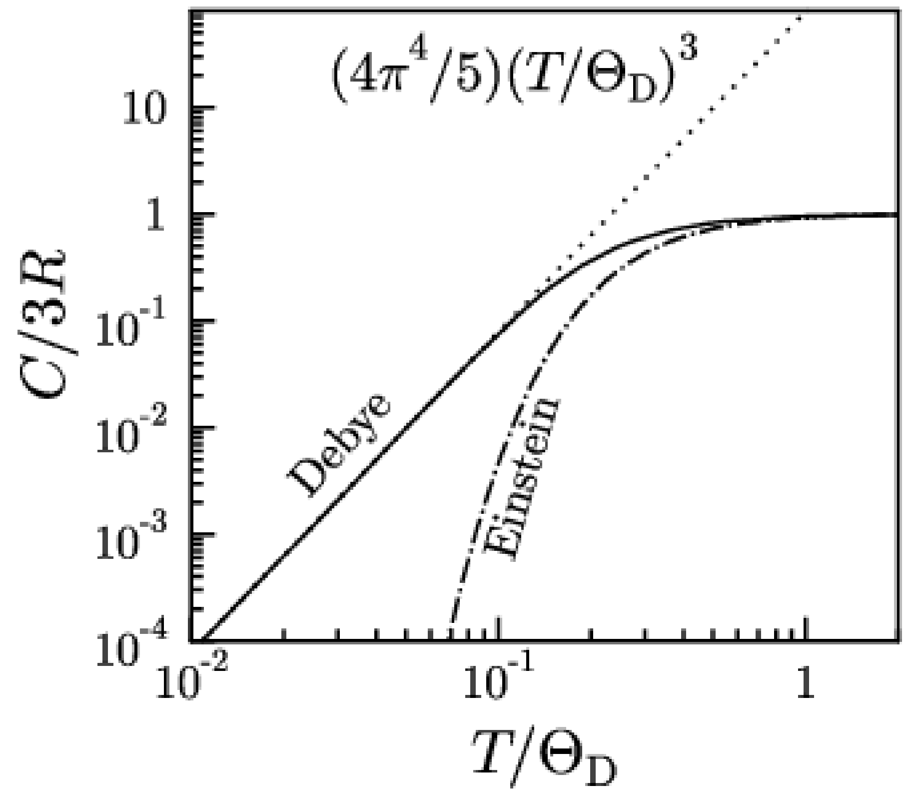
$$U = \frac{9}{8}N\hbar\omega_{\rm D} + \frac{9N\hbar}{\omega_{\rm D}^3}\int_0^{\omega_{\rm D}} \frac{\omega^3\,{\rm d}\omega}{{\rm e}^{\hbar\omega\beta}-1}$$

$$C = \frac{9N\hbar}{\omega_{\rm D}^3}\int_0^{\omega_{\rm D}} \frac{-\omega^3\,{\rm d}\omega}{({\rm e}^{\hbar\omega\beta}-1)^2}{\rm e}^{\hbar\omega\beta}\left(-\frac{\hbar\omega}{k_{\rm B}T^2}\right)$$

$$C = \frac{9R}{x_{\rm D}^3}\int_0^{x_{\rm D}} \frac{x^4{\rm e}^x\,{\rm d}x}{({\rm e}^x-1)^2} \qquad x = \hbar\beta\omega$$



Low temperature



Debye in the limiting case (High-T and Low-T)

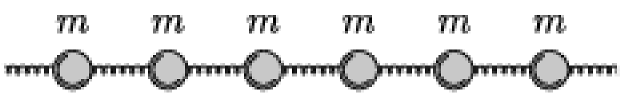
$$C = \frac{9R}{x_{\mathrm{D}}^3}\int_0^{x_{\mathrm{D}}} \frac{x^4 \mathrm{e}^x \,\mathrm{d}x}{(\mathrm{e}^x - 1)^2} \qquad x = \beta\omega$$

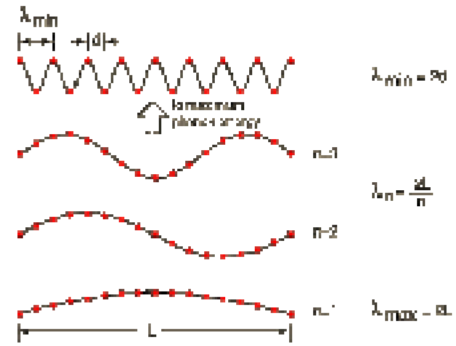
High-T: $C \rightarrow \frac{9R}{x_{\mathrm{D}}^3}\int_0^{x_{\mathrm{D}}} \frac{x^4}{x^2}\,\mathrm{d}x = 3R$ (equipartition result, Dulong-Petit)

Low-T: $C \rightarrow \frac{9R}{x_{\mathrm{D}}^3}\int_0^{\infty} \frac{x^4 \mathrm{e}^x \,\mathrm{d}x}{(\mathrm{e}^x - 1)^2} = \frac{12R\pi^4}{5x_{\mathrm{D}}^3}$

$$C = 3R \times \frac{4\pi^4}{5}\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^3$$

Phonon dispersion ω vs. q





$$m\ddot{u}_n = K(u_{n+1} - u_n) - K(u_n - u_{n-1}) = K(u_{n+1} - 2u_n + u_{n-1})$$

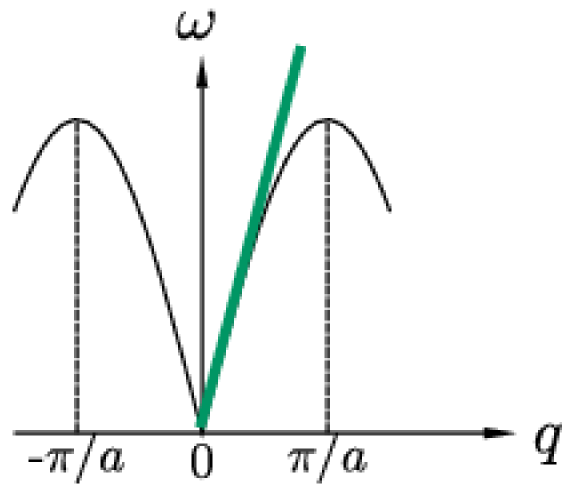
$$u_n = \exp[\mathrm{i}(qna - \omega t)]$$ Wave-like solution

$$-m\omega^2 = K(\mathrm{e}^{\mathrm{i}qa} - 2 + \mathrm{e}^{-\mathrm{i}qa})$$

$$m\omega^2 = 2K(1 - \cos qa)$$

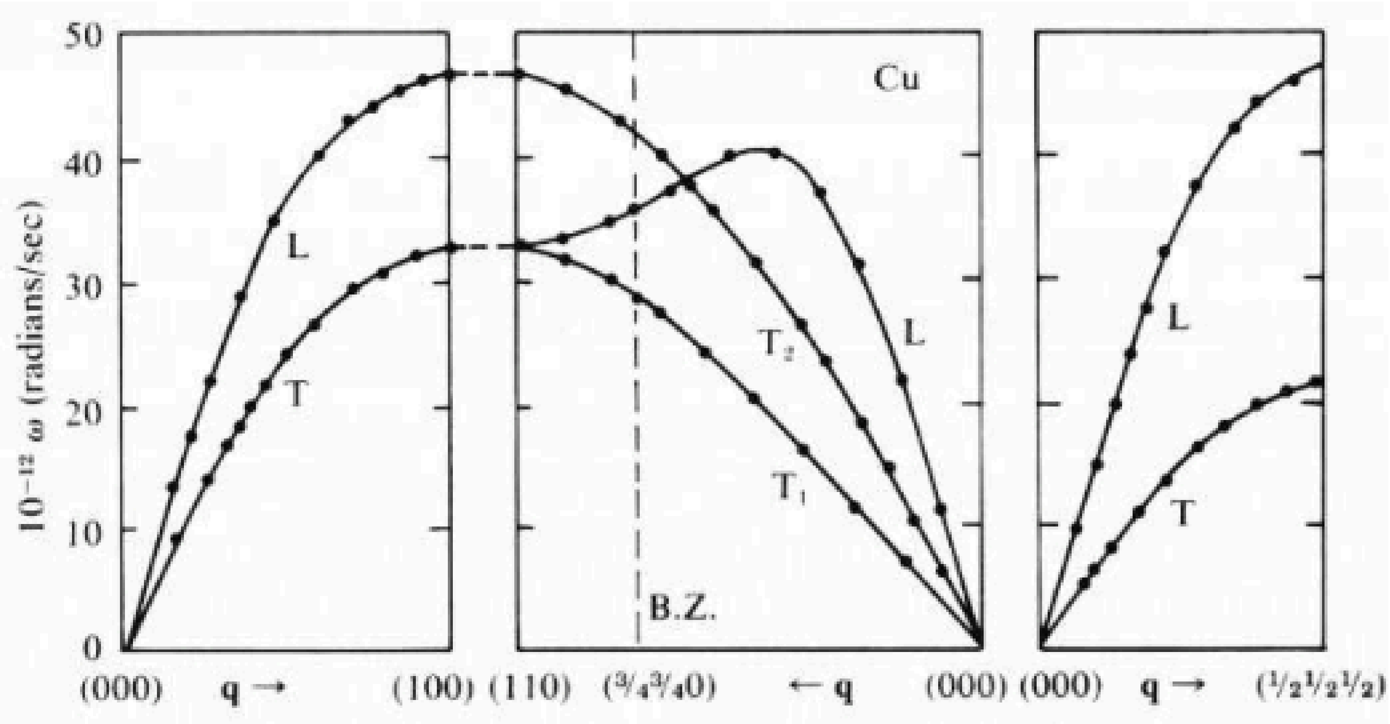
Long wavelength limit:

$$\omega \longrightarrow v_\mathrm{s} q \qquad v_\mathrm{s} = a\left(\frac{K}{m}\right)^{1/2}$$

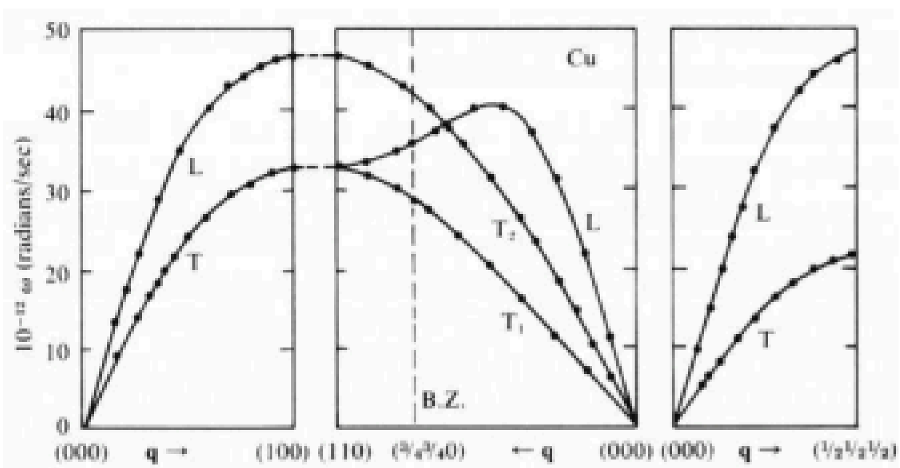


$$\omega^2 = \frac{4K}{m}\sin^2(qa/2)$$

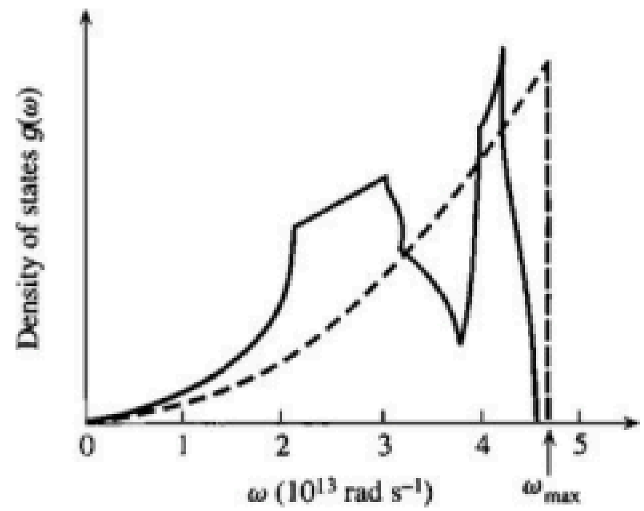
Copper solid



Svensson et al., Phys. Rev. **155**, 619 (1967)

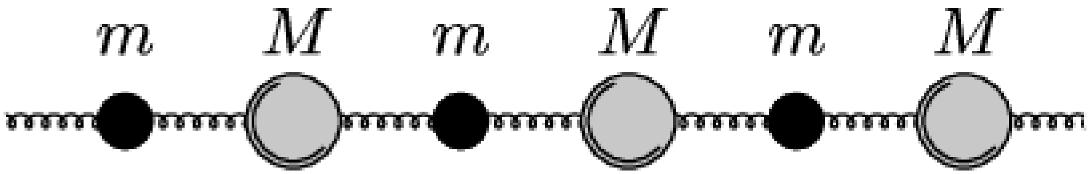


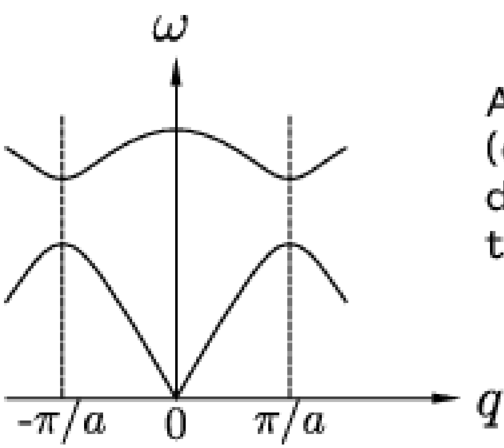
Cu
L
T
T₂
L
T₁
B.Z.
L
T
10⁻¹² ω (radians/sec)
(000) q → (100) (110) (¾¾0) ← q (000) (000) q → (½½½)



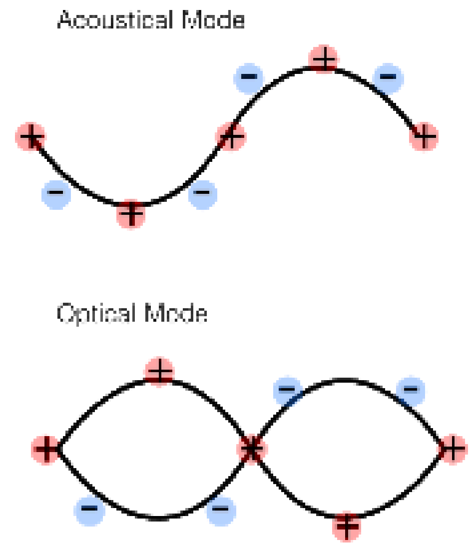
Density of states g(ω)
ω (10¹³ rad s⁻¹)
ω_max

More than one atomic type

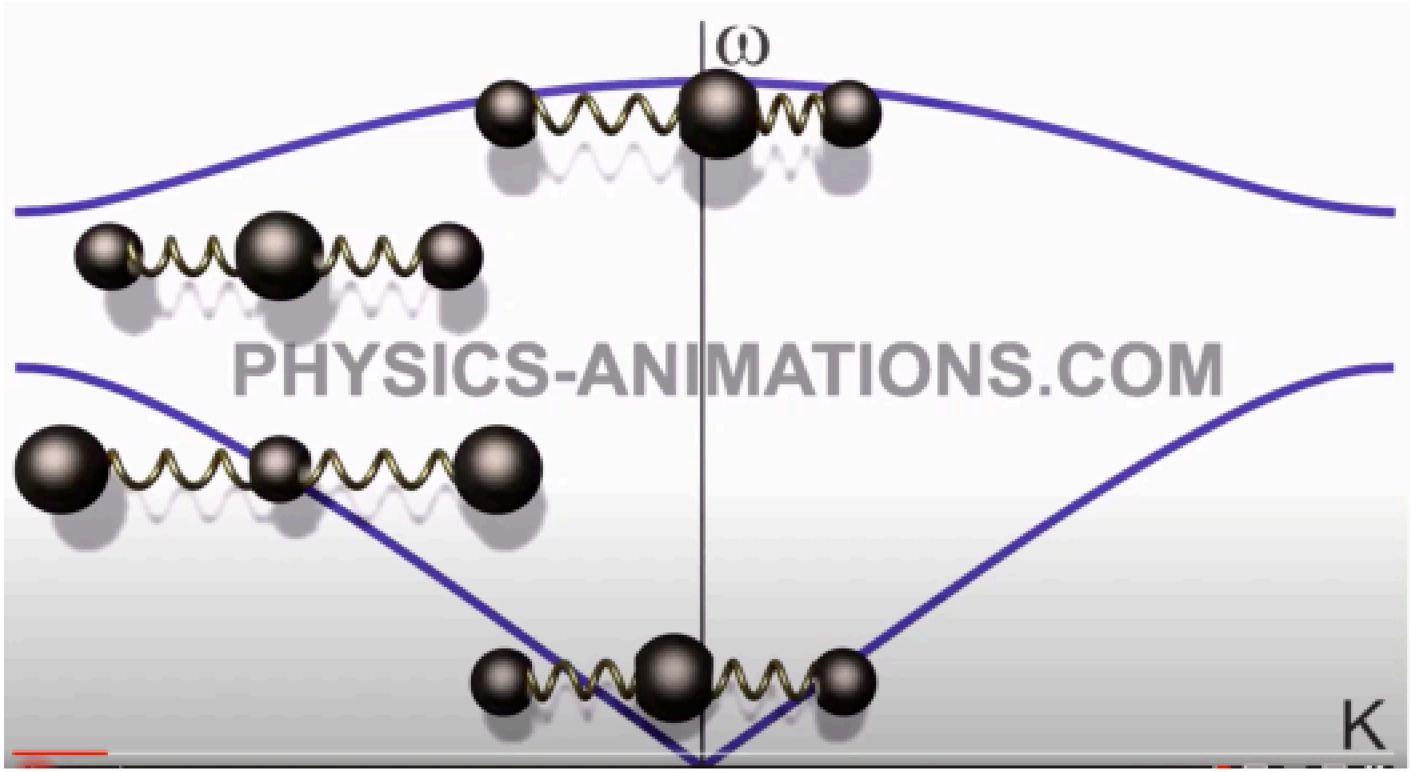




Appearance of **optical modes** (can couple with EM radiation due to the different nature of the atoms)



https://warwick.ac.uk/

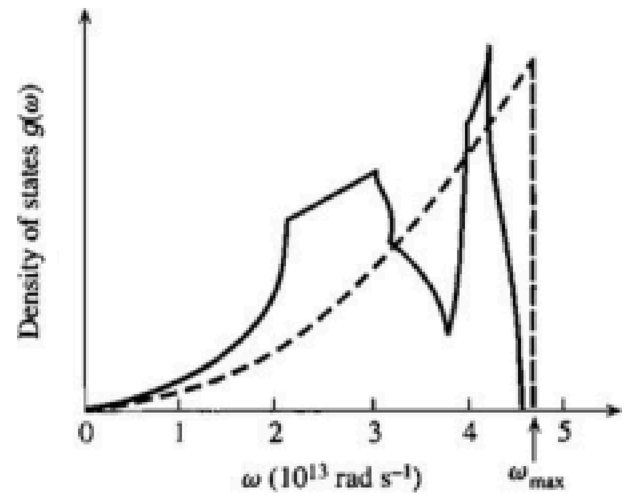


https://www.youtube.com/watch?v=M4WQs_U1nmU

Debye versus Einstein

Debye: good at low T (with T^3 behavior)

Einstein: good for optical modes



Summary

- A phonon is a quantized lattice vibration.
- The Einstein model of a solid assumes that all phonons have the same frequency.

The Debye model allows a range of phonon frequencies up to a maximum frequency called the Debye frequency. The density of states is quadratic in frequency, and this assumes that $\omega = v_s q$

The dispersion relation of a real solid is more complicated and may contain acoustic and optic branches. It can be experimentally determined using inelastic neutron scattering.

- The heat capacity of a three-dimensional solid is proportional to T^3 at low temperature and saturates to a value of $3R$ at high temperature.