NanoEnergy

ECE 597/697 Special Topics:
Energy Transport and Conversion at the Nanoscale
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*Office Hours*: Tue 10:30am, Fri after class, or by appt
Phonons

- When the crystal gains energy, atoms are not trapped at the bottom of the potential well, but can vibrate around their equilibrium position.
- These “lattice vibrations” allow the crystal to store energy.

Since the bottom of the potential is nearly quadratic, we think of the forces between atoms as springs with some spring constant $K$.

Collective vibrations of the lattice are called “phonons” and are the primary means of transmitting thermal energy.
Phonons, cont.

- The motion of each atom is very small (less than an Angstrom)
- Approximate the forces on each atom as springs $K$
- Think of the solid as a collection of masses connected by springs:

$$F_n = K(u_{n+1} - u_n) - K(u_n - u_{n-1})$$
Harmonic Solution

• Use classical F=ma where acceleration is the 2\textsuperscript{nd} derivative of the displacement:
  \[ F = m \frac{d^2u_n}{dt^2} \]

• Formulate the equation of motion for the n’th atom:
  \[ K(u_{n+1} - 2u_n + u_{n-1}) = m \frac{d^2u_n}{dt^2} \]

• To solve, we rely on the fact that phonons are displacement waves:
  \[ u_n = A \exp[i(\omega t \pm kn\alpha)] \]

• So that taking the 2\textsuperscript{nd} derivative wrt time gives us
  \[ m \frac{d^2u_n}{dt^2} = -m\omega^2 A \exp[i(\omega t \pm kn\alpha)] = -m\omega^2 u_n \]
Harmonic Solution, cont.

• On the LHS we simply replace \( n \) by \( n+1 \) or \( n-1 \) to get:

\[
u_{n+1} = A \exp[i(\omega t \pm kna + ka)] = u_n \exp(ika)\]

\[
u_{n-1} = A \exp[i(\omega t \pm kna - ka)] = u_n \exp(-ika)\]

• Combining the two produces:

\[
K \left[ u_n \exp(ika) - 2u_n + u_n \exp(-ika) \right] = -m\omega^2 u_n
\]

• After a few trig substitutions we can simplify this to:

\[
-4K \sin^2 \left( \frac{ka}{2} \right) = -m\omega^2
\]

• Which allows us to write the vibrational frequency as a function of wavevector:

\[
\omega(k) = \sqrt{\frac{4K}{m}} \left| \sin \left( \frac{ka}{2} \right) \right|
\]
Phonon Dispersion

• This relationship between $\omega$ and $k$ is called the dispersion:

\[
\begin{align*}
\omega(k) &= \omega(k + 2\pi/n) \\
\text{Dispersion repeats every } 2\pi/a &- \text{Brilluoin zone is } [-\pi/a, \pi/a]!
\end{align*}
\]

• Two waves whose wavevectors $k$ differ by $2\pi/a$ are equivalent:
Speed of sound

• Let’s examine two limits of our solution: \( k \rightarrow 0 \) and \( k \rightarrow \pi/a \)

  – At \( k \rightarrow 0 \) we can approximate \( \sin(x) \sim x \) to get
    \[
    \omega(k) = \sqrt{\frac{K}{m}} \cdot ka
    \]
    so the phase velocity is
    \[
    v_p = \frac{\omega(k)}{k} = a \sqrt{\frac{K}{m}}
    \]
  – In the opposite limit, \( \sin(\pi/2) \sim 1 \) so
    \[
    \omega_{\text{max}} = 2 \sqrt{\frac{K}{m}}
    \]
  – At the edge of the Brilluoin zone, the wavelength
    \[
    \lambda = \frac{2\pi}{k} = 2a
    \]
    is equal to twice the lattice spacing, so we have a standing wave
  – A standing wave is really two propagating waves moving in opposite
    directions with equal velocity, so the net propagation velocity is zero!
  – However, the phase velocity at this point is almost half the speed of
    sound—what gives?
Homework Quiz 1

- The wavefunction of the lowest ground state (n=0) of the harmonic oscillator is a Gaussian:

\[
\Psi_0(x) = \left( \frac{m \omega}{\pi \hbar} \right)^{1/4} \exp \left( -\frac{m \omega x^2}{2 \hbar} \right) = \left( \frac{\alpha}{\pi} \right)^{1/4} \exp \left( -\frac{\alpha x^2}{2} \right)
\]

a). What is the expectation of position \( \langle x \rangle \)? Hint: \( \langle x \rangle = \int_{-\infty}^{\infty} \Psi^*(x) x \Psi(x) dx \) but no integrals required!

b). What is the expectation of momentum \( \langle p \rangle \)? Hint: no actual integration should be required! Remember \( p = -i\hbar \frac{d}{dx} \)

c). What is the variance of position \( \langle x^2 \rangle \)? Hint: \( \int_{-\infty}^{\infty} x^2 \exp(-\alpha x^2) = \frac{1}{2\alpha} \left( \frac{\pi}{\alpha} \right)^{1/2} \)

d). What is the variance of momentum \( \langle p^2 \rangle \)? Hint: you will also need:

\[
\int_{-\infty}^{\infty} \exp(-\alpha x^2) = \left( \frac{\pi}{\alpha} \right)^{1/2}
\]

e). Show that the uncertainty principle is (just barely) satisfied. Hint:

\[
\sigma(x) = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}
\]
a) \( \langle x \rangle = 0 \) because the integral is a product of even and odd functions:

\[
\langle x \rangle = \int_{-\infty}^{\infty} \Psi^*(x)x\Psi(x)dx = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \exp\left(-\frac{\alpha x^2}{2}\right)x\exp\left(-\frac{\alpha x^2}{2}\right)dx = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x\exp(-\alpha x^2)dx = 0
\]

b) \( \langle p \rangle = 0 \) for the same reason (we end up with the same integral as in part a):

\[
\langle p \rangle = \int_{-\infty}^{\infty} \Psi^*(x)\left(-i\hbar \frac{d}{dx}\right)\Psi(x)dx = -i\hbar \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \exp\left(-\frac{\alpha x^2}{2}\right)\frac{d}{dx}\exp\left(-\frac{\alpha x^2}{2}\right)dx =
\]

\[
= i\hbar \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \exp\left(-\frac{\alpha x^2}{2}\right)\alpha x\exp\left(-\frac{\alpha x^2}{2}\right)dx = i\hbar \alpha \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x\exp(-\alpha x^2)dx = 0
\]

c) \( \langle x^2 \rangle = 1/2\alpha \) using the integral provided and minding the constants:

\[
\langle x^2 \rangle = \int_{-\infty}^{\infty} \Psi^*(x)x^2\Psi(x)dx = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2\exp(-\alpha x^2)dx = \left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{2\alpha} \left(\frac{\pi}{\alpha}\right)^{1/2} = \frac{1}{2\alpha}
\]
**HW Quiz 1 Solutions, cont.**

d) \( <p^2>=\hbar^2 \alpha/2 \) again using the integral provided but carefully taking derivative

\[
\langle p^2 \rangle = \int_{-\infty}^{\infty} \Psi^*(x) \left( -i\hbar \frac{d}{dx} \right)^2 \Psi(x) dx = -\hbar^2 \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \exp \left( -\frac{\alpha x^2}{2} \right) \frac{d^2}{dx^2} \exp \left( -\frac{\alpha x^2}{2} \right) dx = \\
= -\hbar^2 \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \exp \left( -\frac{\alpha x^2}{2} \right) \frac{d}{dx} \left[ -\alpha x \exp \left( -\frac{\alpha x^2}{2} \right) \right] dx = \\
= \alpha \hbar^2 \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \left[ \exp \left( -\frac{\alpha x^2}{2} \right) - \alpha x^2 \exp \left( -\frac{\alpha x^2}{2} \right) \right] dx = \\
= \alpha \hbar^2 \left( \frac{\alpha}{\pi} \right)^{\frac{1}{2}} \left[ \left( \frac{\pi}{\alpha} \right)^{\frac{1}{2}} - \alpha \frac{1}{2\alpha} \left( \frac{\pi}{\alpha} \right)^{\frac{1}{2}} \right] = \frac{\alpha \hbar^2}{2}
\]

d) We want to show the product of the sigmas of \( x \) and \( p \) is exactly equal \( \hbar/2 \)

\[
\sigma(x)\sigma(p) = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \sqrt{\frac{1}{2\alpha} \sqrt{\frac{\alpha \hbar^2}{2}}} = \sqrt{\frac{\hbar^2}{4}} = \frac{\hbar}{2}
\]
Group Velocity

• We noticed that phase velocity does not quite make sense as the speed of propagation of our waves, esp. at BZ edge.
• Phase velocity tells us how fast the wavefront is moving:

\[ u(x) = A \exp\left[i(\omega t - kx)\right] \Rightarrow \omega t - kx = \text{Const}. \]

• Want to know how fast energy is carried (rather than phase).
• Consider a simple wavepacket made up of two waves:

\[ u(x) = A\left[\sin(k_1 x - \omega_1 t) + \sin(k_2 x - \omega_2 t)\right] \]

• We can re-write this by grouping into a product of a wave representing the center of the wavepacket times a modulation.
• The wavepacket is centered at \( k_0 = (k_1 + k_2)/2 \) and \( \omega_0 = (\omega_1 + \omega_2)/2 \).
• The width of the wavepacket is \( \Delta k = (k_2 - k_1)/2 \) and \( \Delta \omega = (\omega_2 - \omega_1)/2 \).
Group Velocity, cont.

- The expression for the wavepacket is now
  \[ u(x) = 2A \sin(k_0 x - \omega_0 t) \cos(\Delta k x - \Delta \omega t) \]

- We now ask how fast the packet [or the modulation pattern \( \cos(\Delta k x - \Delta \omega t) \)] is moving?

- We again look at \( \Delta k x - \Delta \omega t = \text{Const.} \)

- Take a derivative \( \Delta k \ dx - \Delta \omega \ dt = 0 \) to get \( v_g = dx/dt = \Delta \omega / \Delta k \)

- This velocity is called “group velocity” and is the speed at which a wavepacket carries energy rather than phase

- In the limit of a small wavepacket, and in 3d we would replace the “deltas” with a gradient to get the more general definition:

  \[ \vec{v}_g(\vec{k}) = \nabla_{\vec{k}} \omega(\vec{k}) = \begin{pmatrix} \frac{\partial \omega(\vec{k})}{\partial k_x} \\ \frac{\partial \omega(\vec{k})}{\partial k_y} \\ \frac{\partial \omega(\vec{k})}{\partial k_z} \end{pmatrix} \]
Group Velocity in 1d chain

• Let’s go back to our 1d example and examine the group velocity

\[ v_g(k) = \frac{d}{dk} \omega(k) = a \sqrt{\frac{K}{m}} \cos \left( \frac{ka}{2} \right) \]

• At the center of the Brilluoin zone, \( v_g = v_p \) because the dispersion is approaching a linear function (sin(x)\~x)

• This linear approximation is often called the “Debye approximation”

• However, at the edge of the BZ, \( v_g = 0 \) as we expect for a standing wave!

• Most of the semiconductors we discussed are actually diatomic (there are 2 atoms per lattice point).

• Next let us consider a simple 1d model of a diatomic chain with two atoms having different masses (\( m_1 \) and \( m_2 \))

• Keep the same spring constant \( K \) and lattice spacing \( a \)
Phonon dispersion of a diatomic chain

- Each of the two masses has a different displacement function

- Let us call these two functions
  \[ u_n = A_u \exp \left[ i(\omega t \pm k \alpha) \right] \quad \text{and} \quad v_n = A_v \exp \left[ i(\omega t \pm k \alpha) \right] \]

- We end up with two equations for these two waves
  \[
  K(v_n - 2u_n + v_{n-1}) = m_1 \frac{d^2 u_n}{dt^2} \\
  K(u_{n+1} - 2v_n + u_n) = m_2 \frac{d^2 v_n}{dt^2}
  \]

- Combining the expressions together gives us
  \[
  K \left[ v_n - 2u_n + v_n \exp(-ika) \right] = -m_1 \omega^2 u_n \\
  K \left[ u_n \exp(ika) - 2v_n + u_n \right] = -m_2 \omega^2 v_n
  \]
Phonon dispersion of a diatomic chain

- We now have two equations in two unknowns

\[
\begin{pmatrix}
2K - m_1 \omega^2 & -K [1 + \exp(-ika)] \\
-K [1 + \exp(ika)] & 2K - m_2 \omega^2 \\
\end{pmatrix}
\begin{pmatrix}
u_n \\
v_n \\
\end{pmatrix} = 0
\]

- Solve by setting the determinant equal to zero

\[
\omega^2 = \frac{K}{m_1 m_2} \left( m_1 + m_2 \pm \sqrt{m_1^2 + m_2^2 + 2m_1 m_2 \cos(ka)} \right)
\]

- Special case \(m_1 = m_2\):

\[
\omega^2 = \frac{K}{m} \left( 2 \pm \sqrt{2 + 2 \cos(ka)} \right)
\]
Phonons in 3D crystals

• In 3D structures, atoms are free to move in 3 orthogonal directions
• We talk about direction relative to the direction of propagation of the lattice wave
• If the displacement of the atoms is along the direction of travel of the wave, then we call it a “longitudinal” wave
• If the motion of the atoms is perpendicular to the direction of propagation, such a wave is called “transverse”
• Two transverse branches and one longitudinal
• Every crystal has these 3 acoustic modes
• If there are n>1 atoms per lattice points, then we have 3*(n-1) optical branches
Lattice Dynamics and Phonon Dispersion

Anisotropy

- Anisotropy means that a quantity like electronic structure or dispersion is not the same in every direction:

\[ E(\vec{k}) \neq E(|\vec{k}|) \]

- Leads to things like phonon focusing in certain directions

Longitudinal Acoustic (LA) branch

Transverse Acoustic (TA) branch
