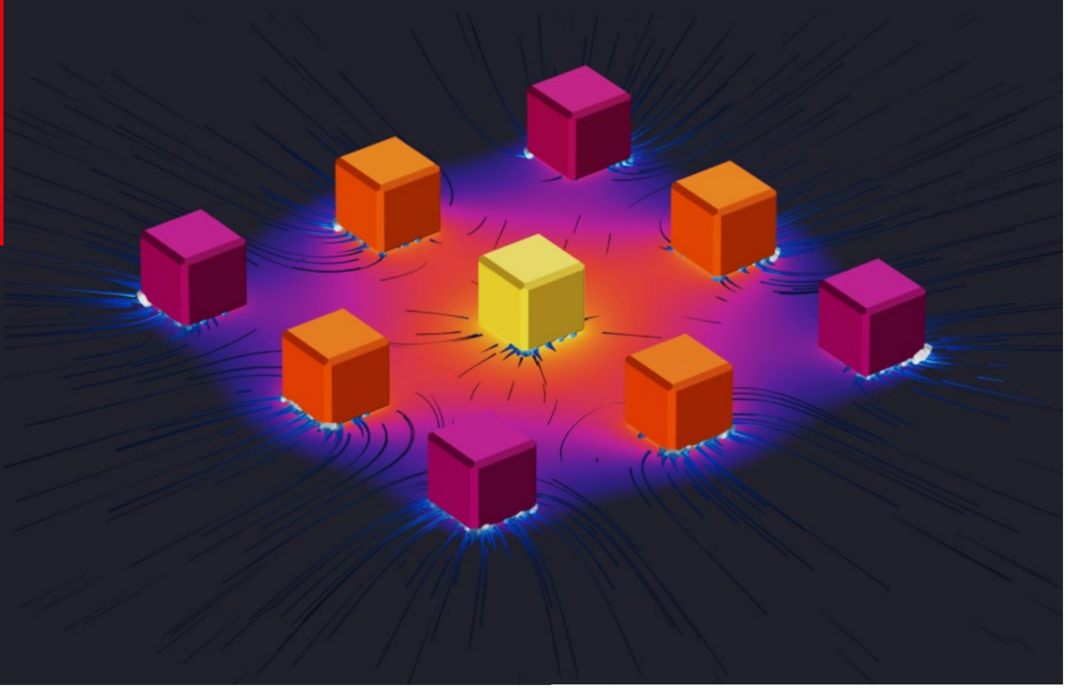
Nanoscale Heat Transfer (and Energy Conversion) ME469

Instructor: Giulia Tagliabue



École
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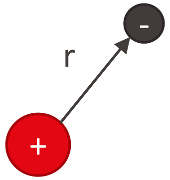
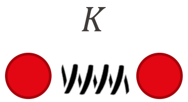
Spring Semester 2020

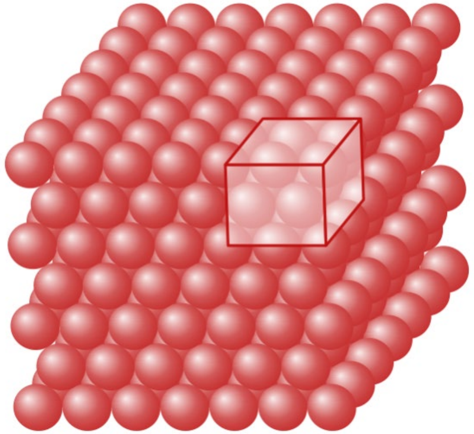
From Individual Elements to Periodic Arrangements



Individual Atom
(electron)

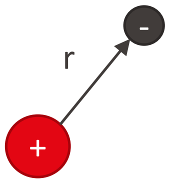


Individual Molecule
Single pair of Particles
(phonons)



3D Periodic Arrangement

From Individuals to Crystals



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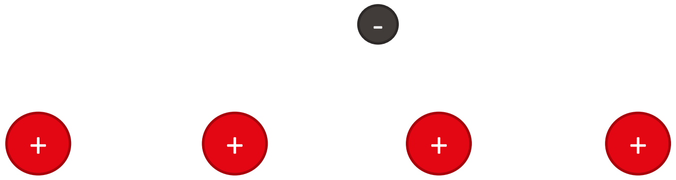

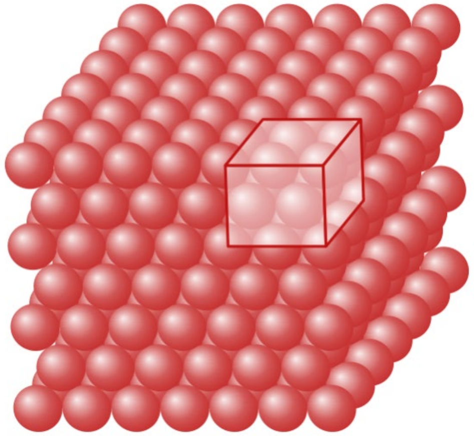

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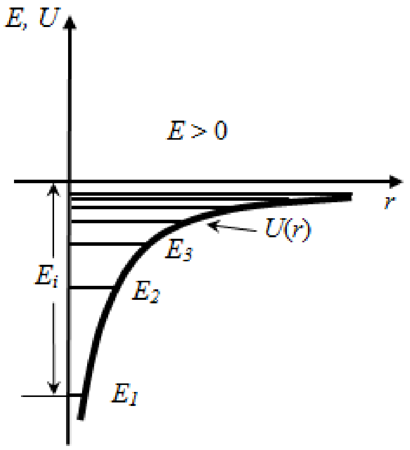
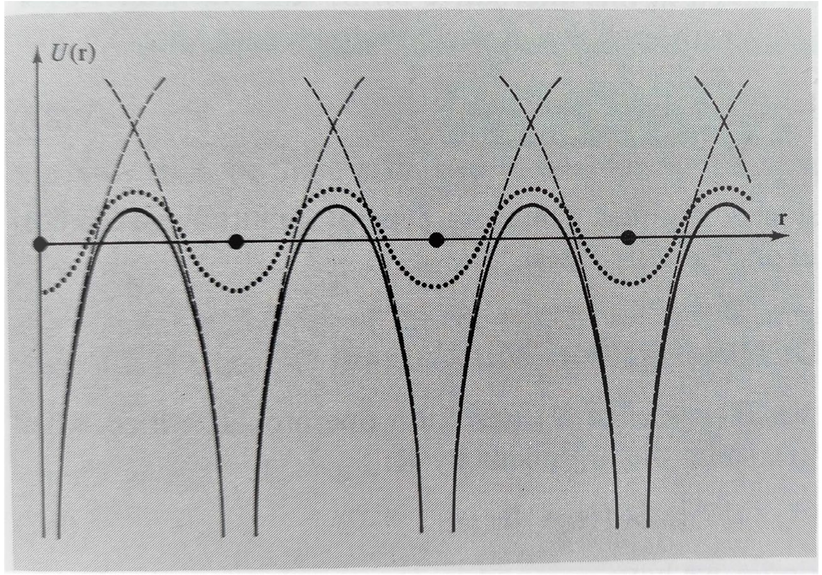




What are the electronic energy levels and wavefunctions in a periodic potential?

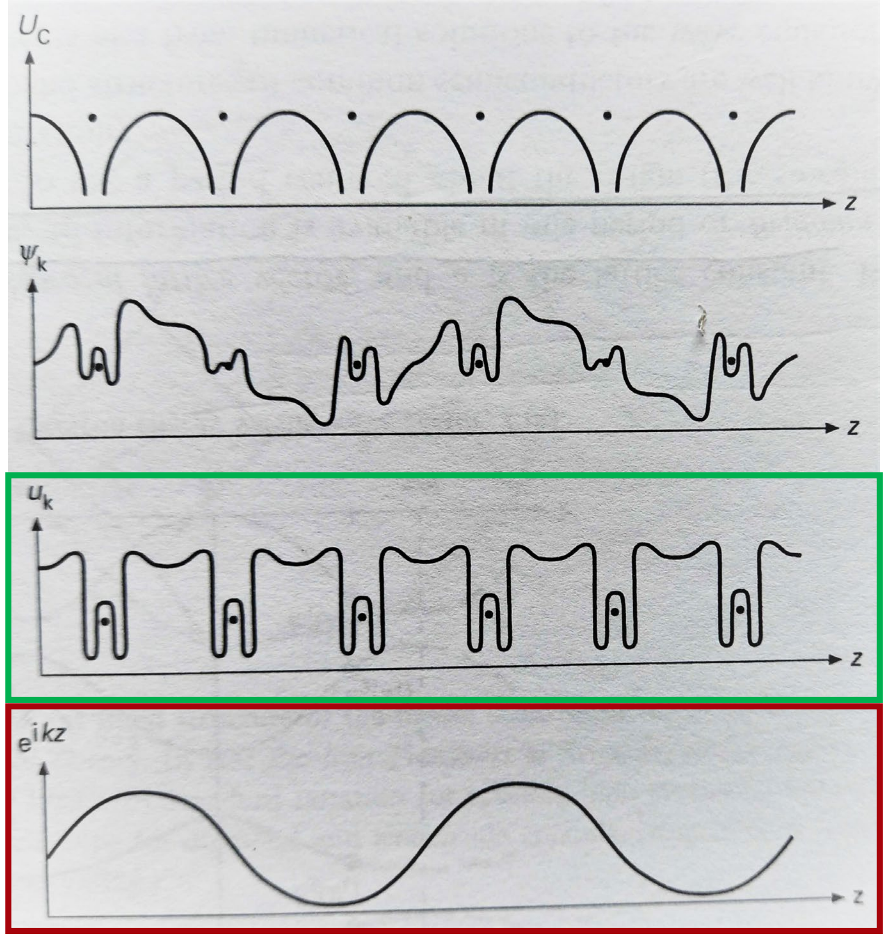
Electron Energy States in a Periodic Potential

Bloch's Theorem demonstrates that we can write a wavefunction in a periodic potential as follows:

$$\Psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}} \qquad \text{where} \qquad u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r}) \quad \forall \vec{R}$$

Plane wave (phase factor)

Function with the periodicity of the lattice



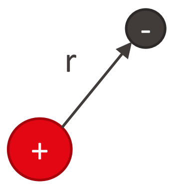
Indeed it is straightforward to show that if the wavefunction has this structure, then:

$$\Psi_{n\vec{k}}(\vec{r}+\vec{R}) = \Psi_{n\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{R}}$$

It is important to recognize that:

- $\vec{k} \neq K$
- While in the case of a free particle with wavefunction $\Psi \propto e^{i\vec{k}\cdot\vec{r}}$, $\vec{k}$ was proportional to the electron momentum, in a periodic potential this is not the case. Yet, the quantity $\hbar\vec{k}$ is known as ***crystal momentum*** and plays an important role in the dynamics of electrons in a solid.
- For every value of $\vec{k}$ there are infinite solutions $u_{n\vec{k}}(\vec{r})$, this is why we have introduced the index n to distinguish different wavefunctions with the same $\vec{k}$.

From Individuals to Crystals



Individual Atom
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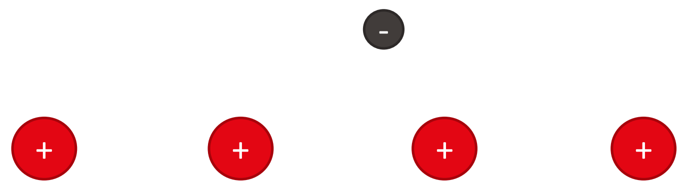
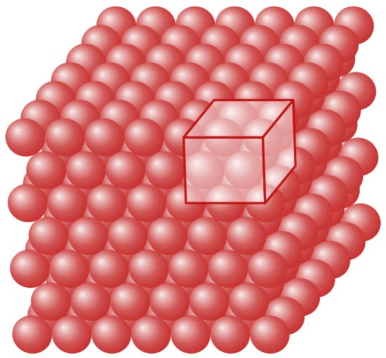
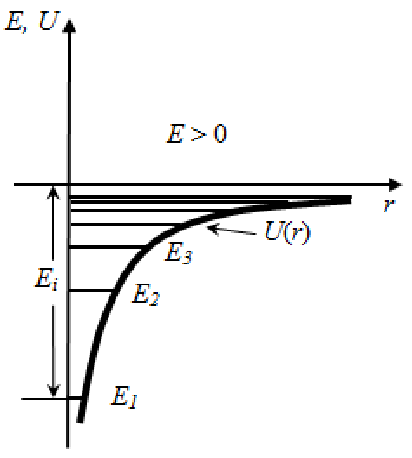
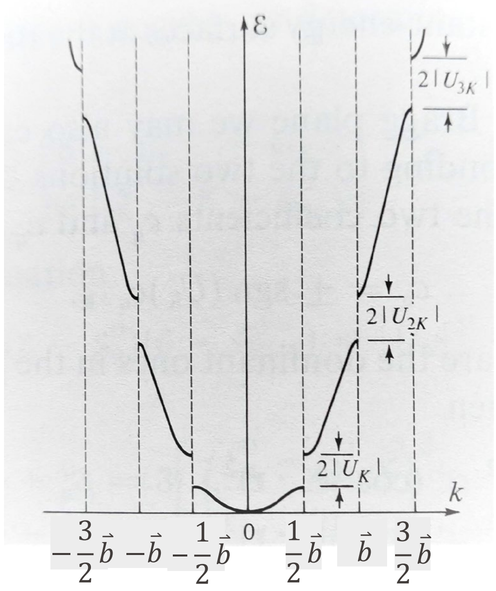




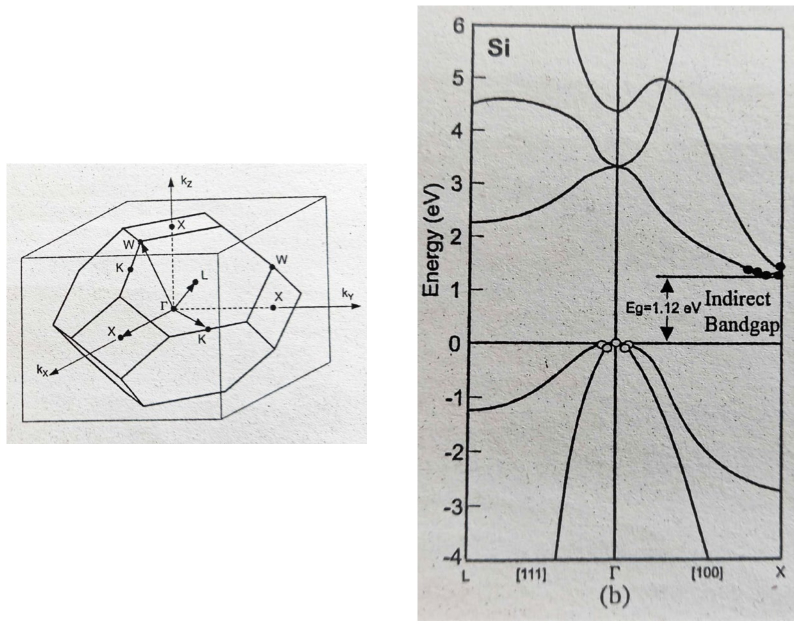
3D Periodic Arrangement



Discrete energy levels



Band-structure
(N discrete k values in each band)



3D Band-structure
(each direction in space has a different periodic potential)

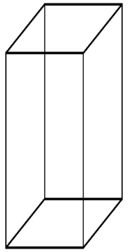
In This Lecture…

- Electron Energy States in Periodic Lattices
  - **Density of States**
  - Nanoscale Confinement
- Phonons
  - Energy states in Periodic Lattices
  - Phonon Density of States
- Photons Density of States

Electron Density of States

We can observe that often, for 3D lattices, for a given value of E, there are many possible combinations of k_i

Example 1 – particle in a box

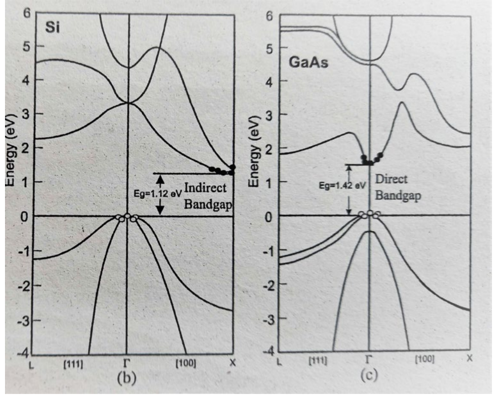


$$E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

$$k_x = \frac{\pi}{L_x} n$$

parabolic band structure

Example 2 – conduction band of a semiconductor (periodic potential)



Close to the conduction band minimum we can use a parabolic band approximation (Taylor expansion):

$$E - E_c = \frac{\hbar^2}{2m^*}\left(k_x^2 + k_y^2 + k_z^2\right) \qquad k_i = \frac{2\pi}{Na} n = \frac{2\pi}{L} n$$

$$n = \pm 0, \pm 1, \ldots \pm \frac{N}{2} \qquad m^* = effective\ mass$$

➡ $$E - E_c = \frac{\hbar^2}{2m^*} k^2 \qquad k^2 = k_x^2 + k_y^2 + k_z^2$$

Electron Density of States

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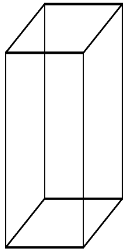

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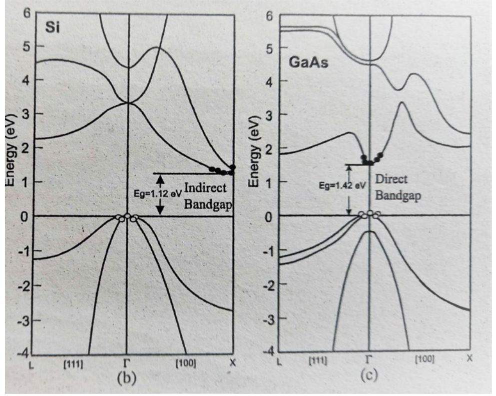

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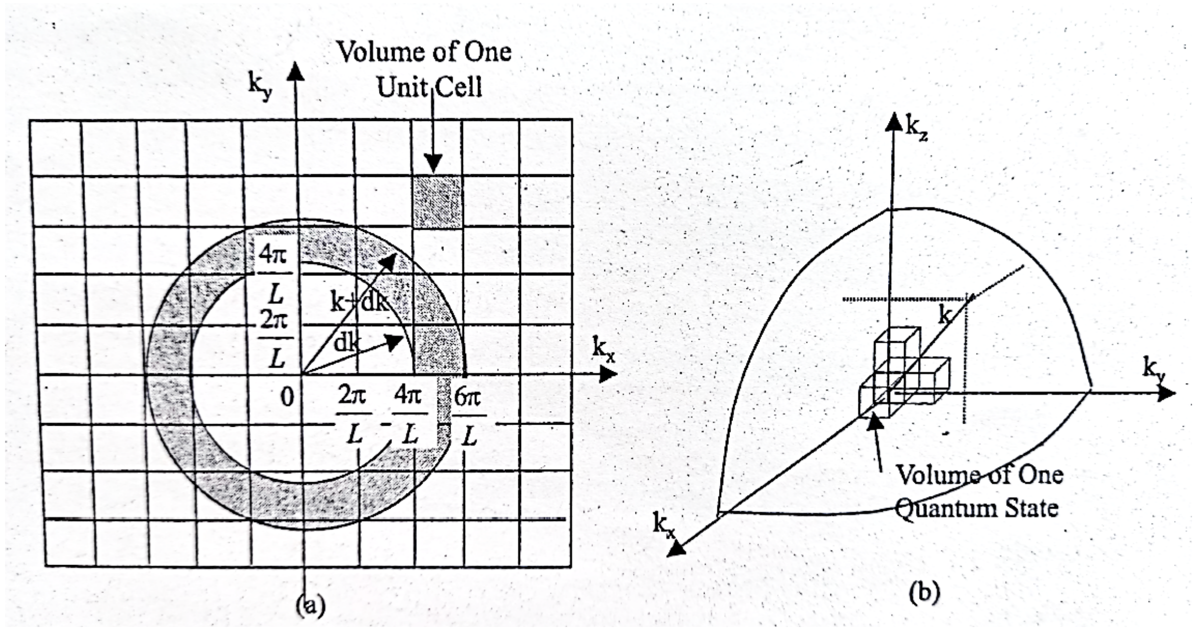
We have also discussed previously that the Born-Von Karmann condition results in discrete values of k, i.e. quantum states.

It is often convenient to know the number of quantum states available in an energy interval $E + dE$ and per unit volume of the crystal.

We call this quantity **density of states**.

Electron Density of States



$$E - E_c = \frac{\hbar^2}{2m^*}k^2 \qquad k^2 = k_x^2 + k_y^2 + k_z^2 \qquad k_i = \frac{2\pi}{L}n \qquad n = \pm 0, \dots \pm \frac{N}{2}$$

Observations:

- In 3D each quantum mechanical state occupies a volume $(2\pi/L)^3$
- the iso-energy surface is a circle (2D) / sphere (3D).

Thus, in 3D the number of energy states between k and $k + \Delta k$ is:

$$\# = \underset{\substack{\uparrow \\ spin}}{2} \cdot \frac{4\pi k^2 dk}{(2\pi/L)^3} = \frac{Vk^2 dk}{\pi^2} \qquad V = L^3 = crystal\ volume$$

We can first define the **density of states** as the number of quantum states per unit interval of the wavevector, dk, per unit volume, V:

$$D(k) = \frac{\#states\ between\ k\ and\ k + dk}{Vdk} = \frac{k^2}{\pi^2}$$

Re-writing as a function of energy we have:

$$d(E - E_c) = \frac{\hbar^2}{m^*}kdk$$

$$dk = \frac{m^* d(E - E_c)}{\hbar^2\sqrt{\frac{2m^*}{\hbar^2}(E - E_c)}}$$

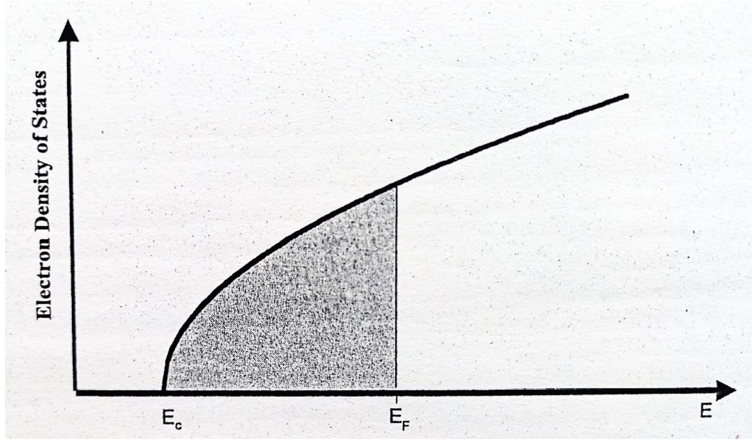
➡

$$D(E) = \frac{\#states\ between\ E\ and\ E + dE}{VdE} = \frac{2m^*}{\hbar^2}(E - E_c)\frac{m^*}{\hbar^2\sqrt{\frac{2m^*}{\hbar^2}(E - E_c)}}$$

➡

$$\boldsymbol{D(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E - E_c}}$$

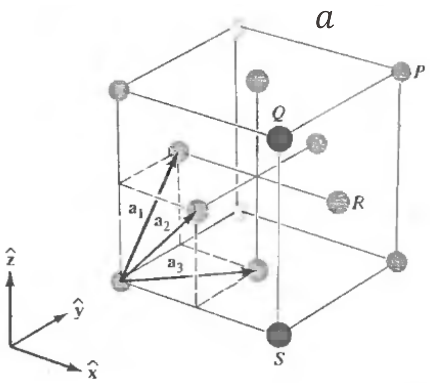
Electron Density of States



$$D(E) = \frac{\mathbf{1}}{\mathbf{2\pi^2}}\left(\frac{\mathbf{2m^*}}{\hbar^2}\right)^{3/2}\sqrt{\boldsymbol{E-E_c}}$$

To see how this is useful, we now want to find the Fermi level for a gold crystal at $T = 0K$. Being gold a metal we can set $E_c = 0$

Gold as an FCC lattice with one atom per lattice point and a lattice constant $a = 4.08$ Å.
Using the conventional FCC lattice cell we have 4 lattice points. Furthermore, each lattice point has one electron. Thus we have 4 electrons per conventional cell.



➡ $$n = \frac{\#electrons\ cell}{V_{cell}} = \frac{4}{(4.08\cdot 10^{-10})^3} = 5.89\cdot 10^{28}\ m^{-3} = 5.89\cdot 10^{22}\ cm^{-3}$$

At the same time we observe that we can write: $$n = \frac{N_{electrons}}{V_{crystal}} = \int_0^{E_F} D(E)dE = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} {E_F}^{3/2}$$

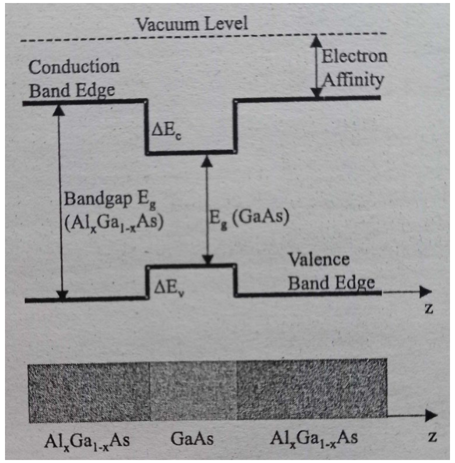
➡ $$E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} = 8.66\cdot 10^{-19}\,J = 5.4\ eV$$

In This Lecture…

- Electron Energy States in Periodic Lattices
  - ➢ Density of States
  - ➢ **Nanoscale Confinement**
- Phonons
  - ➢ Energy states in Periodic Lattices
  - ➢ Phonon Density of States
- Photons Density of States

Nanoscale Confinement and Artificial Structures

So far we have discussed infinite bulk crystals. Let's now confine one of the spatial directions such that quantization effects become important.



Quantum well: by using two semiconductors with different values of the electron affinity, we can create a potential well. If the thickness (z) of such potential well is sufficiently small (d< 200 nm) it will behave like a quantum well, giving rise to quantization of the electronic energy levels along z.

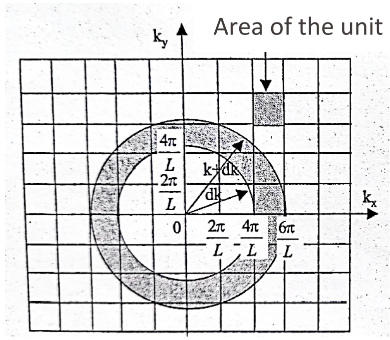
$$E = \frac{\hbar^2}{2m^*}\left(k_x^2 + k_y^2\right) + n^2\frac{\hbar^2\pi^2}{2m^*d^2}$$

$$k_x, k_y = \pm\frac{2\pi}{Na}n = \pm\frac{2\pi}{L}n$$

$$E = \frac{\hbar^2}{2m^*}k_{xy}^2 + n^2\frac{\hbar^2\pi^2}{2m^*d^2}$$

$$k_{xy}^2 = k_x^2 + k_y^2$$

Area of the unit cell



We observe that if $E_n = n^2\frac{\hbar^2\pi^2}{2m^*d^2}$, $E_n < E < E_{n+1}$ can be obtained with n-combinations:

$$\left\{\begin{aligned} E_n &= \frac{\hbar^2}{2m^*}k_{xy,1}^2 + \frac{\hbar^2\pi^2}{2m^*d^2} \\ E_n &= \frac{\hbar^2}{2m^*}k_{xy,2}^2 + 4\frac{\hbar^2\pi^2}{2m^*d^2} \\ &\vdots \\ E_n &= n^2\frac{\hbar^2\pi^2}{2m^*d^2} \end{aligned}\right.$$

We also observe that for each combination, the number of states between k_{xy} and $k_{xy} + dk_{xy}$

$$\# = \frac{4\pi k_{xy}dk_{xy}}{(2\pi/L)^2}$$

while

$$dE = \frac{\hbar^2}{m^*}k_{xy}dk_{xy}$$

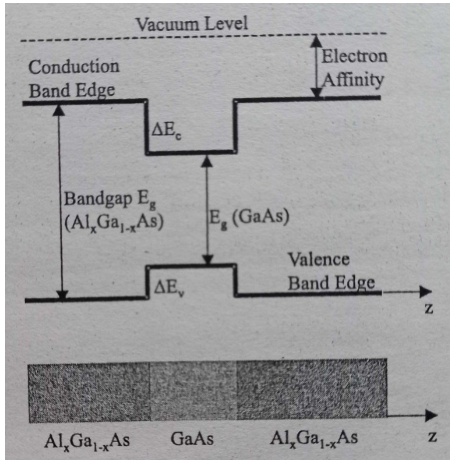
For each allowable k_{xy} series the density of states is

$$D_1(E) = \frac{\#}{AdE} = \frac{m^*}{\pi\hbar^2} \qquad \text{with} \qquad A = L^2$$

Thus for the energy state $E_n < E < E_{n+1}$

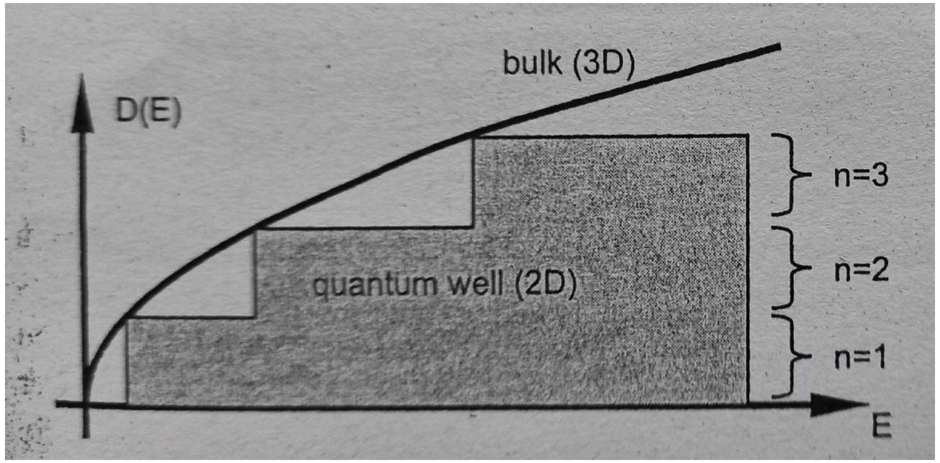
$$D(E) = nD_1(E)$$

Nanoscale Confinement and Artificial Crystal



$$D_1(E) = \frac{\#}{AdE} = \frac{m^*}{\pi\hbar^2}$$

$$D(E) = nD_1(E)$$

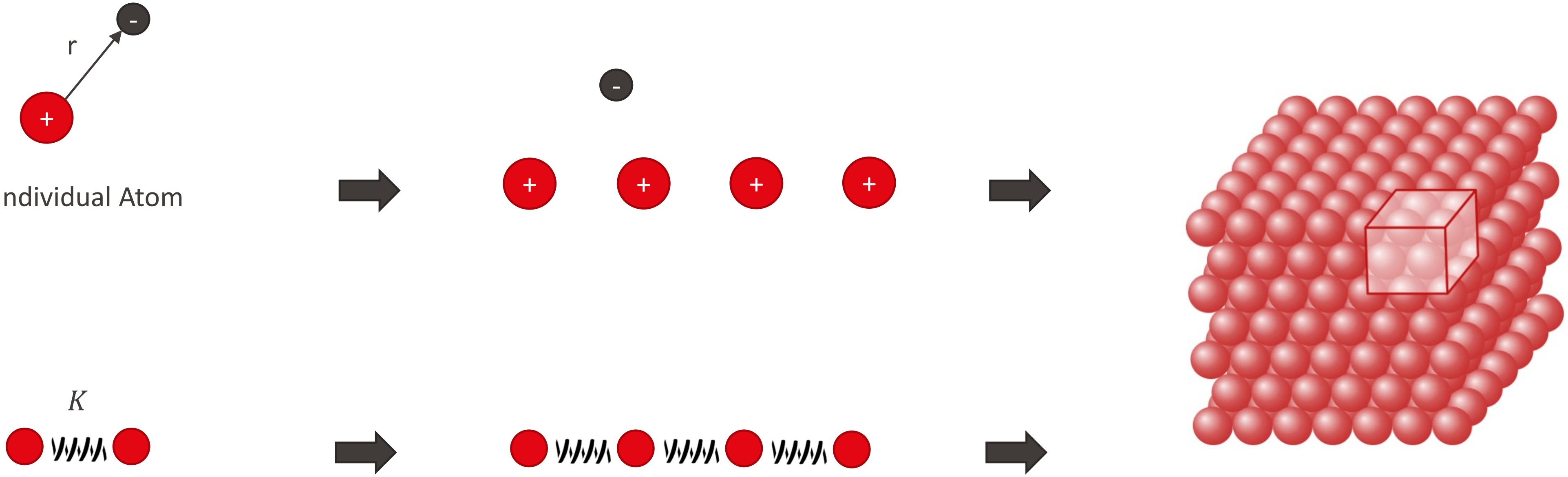


- **What happens if we have 2D confinement, i.e. a nanowire?**
- **And for 3D confinement, i.e. a quantum dot?**

In This Lecture…

- Electron Energy States in Periodic Lattices
  - Density of States
- Phonons
  - **Energy states in Periodic Lattices**
  - Phonon Density of States
- Photons Density of States

From Individuals to Crystals



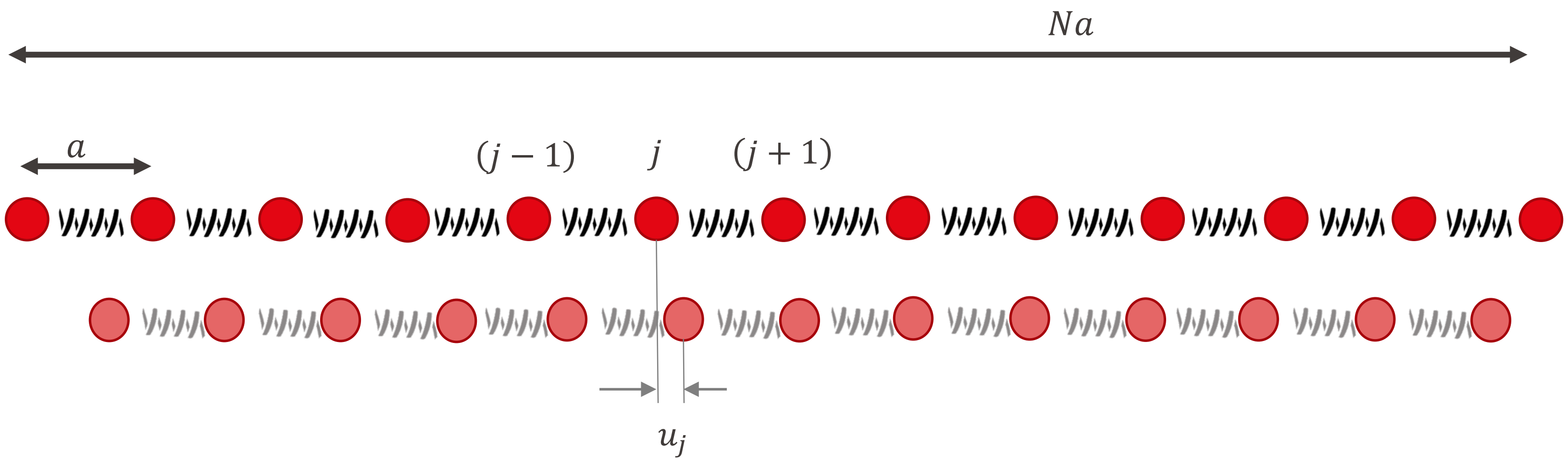
Individual Atom

Individual Molecule
Single pair of Particles

1D Periodic Arrangement

3D Periodic Arrangement

Phonon Modes of a Crystal – 1D monoatomic lattice



Hypothesis:

1. Force interactions occur only between nearest neighbors
2. Harmonic interaction force (Hooke's law)
3. Equal mass M and spring constant K

⇒

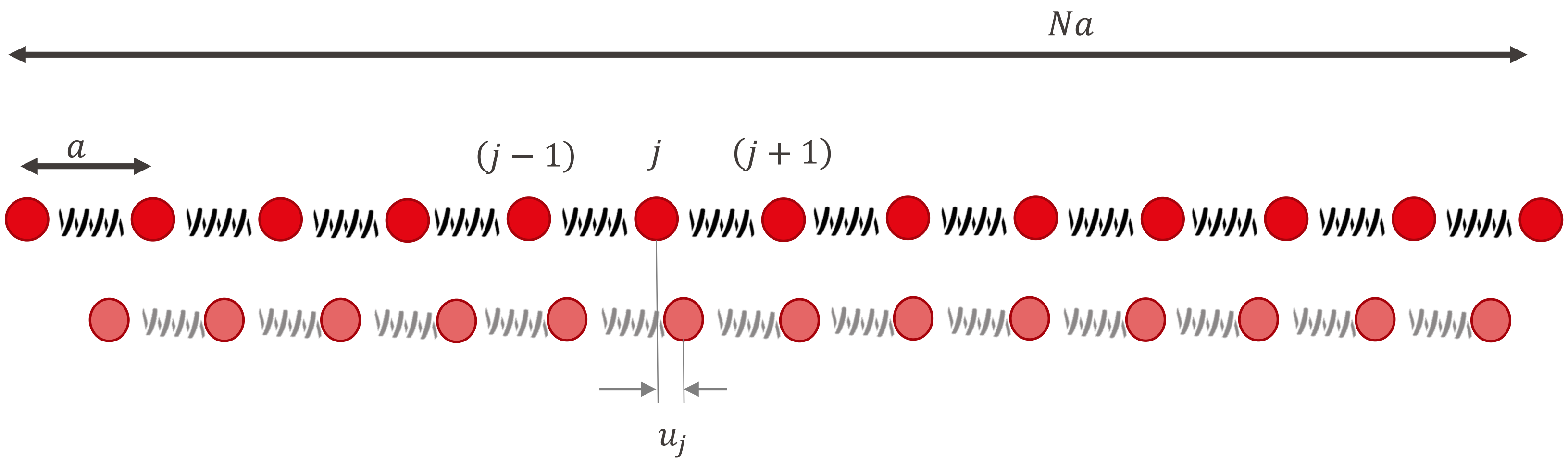
$$\begin{cases} u_j = x_j - x_j^0 & \text{displacement} \\ U^{harm} = \frac{1}{2}K\sum_j \left[u_j - u_{j+1}\right]^2 & \text{potential} \\ F_j = -\frac{\partial U^{harm}}{\partial u_j} = K\left(u_{j+1} - u_j\right) - K\left(u_j - u_{j-1}\right) & \text{force} \end{cases}$$

To find the energy states of this system we can use:

- Schrodinger equation with periodic harmonic potential
- Classical solution of the vibration modes of this system + quantization of the energy states as for the quantum harmonic oscillator

We follow the second option.

Phonon Modes of a Crystal – 1D monoatomic lattice



Hypothesis:

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$u_j = x_j - x_j^0$ displacement

$U^{harm} = \frac{1}{2} K \sum_j \left[u_j - u_{j+1}\right]^2$ potential

$F_j = -\frac{\partial U^{harm}}{\partial u_j} = K\left(u_{j+1} - u_j\right) - K\left(u_j - u_{j-1}\right)$ force

Dynamical equations (Newton's law):

$$m \frac{d^2 u_j}{dt^2} = K\left(u_{j+1} - u_j\right) - K\left(u_j - u_{j-1}\right)$$

This equation has the typical form :

$$m \frac{\partial^2 u_j}{\partial t^2} = K a^2 \frac{\partial^2 u_j}{\partial x^2}$$

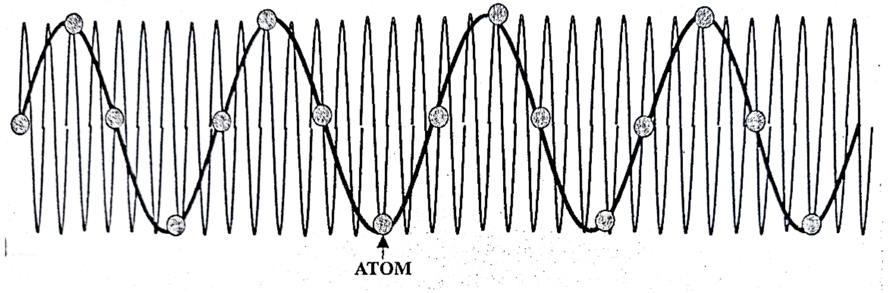
with solution of the form $u_j = A e^{-i(\omega t - kx)}$

Phonon Modes of a Crystal – 1D monoatomic lattice

$$m\frac{d^2u_j}{dt^2} = K\left(u_{j+1} - u_j\right) - K\left(u_j - u_{j-1}\right) \qquad u_j = Ae^{-i(\omega t - kx)}$$

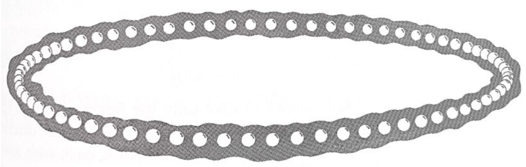
Observations:

1. The displacement is defined only at DISCRETE lattice coordinates $x = ja$. Indeed, talking about vibration at locations other than the atomic sites is meaningless.



$$u_j = Ae^{-i(\omega t - kx)} \Rightarrow u_j = Ae^{-i(\omega t - kja)}$$

2. The real lattice is infinite so we should use the Born-von Karmann boundary condition to describe it correctly:



$$u_N = u_0 \quad \text{or} \quad u_{(N+1)} = u_1 \Rightarrow e^{-ikNa} = 1 \Rightarrow k = \frac{2\pi}{Na}n$$

3. There are just N values of k . Indeed $n = N + 1 \Rightarrow u_j = Ae^{-i(\omega t - \frac{2\pi}{Na}(N+1)ja)} = Ae^{-i(\omega t - \frac{2\pi}{Na}ja)}$

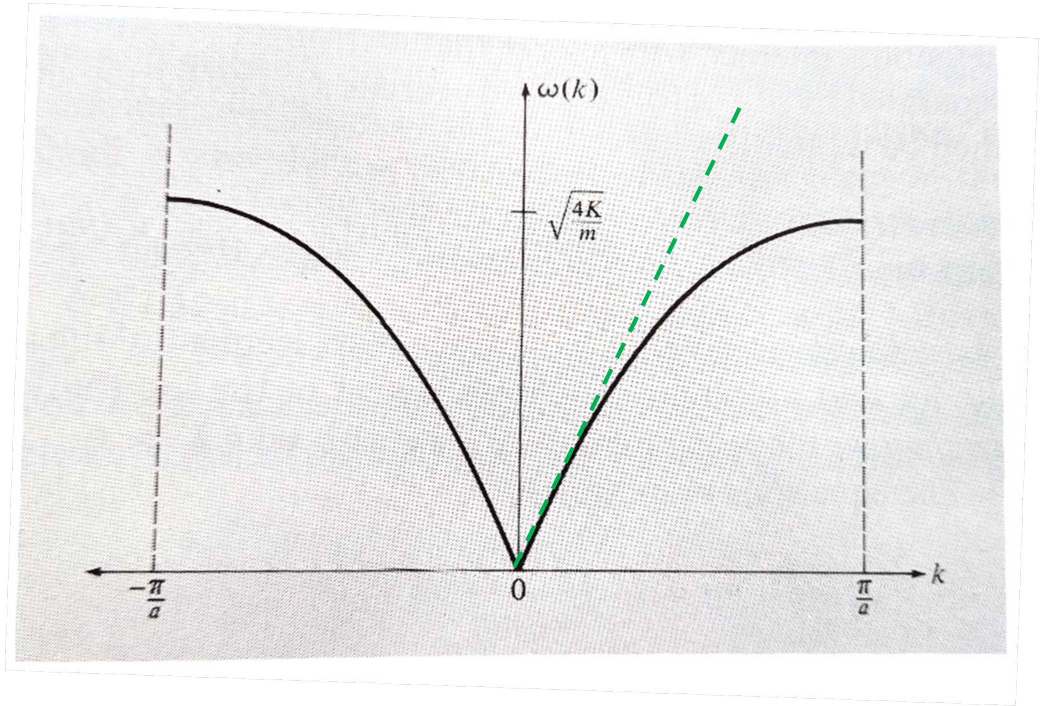
Phonon Modes of a Crystal – 1D monoatomic lattice

$$m\frac{d^2u_j}{dt^2} = K\left(u_{j+1}-u_j\right) - K\left(u_j-u_{j-1}\right) \qquad u_j = Ae^{-i(\omega t-kx)} \qquad k=\frac{2\pi}{Na}n \qquad n=\pm0,\pm1,\ldots\pm\frac{N}{2}$$

➡ $$\boldsymbol{-m\omega^2 e^{-i(\omega t-kja)}} = K\left(e^{-i(\omega t-k(j+1)a)} - 2e^{-i(\omega t-kja)} + e^{-i(\omega t-k(j-1)a)}\right) = K\left(e^{ka}-2+e^{-ka}\right)e^{-i(\omega t-kja)} = \boldsymbol{-2K(1-\cos(ka))e^{-i(\omega t-kja)}}$$

➡ $$\omega = \sqrt{\frac{2K(1-\cos(ka))}{m}} = 2\sqrt{\frac{K}{m}}\left|\sin\left(\frac{1}{2}ka\right)\right|$$

➡ $$u(ja,t) \propto Re\left\{e^{-i(\omega t-kja)}\right\}$$



The solutions $u(ja,t)$ describe plane waves propagating along the chain with:

- *Phase velocity* $c = \omega/k$
- *Group velocity* $v = \partial\omega/\partial k$

Dispersion relation $\omega(k)$

- For $k \ll \pi/a$, i.e. wavelength much larger than inter-atomic spacing, we can assume a linear dispersion $\omega = a\sqrt{\frac{K}{m}}|k|$ **Debye Approximation**
- For $k\sim\pi/a$ we have v~0

Phonon Modes of a Crystal – 1D monoatomic lattice

$$\omega = \sqrt{\frac{2K(1-\cos(ka))}{m}} = 2\sqrt{\frac{K}{m}}\left|\sin(\frac{1}{2}ka)\right| \qquad u(ja,t) \propto Re\{e^{-i(\omega t - kja)}\} \qquad k = \frac{2\pi}{Na}n \qquad n = \pm 0, \pm 1, \ldots \pm \frac{N}{2}$$

For the classical resonator, the vibrational energy at each frequency is determined by the amplitude of oscillation A

For the quantum mechanical oscillator we have previously demonstrated that the energy of the lattice vibration is quantized: $E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad n = 0,1, \ldots$

➡ **We call PHONON the minimum quantum of lattice vibration (normal mode). This collective excitation has a zero rest mass.**

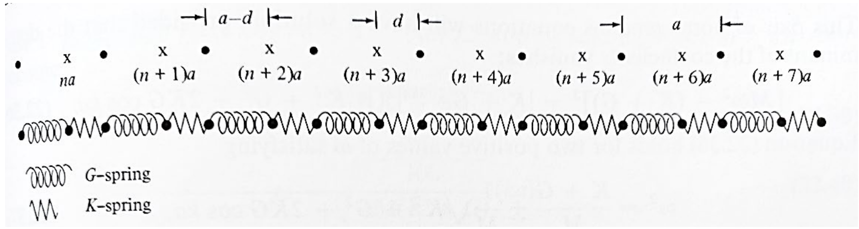
Each phonon has an energy $\mathrm{E} = \hbar\omega$ where $\omega = 2\sqrt{\frac{K}{m}}\left|\sin(\frac{1}{2}ka)\right|$

and the amplitude of the mode will be related to the number of phonons in that mode (L3, slide 8).

For phonons, one quantum state corresponds to one set of wavevectors k. We note that there are N frequencies and hence phonon energies for a monoatomic 1D lattice.

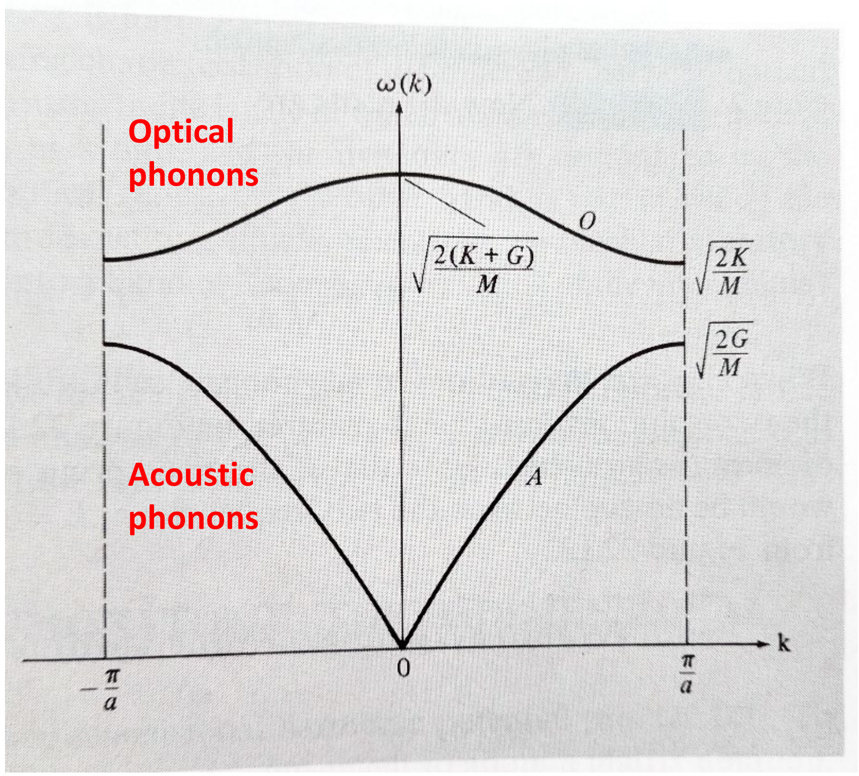
Finally, we observe that, contrary to the electron case where the Pauli exclusion principle restrict the occupancy of a quantum state to just two electrons, many phonons can occupy the same quantum state.

Phonon Modes of a Crystal – 1D polyatomic lattice



If we consider a lattice with two ions per primitive cell we will have to consider to different coupling constants, K, G.

Masses could also be different but for simplicity we consider identical ions with mass m

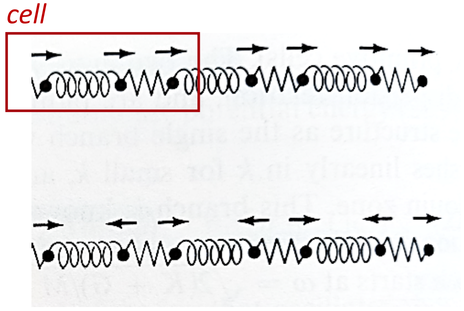


The solutions for this system gives: $\omega^2 = \frac{K+G}{m} \pm \frac{1}{m}\sqrt{K^2 + G^2 + 2KG\cos(ka)}$

- For $k \ll \pi/a$ subsequent primitive cells oscillate in phase. Yet, ions within the cell have different phase

$$\omega_- = \omega_{acu} = \sqrt{\frac{KG}{2m(K+G)}}(ka)$$

$$\omega_+ = \omega_{opt} = \sqrt{\frac{2(K+G)}{m}}$$



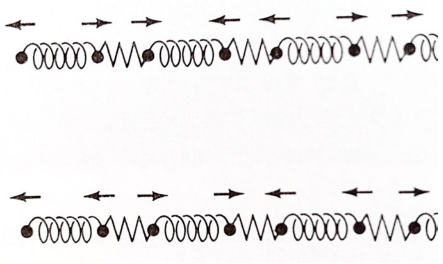
In-phase ion oscillation

Out-of-phase ion oscillation

- For $k \sim \pi/a$ subsequent primitive cells oscillate out of phase. Ions within the cell have different phase

$$\omega_- = \omega_{acu} = \sqrt{\frac{2G}{m}}\left|sin\left(\frac{1}{2}ka\right)\right|$$

$$\omega_+ = \omega_{opt} = \sqrt{\frac{2K}{m}}$$

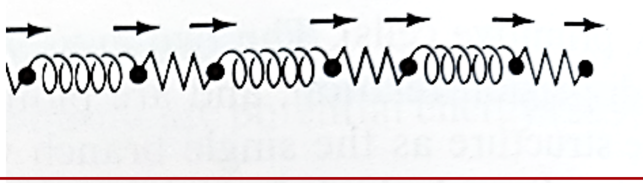
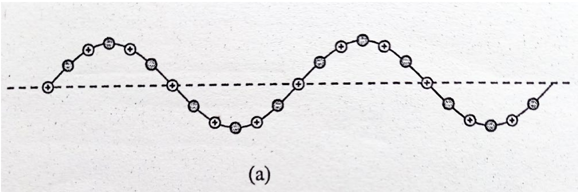
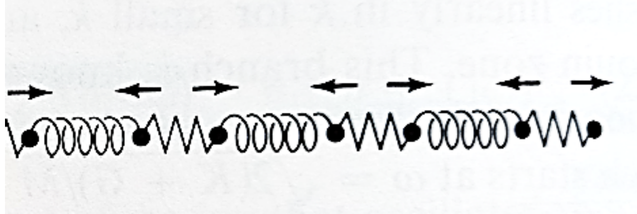
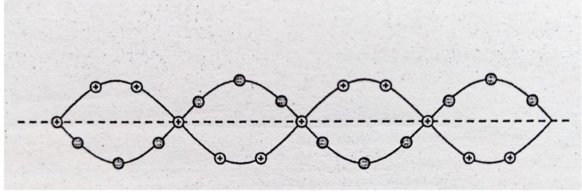


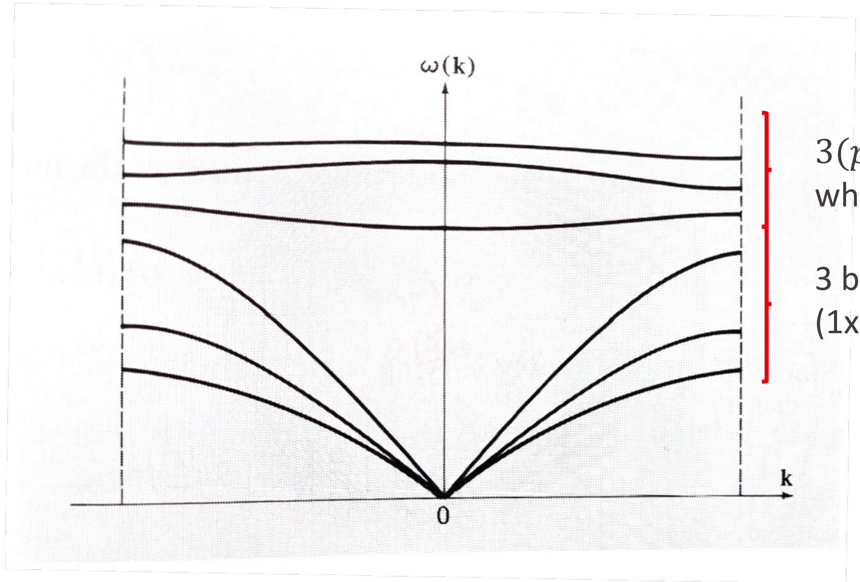
In-phase ion oscillation

Out-of-phase ion oscillation

Phonon Modes of a Crystal – 3D lattices

For a 3D lattice we have more degrees of freedoms. Thus every lattice point can vibrate along all three spatial directions. This results in two types of waves:

	Longitudinal Waves	**Transversal Waves**
Acoustic Phonons		
Optical Phonons		

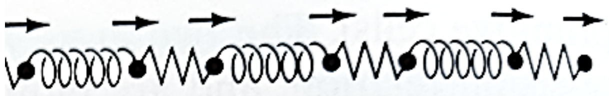
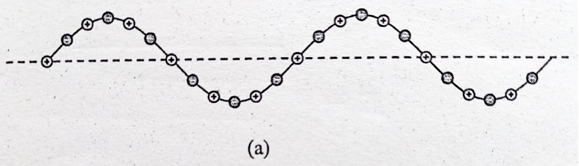
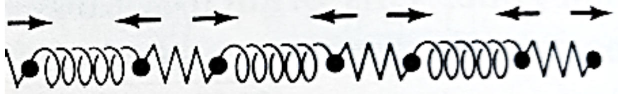
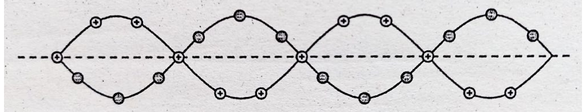


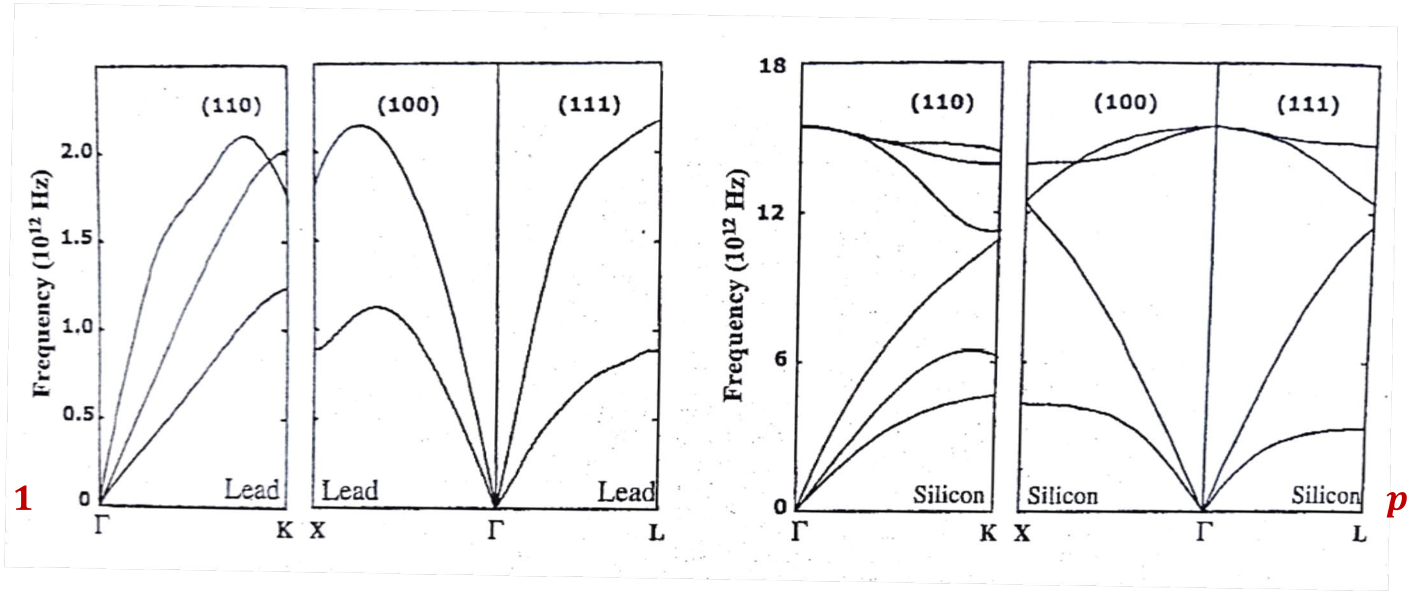
$3(p-1)$ branches of acoustic phonons
where $p = \#atoms\ per\ lattice\ point$

3 branches of acoustic phonons
(1x longitudinal, 2x transversal)

Phonon Modes of a Crystal – 3D lattices

For a 3D lattice we have more degrees of freedoms. Thus every lattice point can vibrate along all three spatial directions. This results in two types of waves:

	Longitudinal Waves	**Transversal Waves**
Acoustic Phonons		
Optical Phonons		



$p = 1$

$p = 2$

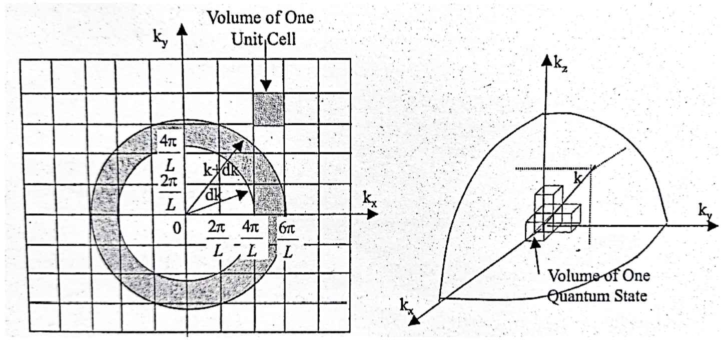
In This Lecture…

- Electron Energy States in Periodic Lattices
    - Density of States
- Phonons
    - Energy states in Periodic Lattices
    - **Phonon Density of States**
- Photons Density of States

Phonon Density of States

We now want to determine the phonon density of states.
To obtain an analytical expression we limit ourselves to a monoatomic lattice and to the Debye regime $k \ll \pi/a$ where $\omega = a\sqrt{\frac{K}{m}}|k| = v_D k$

with $v_D = propagation\ velocity$



In 1D we have: $k = \frac{2\pi}{Na}n = \frac{2\pi}{L}n$

Therefore, for a 3D crystal in k-space the volume of one phonon state is: $V_k = (2\pi/L)^3$

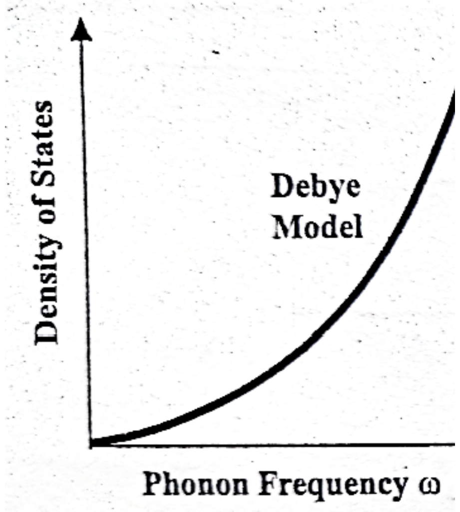
Also, the isofrequency surface will be a sphere in 3D.

Finally the total volume of the crystal is $V = L^3$

While electrons have spin, phonons have different polarizations and we know that we will have 3 polarization states for the acoustic phonons.

$$D(k) = \frac{\#states\ between\ k\ and\ k+dk}{Vdk} = 3\frac{\frac{4\pi k^2 dk}{(2\pi/L)^3}}{Vdk}$$

$$D(\omega) = \frac{\#states\ between\ \omega\ and\ \omega + d\omega}{Vd\omega} = \frac{3\omega^2}{2\pi^2 {v_D}^3}$$



Phonon Density of States

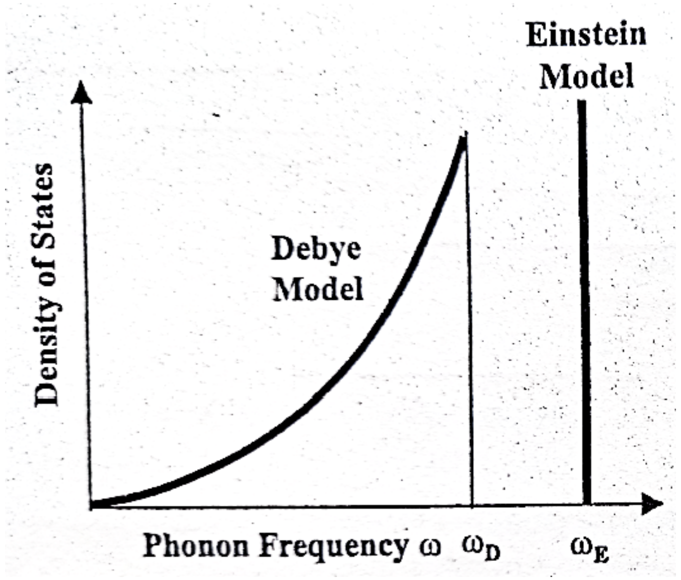
Acoustic Phonons $D(\omega) = \dfrac{3\omega^2}{2\pi^2 {v_D}^3}$

For a 3D lattice this results implies that the propagation velocity v_D is the same in all directions in the lattice. However, even in a cubic lattice, different crystallographic directions have different velocities.

We can nonetheless define a fictitious **Debye crystal** with lattice constant a_D that satisfies the isotropic v_D. To do so, we require that the total number of phonon states in the isotropic crystal equals the total number of states in the real crystal, i.e. $3N$ where N is the number of ions in the crystal, :

$$\left.\begin{aligned} 3N = 3\frac{4/3\pi {k_D}^3}{(2\pi/L)^3} \quad &\Rightarrow \quad k_D = \left(\frac{6\pi^2 N}{V}\right)^{1/3} \\ k_D = \frac{\pi}{a_D} \quad &\Rightarrow \quad a_D = \left(\frac{\pi V}{6N}\right)^{1/3} \end{aligned}\right\} \quad \omega_D = v_D k_D$$

The usefulness of this approximation will become more clear later in the course

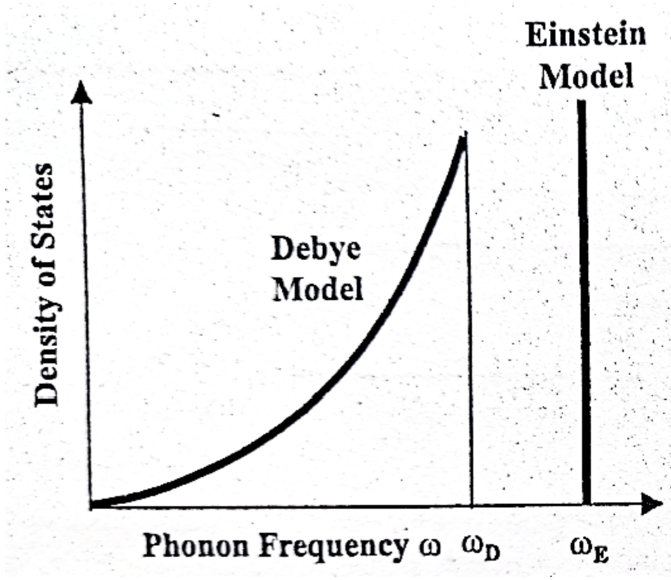


Optical Phonons

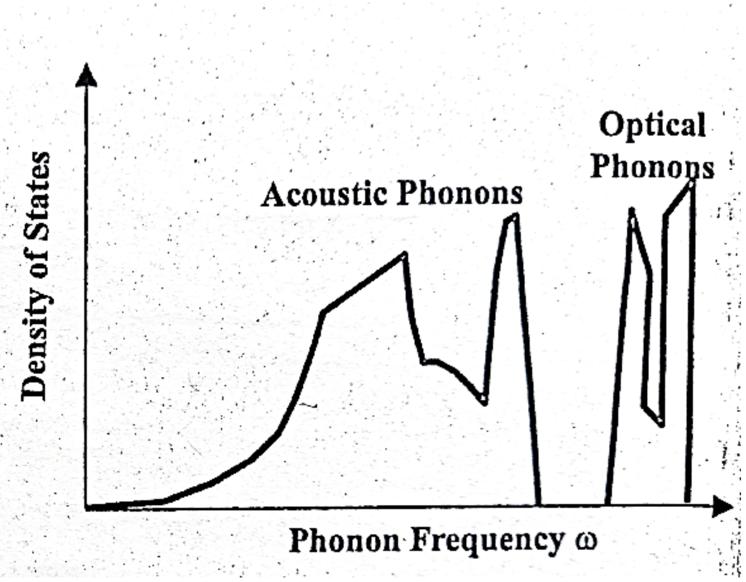
For the optical phonons, a better approximation is $\omega = \omega_E$ for each branch.
Hence, for a lattice with N points, there will be N modes for each branch with N degeneracy.

This approximation is called **Einstein model**.

Phonon Density of States



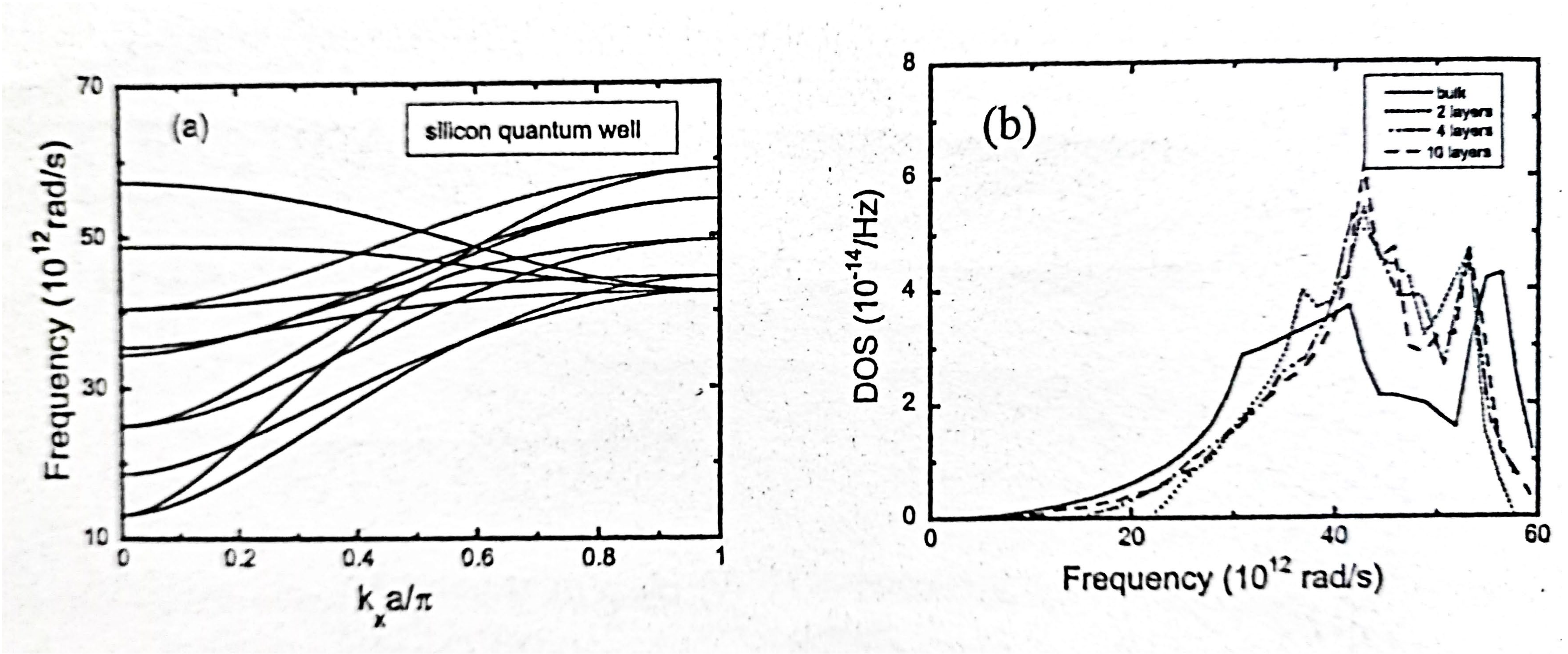
Debye Crystal



Real Crystal

Nanoscale Confinement and Artificial Structures

Similar to what we can do for electrons, we can create quantum wells also for phonons, for example by creating a free-standing ultra-thin film.



We will see that we can use optical tool, such as Raman spectroscopy, to probe the change in the vibrational modes of the structure.

As we will see, controlling the phonon dispersion enables controlling heat flow in the material.

In This Lecture…

- Electron Energy States in Periodic Lattices
    - Density of States
- Phonons
    - Energy states in Periodic Lattices
    - Phonon Density of States
- **Photons Density of States**

Photon Density of States

Photons are the other important particle we will encounter often. It is a quantum of an electromagnetic field oscillation.
Similar to phonons in the Debye approximation, photons have a linear dispersion relation:

$$\omega = ck \qquad\qquad c = speed\ of\ light^*$$

If we consider the electromagnetic field in a cubic box of length L we will find that the allowable wavevectors are: $k_x, k_y, k_z = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots$

Contrary to phonons, however:

- Photons can have only two (transverse) polarizations (factor of 2 instead of 3 for the D(k))
- There is no cut-off frequency for the photons (no minimum wavelength required by the interatomic spacing)

Using the same derivation of the density of states as for phonons we obtain:

$$D(k) = \frac{\#states\ between\ k\ and\ k+dk}{Vdk} = 2\frac{\frac{4\pi k^2 dk}{(2\pi/L)^3}}{Vdk}$$

$$D(\omega) = \frac{\#states\ between\ \omega\ and\ \omega+d\omega}{Vd\omega} = \frac{\omega^2}{\pi^2 c^3}$$

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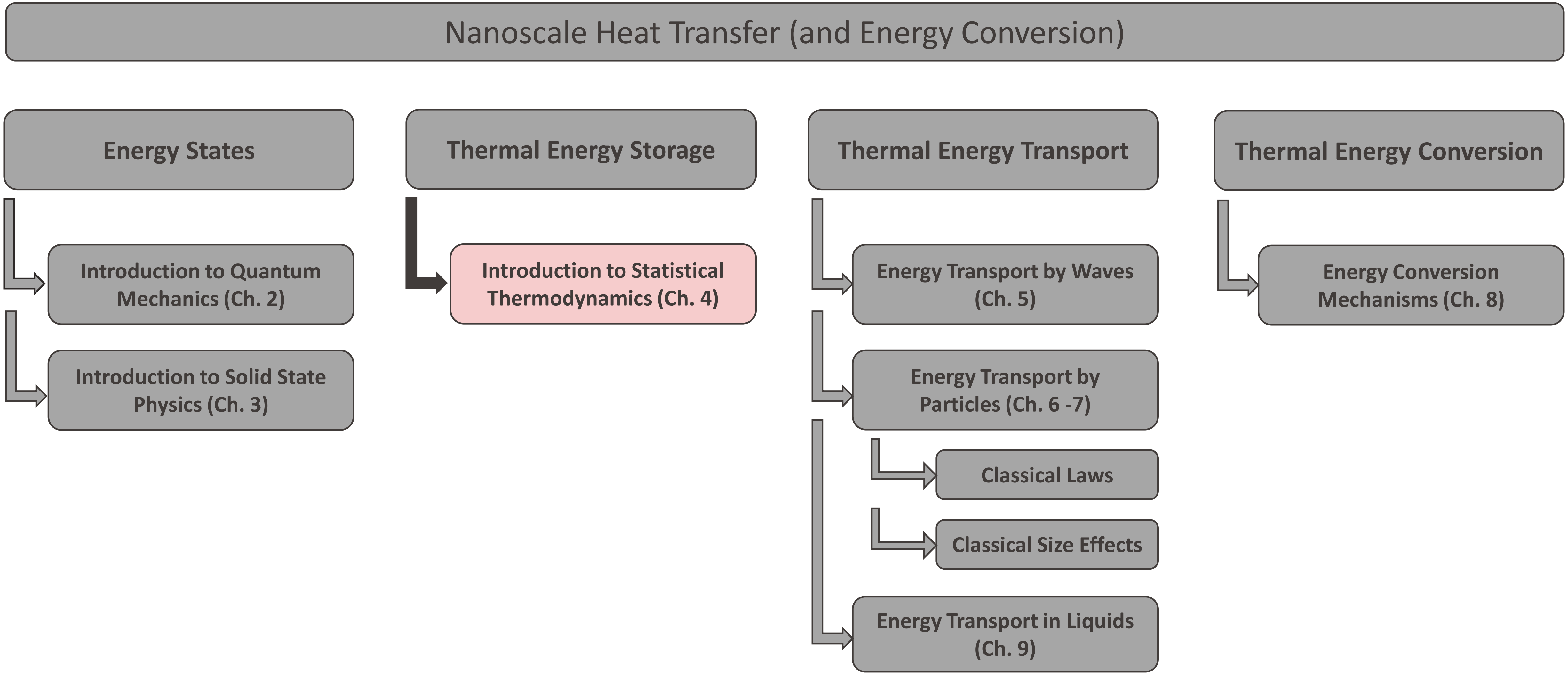
* When travelling inside a material the light can be slowed down compared to its vacuum value. The dispersion relation remains linear

Next Week



Nanoscale Heat Transfer (and Energy Conversion)

Energy States
- Introduction to Quantum Mechanics (Ch. 2)
- Introduction to Solid State Physics (Ch. 3)

Thermal Energy Storage
- Introduction to Statistical Thermodynamics (Ch. 4)

Thermal Energy Transport
- Energy Transport by Waves (Ch. 5)
- Energy Transport by Particles (Ch. 6 -7)
  - Classical Laws
  - Classical Size Effects
- Energy Transport in Liquids (Ch. 9)

Thermal Energy Conversion
- Energy Conversion Mechanisms (Ch. 8)