

DPMS:
Chemistry and Technology of Materials

Lecture:
Theory of the Harmonic Lattice

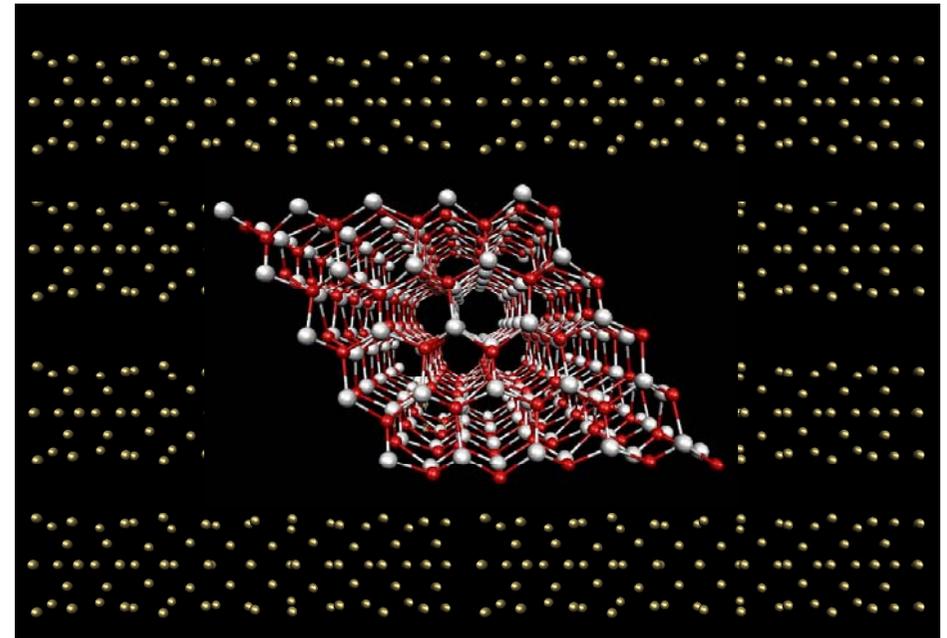
Eleferios Lidorikis

Room Π1, 26510 07146

elidorik@cc.uoi.gr

<http://cmsl.materials.uoi.gr/lidorikis>

Ionic motion

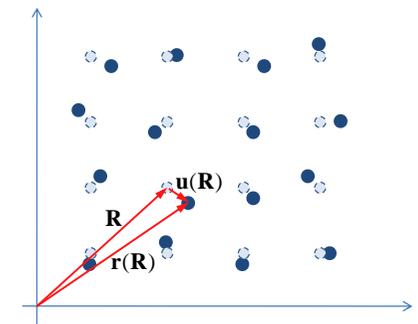
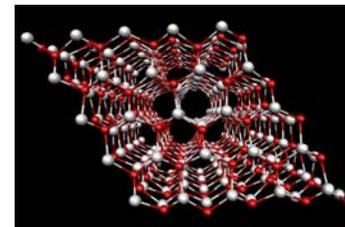


Outline

- Classical theory of the harmonic crystal
 - spectrum of the vibrational modes
 - normal modes and phonons
- Quantum theory
 - quantization of vibrational modes
 - thermal capacitance

Assumptions

- Average position of ions is their Bravais lattice site
 - no diffusion, defects, etc are allowed
- Motion around the equilibrium is much smaller than the ionic spacing
 - assume a harmonic approximation (Hook's law)
- Adiabatic approximation
 - electrons move fast enough so they are always at their ground state



- We define
 - Bravais lattice site \mathbf{R}
 - ion position $\mathbf{r}(\mathbf{R})$
 - ion displacement $\mathbf{u}(\mathbf{R}) = \mathbf{r}(\mathbf{R}) - \mathbf{R}$

Total energy

- For ions fixed at equilibrium positions

- potential energy $U^{pot} = \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \phi(\mathbf{R} - \mathbf{R}')$
- kinetic energy $U^{kin} = 0$
- total energy $H = U^{pot}$

- For ions moving around their equilibrium

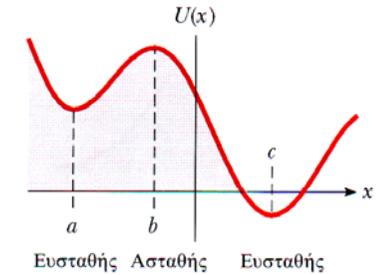
- potential energy $U^{pot} = \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \phi(\mathbf{r}(\mathbf{R}) - \mathbf{r}(\mathbf{R}')) = \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \phi(\mathbf{R} - \mathbf{R}' + \mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}'))$
- kinetic energy $U^{kin} = \sum_{\mathbf{R}} \mathbf{p}(\mathbf{R})^2 / 2M$
- total energy $H = U^{pot} + U^{kin}$

Taylor expansion in 1D

- General case of potential energy in 1D

- potential energy $U(x)$
- potential minima: points of equilibrium

$$\frac{dU}{dx} = 0 \quad \frac{d^2U}{dx^2} > 0$$



- we can expand around an equilibrium point

$$U(x) = U(a) + \frac{U'(a)}{1!} (x-a) + \frac{U''(a)}{2!} (x-a)^2 + \frac{U'''(a)}{3!} (x-a)^3 + \dots$$

- Close to the equilibrium point $x \approx a$

$$U(x) \approx U(a) + \frac{1}{2} U''(a) (x-a)^2$$

restoring force:
Hook's law

- Harmonic oscillator

$$U(x) = U_0 + \frac{1}{2} K (x-a)^2 \quad K = \left. \frac{d^2U}{dx^2} \right|_{x=a}$$

$$F = - \frac{dU(x)}{dx} = -Kx$$

Harmonic approximation in 3D

- Motion around equilibrium is small

- Taylor expansion around equilibrium

$$\phi(\mathbf{r}) = \phi(\mathbf{R}) + (\mathbf{u} \cdot \nabla) \phi(\mathbf{R}) + \frac{1}{2!} (\mathbf{u} \cdot \nabla)^2 \phi(\mathbf{R}) + \frac{1}{3!} (\mathbf{u} \cdot \nabla)^3 \phi(\mathbf{R}) + \dots$$

- the potential energy

$$U^{pot} = \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \phi(\mathbf{R} - \mathbf{R}' + \mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}'))$$

- use the Taylor expansion above with $\mathbf{R} \rightarrow \mathbf{R} - \mathbf{R}'$ and $\mathbf{u} \rightarrow \mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}')$

- Total potential energy close to equilibrium $U^{pot} = U^{eq} + U^{harm}$

$$U^{eq} = \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \phi(\mathbf{R} - \mathbf{R}') = \frac{N}{2} \sum_{\mathbf{R}} \phi(\mathbf{R})$$

$$U^{harm} = \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} D_{\mu\nu}(\mathbf{R} - \mathbf{R}') u_{\mu}(\mathbf{R}) u_{\nu}(\mathbf{R}')$$

Specific heat of a classical crystal the law of Dulong and Petit

- From classical statistics the average energy density is

$$\langle H \rangle = \frac{\int H e^{-H/k_B T} d\Omega}{\int e^{-H/k_B T} d\Omega} \quad d\Omega = \prod_{\mathbf{R}} d\mathbf{u}(\mathbf{R}) d\mathbf{p}(\mathbf{R})$$

$$H = U^{kin} + U^{eq} + U^{harm}$$

$$H = \sum_{\mathbf{R}} \frac{\mathbf{p}(\mathbf{R})^2}{2M} + \frac{N}{2} \sum_{\mathbf{R}} \phi(\mathbf{R}) + \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} D_{\mu\nu}(\mathbf{R} - \mathbf{R}') u_{\mu}(\mathbf{R}) u_{\nu}(\mathbf{R}')$$

- It can be proved that this is simply

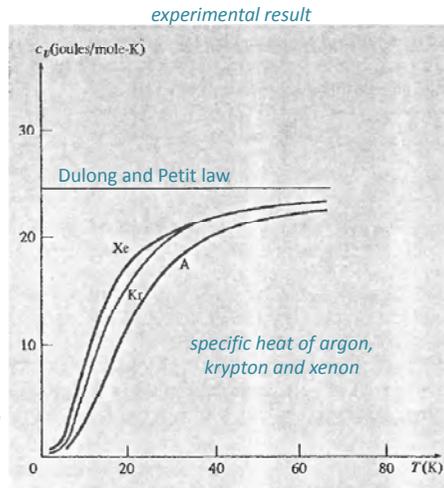
$$\langle H \rangle = U^{eq} + 3Nk_B T$$

- And the specific heat $c_v = \frac{1}{V} \frac{\partial \langle H \rangle}{\partial T} = 3nk_B$ law of Dulong and Petit

Specific heat

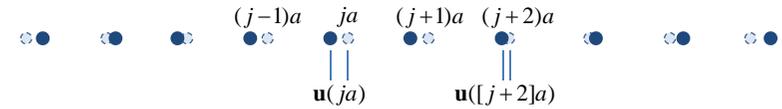
- Classical result for insulators (Dulong and Petit law)

$$c_v = 3nk_B$$
- In reality
 - it reaches the classical result at high T
 - it goes to zero at low T
 - for metals $c_v = \gamma T + AT^3$
 - for insulators $c_v = AT^3$
- So we cannot use classical theory!
- But before we consider the quantum case
 - which are the allowed modes?
 - what is the number of modes?



1D monoatomic lattice: normal modes

- Assume 1D chain with lattice spacing a



- Assume only nearest neighbor interactions



$$U^{ham} = \frac{1}{2} K \sum_{j=1}^N [u(ja) - u((j+1)a)]^2$$

- Equation of motion for ion j

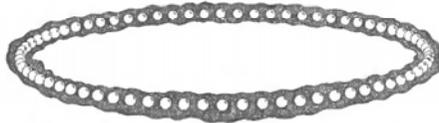
$$M \frac{\partial^2 u(ja)}{\partial t^2} = -K[u(ja) - u((j+1)a)] - K[u(ja) - u((j-1)a)]$$

$$M \ddot{u}(ja) = K[u((j+1)a) + u((j-1)a) - 2u(ja)]$$

- But what about ions at the boundaries?

Boundary conditions

- Assume periodic (Born-von Karman) boundary conditions $u(Na) = u(0)$
 - they are equivalent to assuming a ring of ions



- Assume harmonic solution $u(x,t) = \alpha e^{i(kx - \omega t)}$ or $u(ja,t) = \alpha e^{i(kja - \omega t)}$

so the boundary condition $e^{ikNa} = 1$

thus $\Rightarrow kNa = n2\pi \Rightarrow k = n \frac{2\pi}{Na}$ $n = 1, 2, 3, \dots, N$

- From N ions we get N modes

if $n > N$ $n = N + n'$ $k = \frac{2\pi}{Na}(N + n') = \frac{2\pi}{a} + n' \frac{2\pi}{Na} = \frac{2\pi}{a} + k'$

$$e^{ikja} = e^{i\left(\frac{2\pi}{a} + n' \frac{2\pi}{Na}\right)ja} = e^{i2\pi j} e^{i2\pi n' j / N} = e^{ik'ja}$$

Dispersion relation

- Equation of motion $M \ddot{u}(ja) = K[u((j+1)a) + u((j-1)a) - 2u(ja)]$
 - assume for solution $u(ja,t) = \alpha e^{i(kja - \omega t)}$ (the real part or imaginary part)

- Substitute in equation

$$-M\omega^2 e^{i(kja - \omega t)} = K[e^{ika} + e^{-ika} - 2]e^{i(kja - \omega t)}$$

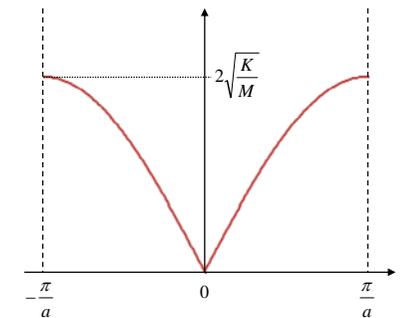
$$\omega^2 = 2 \frac{K}{M} [1 - \cos(ka)]$$

- Dispersion relation

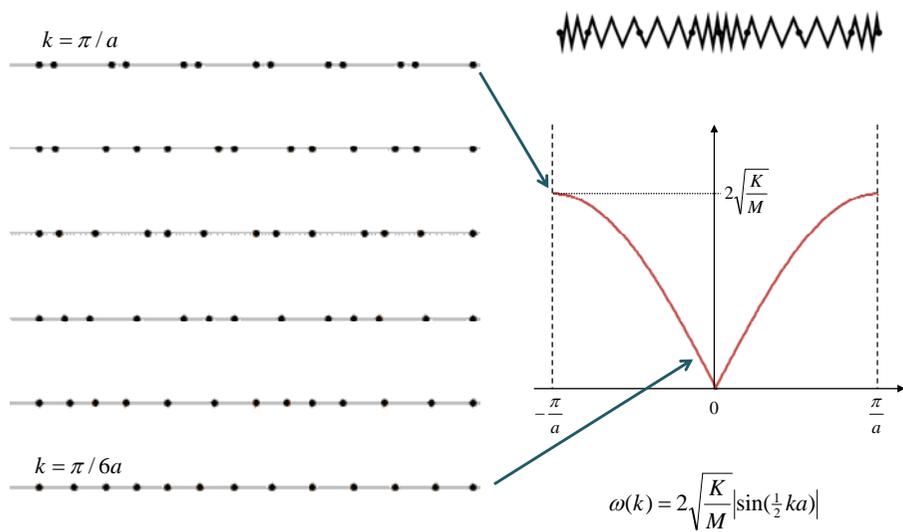
$$\omega(k) = 2 \sqrt{\frac{K}{M}} \left| \sin\left(\frac{1}{2}ka\right) \right|$$

linear dispersion at $k \rightarrow 0$ $\omega = a \sqrt{\frac{K}{M}} |k|$

flat dispersion at $k \rightarrow \pm\pi/a$ $\omega \rightarrow 2\sqrt{K/M}$

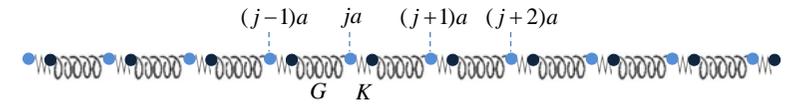


1D acoustic oscillations



1D lattice with a basis

- Two ions of mass M in each period a

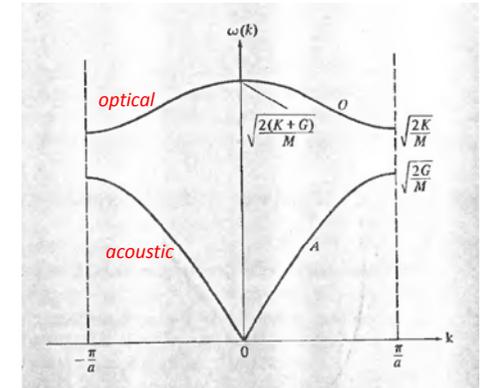


- two spring constants K and G
- two separation distances

- Now we have two branches of states
 - $2N$ ions give us $2N$ modes

$$\omega(k) = \left| \frac{K + G \pm \sqrt{K^2 + G^2 + 2KG \cos(ka)}}{M} \right|^{1/2}$$

- The lower branch is the acoustic
 - always present
- The upper branch is the optical
 - enabled by having 2 ions in unit cell



1D acoustic and optical branches

- At $k \rightarrow 0$ (zone center)
 - acoustic branch: all ions move together

$$\omega(k) = \sqrt{KG/[2M(K+G)]}ka$$

- optical branch: ions move in pairs

$$\omega(k) = \sqrt{2(K+G)/M}$$

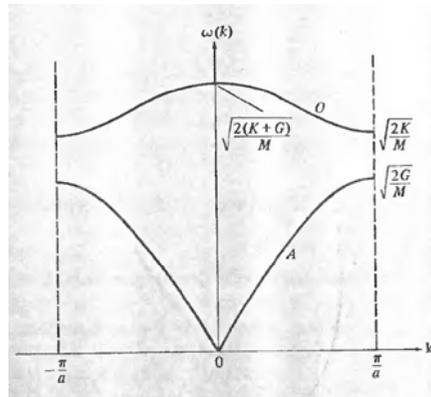
- At $k \rightarrow \pi/a$ (zone edge)

- acoustic branch: soft springs active

$$\omega(k) = \sqrt{2G/M}$$

- Optical branch: stiff springs active

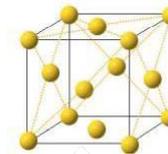
$$\omega(k) = \sqrt{2K/M}$$



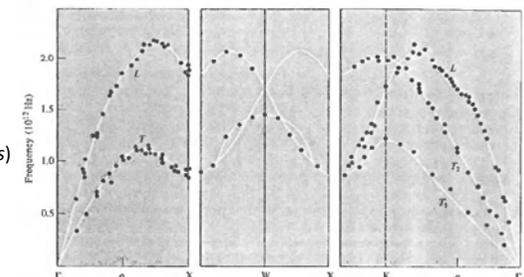
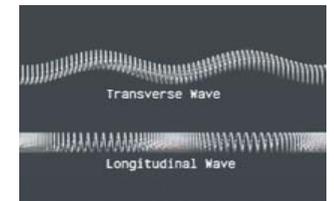
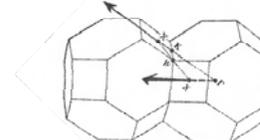
3D monoatomic lattice

- We can generalize equations to 3D
 - the lattice symmetry determines the available k -points and their symmetries
 - reciprocal lattice - Brillouin zone
- We have 1 longitudinal and 2 transverse modes

fcc lattice
(real space configuration of atoms)



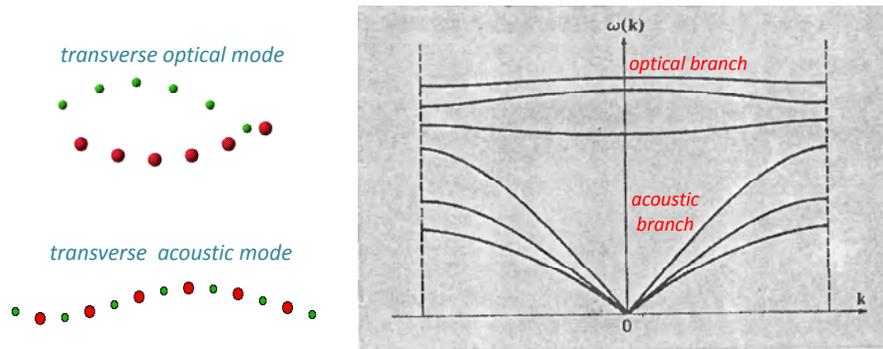
fcc Brillouin zone
(reciprocal space configuration of k -points)



phonon dispersion relations for lead (fcc)

3D lattice with basis

- If we have p atoms in the basis
 - 1 acoustic branch with 1 longitudinal and 2 transverse modes
 - $p-1$ optical branches with $p-1$ longitudinal and $2(p-1)$ transverse modes
- $3N$ modes in total



Thermal energy in quantum theory

- The modes are described by wavevector \mathbf{k} and branch s

- quantized energies - phonons, with energy per mode

$$\mathcal{E}_{\mathbf{k}s} = (n_{\mathbf{k}s} + \frac{1}{2})\hbar\omega_s(\mathbf{k})$$

- $n_{\mathbf{k}s}$ is the number of phonons with \mathbf{k} and s

- Total energy

$$\langle \mathcal{E} \rangle = U^{eq} + \sum_{\mathbf{k}s} \frac{1}{2} \hbar\omega_s(\mathbf{k}) + \sum_{\mathbf{k}s} \frac{\hbar\omega_s(\mathbf{k})}{e^{\hbar\omega_s(\mathbf{k})/k_B T} - 1}$$

- where $(e^{\epsilon/k_B T} - 1)^{-1}$ corresponds to the Bose-Einstein distribution

- Specific heat

$$c_v = \frac{1}{V} \frac{\partial \langle \mathcal{E} \rangle}{\partial T} = \frac{1}{V} \sum_{\mathbf{k}s} \frac{\partial}{\partial T} \frac{\hbar\omega_s(\mathbf{k})}{e^{\hbar\omega_s(\mathbf{k})/k_B T} - 1}$$

- to evaluate this we need the number of possible states

High temperature specific heat

- At very high temperatures $\hbar\omega_s(\mathbf{k}) \ll k_B T$

$$\frac{1}{e^{\hbar\omega_s(\mathbf{k})/k_B T} - 1} \rightarrow \frac{k_B T}{\hbar\omega_s(\mathbf{k})}$$

$$c_v = \frac{1}{V} \sum_{\mathbf{k}s} \frac{\partial}{\partial T} \frac{\hbar\omega_s(\mathbf{k})}{e^{\hbar\omega_s(\mathbf{k})/k_B T} - 1} \rightarrow \frac{1}{V} \sum_{\mathbf{k}s} \frac{\partial}{\partial T} (k_B T) = \frac{k_B}{V} \sum_{\mathbf{k}s} = \frac{3Nk_B}{V} = 3nk_B$$

- which is just the Dulong and Petit law
- at very high temperatures, all phonon modes are activated with high occupation numbers

- At very low temperatures $\hbar\omega_s(\mathbf{k}) \gg k_B T$

- assume only the linear part of the acoustic branch $\omega_s(\mathbf{k}) \rightarrow v_s(\hat{\mathbf{k}})k$

$$c_v \rightarrow \frac{\partial}{\partial T} \sum_s \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\hbar v_s(\hat{\mathbf{k}})k}{e^{\hbar v_s(\hat{\mathbf{k}})k/k_B T} - 1}$$

- set $d\mathbf{k} = k^2 dk d\Omega$ $\frac{1}{v^3} = \frac{1}{3} \sum_s \int \frac{d\Omega}{4\pi} \frac{1}{v_s(\hat{\mathbf{k}})^3}$

$$c_v = \frac{\partial}{\partial T} \frac{(k_B T)^4}{(\hbar v)^3} \frac{3}{2\pi^2} \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\partial}{\partial T} \frac{\pi^2 (k_B T)^4}{10(\hbar v)^3} = \frac{2\pi^2}{5} k_B \left(\frac{k_B T}{\hbar v} \right)^3$$

Debye and Einstein models

Summary

- **Classical (Drude) theory of metals**
 - electrons scatter with relaxation time τ
 - Classical statistical distribution of velocities
 - Quantities that include the velocity or c_v are not accurate:
 - velocities are underestimated by an order of magnitude
 - thermal capacity is overestimated by 2 orders of magnitude
- **Sommerfeld theory of metals**
 - Pauli exclusion principle, velocities follow a Fermi-Dirac distribution
 - Definition of Fermi quantities: energy, velocity etc of the last occupied state
 - Quantities with velocity and c_v are now accurate
 - velocity to be used is the Fermi velocity
 - only the electrons close to the Fermi energy can be thermally excited