Outline:

- Quantization of vibrational modes in a 1D chain;
- Concept of Phonons;
- Phonon scattering.
The goal is to understand, at the qualitative level, $g(\omega)$ for real materials.

- Total number of vibrational modes: $8 \times 3 = 24$ (3 translational, some modes could be degenerate, but still a lot of modes).

- Strong deviations from Debye model are observed at high frequencies - $\omega \sim 10^{13} \text{rad}^{-1}$. $c(Si) \sim (5 - 8) \times 10^3 \text{m/s}$, so $k \sim \omega/c \sim 10^9 \text{m}^{-1}$ - approaches $\pi/a$. 

Unit cell: 8 atoms at corners at $1/8$ each in cell 6 atoms in faces at $1/2$ each in cell 4 atoms within cell. Thus total of 8 Si atoms per unit cell.
Importance of $g(\omega)$

**Example:** electron scattering by phonons (vibrations of the lattice). The larger the phonon DoS, the greater the scattering probability.

Analogy: the probability of energy relaxation of an excited atom in an optical resonator is much reduced if the energy of the emitted photon doesn’t match one of the resonator’s modes.
Debye Model, Continuum Approximation

Isotropic continuous medium: \[ u_i = u_{i0} \exp(i\omega t - i\vec{k} \cdot \vec{r}) \]

Dispersion relation is linear \[ \omega = ck \]

What happens when the wave length \( \lambda \) approaches the inter-atomic distance \( a \)? Something **should** happen: all waves, including the elastic ones, should undergo reflection at the Brillouin zone boundary...

The continuum approximation breaks down when the wavelength approaches the inter-atomic distance.

\[ \lambda \sim 2a \quad k \sim \frac{\pi}{a} \quad \text{close to the Brillouin zone boundary} \]

\[ \omega = ck \sim \frac{10 \cdot 10^3}{10^{-10}} \sim 10^{14} \text{rad}^{-1} \leftrightarrow 10^{13} \text{Hz} \leftrightarrow 500K \]

Thus, these effects should be significant at RT!
Let’s consider a 1D chain of identical atoms of mass $m$ coupled to their nearest neighbors by springs of stiffness $\beta$.

Assumptions:
- nearest-neighbor interactions;
- harmonic approximation holds;
- we assume that $\delta x_n \ll a$ (see HW2). In conventional crystals, the assumption is valid except near melting point. The assumption fails in solid $He$ (very light atoms) where the zero–point fluctuations $\sim a$ (quantum crystals).
From stiffness $\beta$ to Young’s Modulus $E$

$\beta' = \beta / n$

$\beta' = \beta n$

$E = \frac{stress}{strain} = \frac{F/A}{\Delta l/l} [N/m^2]$

$strain = \frac{\Delta l}{l}$

HW2: relationship between $E$ and $\beta$. 
1D chain of identical atoms of mass $m$ coupled to their nearest neighbors by springs of stiffness $\beta$.

$\delta x_n$ - displacement from the equilibrium position

$$f_n = \beta(\delta x_{n+1} - \delta x_n) - \beta(\delta x_n - \delta x_{n-1})$$

$$m\frac{\partial^2 \delta x_n}{\partial t^2} = \beta(\delta x_{n+1} + \delta x_{n-1} - 2\delta x_n)$$

We are looking for solutions in the wave form:

$$\delta x_n = \delta x_0 e^{i(nka - \omega t)}$$

Phase difference between oscillations of two neighboring atoms is meaningful only within $\pm \pi$. So allowed values of $k$ are between $-\frac{\pi}{a}$ and $\frac{\pi}{a}$, which is the first Brillouin zone.
Dispersion Relation for a 1D Chain of Identical Atoms

\[ m \frac{\partial^2 \delta x_n}{\partial t^2} = \beta (\delta x_{n+1} + \delta x_{n-1} - 2\delta x_n) \quad \delta x_n = \delta x_0 e^{i(nka - \omega t)} \]

\[-m\omega^2 = \beta [e^{ika} + e^{-ika} - 2] \]

\[ m\omega^2 = \beta [2 - e^{ika} - e^{-ika}] = 2\beta (1 - \cos ka) = 4\beta \sin^2 \frac{ka}{2} \]

\[ \omega = 2 \sqrt{\frac{\beta}{m} \left| \sin \frac{ka}{2} \right|} \quad \text{- dispersion relation} \]
Dispersion Relation for a 1D Chain of Identical Atoms (cont’d)

\[ \omega = 2 \sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right| \]

At small \(|k| \ll \pi / a\), the dispersion relation is the same as for the long-\(\lambda\) sound waves (Debye approximation)

\[ \omega \approx 2 \sqrt{\frac{\beta}{m} \frac{ka}{2}} = \sqrt{\frac{\beta a^2}{m}} k = ck \]

\[ c = \sqrt{\frac{\beta}{m} a} \] - the speed of sound

\[ \omega_{\text{max}} = 2 \sqrt{\frac{\beta}{m}} \]
The Phase and Group Velocities

\[ v_\phi(k) \equiv \frac{\omega(k)}{k} = c(k) \]

- the phase velocity

\[ v_g(k) \equiv \frac{d\omega(k)}{dk} \]

- the group velocity

\[ \omega = 2 \sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right| \implies \]

\[ c(k) = \frac{2}{k} \sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right| \]

\[ c(k \to 0) = \sqrt{\frac{\beta}{m}} a \]

\[ v_g(k \to 0) = \sqrt{\frac{\beta}{m}} a \]
Reflection at the Boundary of the Brillouin zone

At \( k = \pm \pi / a \) the ratio of displacements of two neighboring ions (ionic planes in 3D) is

\[
\frac{\delta x_{n+1}}{\delta x_n} = \frac{e^{i[k(a+1)-\omega t]}}{e^{i[ka-\omega t]}} = e^{ika} = e^{\pm i\pi} = \pm 1
\]

The alternate atoms oscillate with the same amplitude but out of phase – the wave moves neither to the left nor to the right – the standing wave.

This is consistent with \( v_g = 0 \). This is also consistent with the reflection of waves at the Brillouin zone boundary – reflection of lattice waves leads to the formation of standing waves.
DoS for an Arbitrary Dispersion Relation

For an \textbf{arbitrary} dispersion relation $\omega(k)$ (not necessarily linear):

$$g_{3D}(k) = \frac{3}{2\pi^2} k^2$$

$$g_{2D}(k) = \frac{1}{\pi} k$$

$$g_{1D}(k) = \frac{1}{\pi}$$

$$g(\omega) = g(k) \frac{dk}{d\omega} \propto \frac{1}{v_g(\omega)}$$

$$\frac{d\omega(k)}{dk} \equiv v_g(k)$$ \quad - the group velocity

$$\frac{\omega(k)}{k} \equiv v_{phase} = c(k)$$ \quad - the phase velocity

DoS $g(\omega)$ depends on (a) dimensionality and (b) the dispersion relation $\omega = c(k)k$. 

For an arbitrary dispersion relation:

\[
g_{3D}(\omega) = \frac{3\omega^2}{2\pi^2 [c(\omega)]^2} \frac{1}{\nu_g(\omega)}
\]

\[
\nu_g(k) = 2 \sqrt{\frac{\beta}{m}} \cos \frac{ka}{2} = a \sqrt{\frac{\beta}{m}} \sqrt{1 - \sin^2 \left(\frac{ka}{2}\right)}
\]

\[
\nu_g(\omega) = a \sqrt{\frac{\beta}{m}} \sqrt{1 - \omega^2 m / 4\beta}
\]

\[
\omega = 2 \sqrt{\frac{\beta}{m}} \sin \frac{ka}{2}
\]

non-singular behavior at \(\omega \to 2\sqrt{\beta / m}\)

singular behavior

\[
c(k) = \frac{\sin \frac{ka}{2}}{\sqrt{\frac{\beta}{m}}}
\]
$g(\omega)$ for Acoustic Phonons in 2D crystals

In 2D $g(\omega)$ is logarithmically divergent at a saddle point (see, e.g. https://en.wikipedia.org/wiki/Van_Hove_singularity).
Our treatment included an unrealistic assumption that the solid is isotropic. In reality, all crystals are anisotropic – the dispersion relations along different $k$ directions are different, and the first B. zone is not a sphere.

Van Hove singularities (correspond to extrema of $E(k)$). In 3D, the DOS itself is not divergent although its derivative is.
- to be explained in L5
Recall E&M: The electromagnetic field has an infinite number of modes (standing waves) in the cavity. The black-body radiation field is a superposition of plane waves of different frequencies. The characteristic feature of the radiation is that a mode may be excited only in units of the quantum of energy $\hbar \omega$ (similar to a harmonic oscillator).

This fact leads to the concept of photons as quanta of the electromagnetic field. The state of the el.-mag. field is specified by the average number of photons for each of the modes.

The linearity of Maxwell equations implies that the photons do not interact with each other.

**Quantum Correspondence:**

Classical harmonic system with a normal mode at $\omega$ \quad $\leftrightarrow$ \quad Quantum system with eigenstates $E_n = \hbar \omega \left( n + \frac{1}{2} \right)$

*Phonons: the elementary excitations (the quanta of vibrations) of the lattice.*

Einstein model: the oscillators are not coupled, no propagation.

Debye model: propagating “phonons” with simplified dispersion relation.
Quasiparticles and Collective Excitations

Solids – systems of strongly interacting particles. Exact calculations are impossible, approximation methods are of primary importance.

One of the very powerful methods – the method of quasiparticles and collective excitations (which are closely related). The total energy – the ground-state energy of the system (which can be considered as the reference point) + the energy of all excitations. Elementary excitation can be treated as weakly-interacting particles if their lifetime \( \tau \gg \Delta t = \frac{\hbar}{E} \) where \( E \) is the excitation energy.

Two types of elementary excitations:

1. Excitations which are transformed into the “ideal gas” particles if the interactions are turned off. They are called quasiparticles (“dressed” particles). Example – electronic excitations near the Fermi energy.

2. Excitations that exist only because of interactions, and vanish if the interactions are turned off. They are called collective excitations. Example – phonons which involve collective (coherent) motion of many ions.

The quasiparticle excitations are related to fermions (e.g. electrons and holes), collective excitations - to bosons (e.g. phonons).

Both quasiparticles and collective excitations are emergent phenomena.
**Similarities:**
- both are “unconserved” bosons, Bose-Einstein statistics;
- the dispersion relation for phonons at small $k$ resembles that for photons - $\omega \approx ck$.

**Distinctions:**
- the speed of propagation of phonons ($\sim$ the speed of sound) is by a factor of $10^5$ less than that for photons;
- sound waves can be longitudinal as well as transversal, thus 3 polarizations $\iff$ only 2 for photons;
- because of discreteness of matter, there is a lower limit on the wavelength of phonons and upper limit on their energy $\iff$ no limit on the photon energy;
- because of anharmonicity of $U(r)$ in solids, the phonons can interact with each other, in contrast to photons.
Main Characteristics of Phonons

- Boson statistics
- Energy $E = \hbar \omega$
- Quasi-momentum $p = \hbar k$
- Dispersion relation $E(p)$ or, the same, $\omega(k)$

$$\omega = 2 \sqrt{\frac{\beta}{m}} \left| \sin \frac{ka}{2} \right|$$

for 1D chain

- Density of States: depends on dimensionality and dispersion relation. Diverges in 1D with approaching the B. zone boundary, displays singularities in 2D and 3D
Total Energy of Phonons, Debye Approximation

\[
E(T) = \int_0^\infty \langle n(\omega) \rangle \hbar \omega \ g_{3D}(\omega) \ d\omega
\]

the average number of phonons in a single mode of frequency \( \omega \)

\[
\langle n(\omega) \rangle = \frac{1}{\frac{\hbar \omega}{e^{\frac{\hbar \omega}{k_B T}} - 1}}
\]

\[
g_{3D}(\omega) = \frac{3 \ \omega^2}{2 \pi^2 \ c^3}
\]

Debye model (good approx. of DoS at low \( T \))

HW 2
Thermal Excitation of Phonons

Thermal excitation of phonons involves the interaction of thermal energy with lattice vibrations. The phonon dispersion for a simplified DoS is given by:

\[ g_{3D}(\omega) \propto \omega^2 \]

Two Planck spectra for a simplified DoS are shown. At \( T < 10K \), the Planck spectrum is a reasonable approximation of the actual phonon spectrum.

\[ \langle n(\omega) \rangle \hbar \omega g_{3D}(\omega) \]

At \( T < 10K \), the Planck spectrum is a reasonable approximation of the actual phonon spectrum.

\[ 10^{12} \text{Hz} \leftrightarrow ? K \]

\[ 10^{12} \text{Hz} \leftrightarrow 50K \]

Recap: The Low-T Specific Heat of Lattice

\textbf{Low }T (\ll T_D): \langle n(\omega) \rangle \propto 1 \text{ over the range } \hbar \Delta \omega \propto k_B T

\begin{align*}
\hbar \omega & \propto k_B T \\
g_{3D} \left( \omega \sim \frac{k_B T}{\hbar} \right) & \propto T^2
\end{align*}

\[ E(T) \approx \int_0^{k_B T} 1 \times \hbar \omega \times g_{3D}(\omega) \, d\omega \propto T \times T^2 \times T = T^4 \]

\[ C_{ph} \equiv \frac{dE}{dT} \propto T^3 \]

Roughly speaking, the number of phonons \( \propto T^3 \), each has energy \( \sim k_B T \).

\textbf{High }T (\gg T_D): \langle n(\omega) \rangle \propto T

phonon energy \( \sim k_B T_D \) is \( T \)-independent

\( g_{3D} \) and \( \Delta \omega \) do not grow with \( T \) either

\[ E(T) \propto T \quad C_{ph} \equiv \frac{dE}{dT} = \text{const} \]

Roughly speaking, the number of phonons \( \propto T \), each has energy \( \sim k_B T_D \).
Phonon-Phonon Scattering

Because of anharmonicity, phonons can interact with each other (in contrast to photons).

Examples:

\[ \omega, \vec{k} \]
\[ \omega - \omega', \vec{k} - \vec{k}' \]
\[ \omega', \vec{k}' \]

\( k_1 + k_2 = k_3 + k_4 \pmod{\vec{G}} \)

In all these processes, the energy and quasi-momentum must be conserved.

\[ \omega_1 + \omega_2 = \omega_3 + \omega_4 \]

energy conservation

quasi-momentum conservation
Phonon Quasi-Momentum and Umklapp (flip-over) Processes

Quasi-momentum $p = \hbar k$

$$E = \hbar \omega = \hbar \sqrt{\frac{4\beta}{m} \left| \sin \frac{p}{\hbar} \right|}$$

We have to treat the phonon momentum with caution: $k$ is defined modulo the reciprocal lattice vector ($k$ and $k + m \frac{2\pi}{a}$ are the same because of aliasing) - $k$ is confined within the first Brillouin zone.

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3$$
$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3' = \vec{k}_3 + \vec{G}$$

Example: two phonons with $k = \pi/2a$ can be transformed, as the result of scattering, into two phonons with $k = -\pi/2a$:

$$2 \times \frac{\pi}{2a} = 2 \times \left( -\frac{\pi}{2a} \right) \mod \left( \frac{2\pi}{a} \right)$$

Umklapp processes become important at high $T$ ($\sim T_D$), where the phonon wave vector becomes $\sim \pi/a$.  

Kittel, p.123-8 - home reading
Allowed and Forbidden Processes

The decay of an acoustic phonon shown in the Fig. is forbidden: the quasi-momentum conservation would be possible only for the linear dispersion relation.

In the 3D isotropic approximation, there are two possible decay routes for $L$ phonons:

\[ L \rightarrow L + T \]
\[ L \rightarrow T + T \]
Thermal conductivity in the diffusive regime (the phonon m.f.p. is much smaller than the system size):

\[ Q = -\kappa \frac{dT}{dx} \]

- \( \kappa \) - the energy transmitted per unit time across unit area per unit \( T \) gradient

\[ Q \propto n_{ph} c \left( \varepsilon_{ph}(T[x - c\tau]) - \varepsilon_{ph}(T[x + c\tau]) \right) = n_{ph} c^2 \tau \frac{d\varepsilon_{ph}}{dT} \left( -\frac{dT}{dx} \right) = -c^2 \tau C \frac{dT}{dx} \]

After angle averaging, extra factor \( 1/3 \).

\[ \kappa = \frac{1}{3} c^2 \tau C \]

Thus, the lattice thermal conductivity is determined by the specific heat \( C \) and the m.f.p. of phonons \( c\tau \).

Without phonon scattering, the thermal conductivity by phonons = \( \infty \).

(compare: without electron scattering, the charge conductivity would be \( \infty \)).
Phonons are scattered by lattice imperfections and surfaces (elastic scattering) and $ph - ph$ scattering. The $ph - ph$ scattering doesn’t affect the total momentum of the phonon system if only $N$-processes are considered (low $T$).

$$\frac{T}{T_D} \ll 1 \Rightarrow C \propto T^3$$

all scattering is due to lattice imperfections, the phonon m.f.p. is $T$-independent

$$\Rightarrow \kappa = \frac{1}{3} c^2 \tau C \propto T^3$$

$$\frac{T}{T_D} \geq 1 \Rightarrow C = const.$$ The probability that a phonon will suffer a $U$-type collision is directly proportional to the number of other phonons present.

The number of equilibrium phonons $\sim T$:

$$\langle n \rangle = \frac{1}{e^\hbar \omega/k_B T - 1} \propto T$$

So the phonon m.f.p. due to $U$-processes $\propto 1/T$ at $T/T_D \geq 1$. In this temperature range, the $T$-dependence of $\kappa$ comes from temperature dependence of the phonon m.f.p. - $\kappa \propto 1/T$. 

Figure 18 Thermal conductivity of a highly purified crystal of sodium fluoride, after J. E. Jackson, C. T. Walker, and T. F. McNelly.
Importance of Phonons

- Thermal conductivity of insulators is due to phonon propagation (e.g., thermal conductivity of diamond at RT is 5 times greater than that of copper).
- The resistivity of (clean) metals at RT is mostly due to scattering of electrons by phonons.
- Electron-phonon interaction renormalizes the properties of electrons (the electron effective mass differs from the bare $m_e$).
- Superconductivity (conventional BCS-type) occurs due to the phonon-mediated electron-phonon interactions.
- etc., etc.
Summary

- Phonons – the quanta of lattice vibration with energy $\hbar \omega$ and quasi-momentum $\hbar k$. All phonon wave vectors are within the first Brillouin zone in the $k$ – space. Phonons obey the Bose-Einstein statistics.

- One of the profound consequences of lattice discreteness – the upper limit on the energy of phonons.

- Small $\omega$ or $k \ll \pi / a$ – linear spectrum of acoustic phonons, $v_g \approx c$.

- $k \sim \pi / a$ – more complicated spectrum, $v_g$ drops to 0 at the Brillouin zone boundary, the DOS increases (diverges in 1D).

- In a 3D “isotropic” lattice there are 3 branches of phonon spectra, one longitudinal and two transverse.

- Because of anharmonicity, phonon-phonon scattering and phonon decay into lower-energy phonons are possible.

- Quasi-momentum to be treated with caution at $k \sim \pi / a$ - Umklapp scattering processes.

Today: Simon Ch. 8,9. Next time: Simon Ch. 10.