Review of Last Lecture

- Seebeck effect
- Peltier effect
- Thomson effect
- Device analysis
- Figure of merit ZT
- Applications
Thermoelectric Figure of Merit

\[ ZT = \frac{\sigma S^2 T}{k} = \frac{\sigma S^2 T}{k_p + k_e} \]

- \( \sigma \): Electrical Conductivity
- \( S \): Seebeck Coefficient
- \( T \): Temperature
- \( k \): Thermal Conductivity
- \( k_p \): Phonon Contribution
- \( k_e \): Electron Contribution
Microscopic Formulation of Thermoelectric Properties

- Review of basic concepts in solid states
- Simple kinetic formulation
- Results from formal transport theory
Atomic Vibration

- Classical Oscillator
  - Natural Frequency
    \[ v = \frac{1}{2\pi} \sqrt{\frac{K}{M}} \]
  - From Quantum Mechanics
    - Energy of Mode
      \[ E = \left( n + \frac{1}{2} \right) h \nu \quad n = 0, 1, 2, \ldots \]
  - Basic vibrational energy quanta \( h \nu \) is called a phonon

Potential Energy

\[ U \approx U_o + K(x - x_o)^2 \]

\[ F = -\frac{dU}{dx} = -K(x - x_o) \]
**1D Atomic Chair**

**Monatomic**

![Diagram of a monatomic 1D atomic chain]

Allowable wavelength: \( Na = \frac{\lambda}{2}, 2 \frac{\lambda}{2}, \ldots \)

Standing Wave Picture

\[
k = \frac{2\pi}{\lambda} = \frac{2\pi}{2Na}, \ldots, \frac{(N-1)a\pi}{2Na}, \frac{\pi}{2a}, \ldots
\]

**Diatomic**

![Diagram of a diatomic 1D atomic chain]

Optical Phonons

Acoustic Phonons

\[
k = \frac{2\pi}{\lambda} = -\frac{\pi}{a}, -\frac{(N-1)a\pi}{Na}, \ldots, \frac{(N-1)a\pi}{Na}, \frac{\pi}{a}
\]
Unit Cell in Real and Reciprocal Spaces

• Periodic signal in time with period $T$, Fourier transform gives a frequency $\nu = 2\pi / T$,
• Periodic signal in space with wavelength $\lambda$, Fourier transform gives $2\pi / \lambda$. 

Crystal unit cell in real space

Fourier Transform

Reciprocal Space
Phonons Dispersion in Crystals

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Please see Fig. 1a and 2a in Giannozzi, Paolo, et al. "Ab initio Calculation of Phonon Dispersions in Semiconductors." Physical Review B 43 (March 1991): 7231-7242.
Electronic Energy Levels

- Wavefunction
  \[ \Psi_{n\ell m_s}(r, \theta, \varphi) \]
  \[ n = 1, 2, 3, \ldots \]
  \[ \ell < n \]
  \[ |m| \leq \ell \]
  \[ s = \pm \frac{1}{2} \]

- Degeneracy
  \[ D = 2n^2 \]

Hydrogen Atom

- 1s, n=1 (-13.6 eV)
- 2s, 2p, n=2 (-3.4 eV)
- 3s, 3p, 3d, n=3 (-1.5 eV)
Electrons in an Atomic Chain

\[ \Psi_{ns}(k, x) \]

\[ k = \frac{2\pi}{\lambda} = -\frac{\pi}{a}, -\frac{(N-1)a\pi}{Na}, \ldots, \frac{(N-1)a\pi}{Na}, \frac{\pi}{a} \]

\( k \) has N discrete values between \((-\frac{N}{2}, \frac{N}{2})\)
Different Solids

Energy vs. \( k/(\pi/a) \)

- **Metal**
- **Insulator**
- **n-type Semiconductor**
- **p-type Semiconductor**

- **Fermi Level**
- **Gap \( E_g \)**
- **Conduction Band**
- **Valence Band**
- **Donor Energy Level**
- **Acceptor Energy Level**
Electronic Band Structures of Real Crystals

\[ \text{Si} \]

\[ \text{GaAs} \]

Indirect Band Gap \( E_g = 1.12 \text{ eV} \)

Direct Band Gap \( E_g = 1.42 \text{ eV} \)
Parabolic Band Approximation

- **Free Electrons**

\[ E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{\hbar k^2}{2m} \]

- **Near Minimum (Maximum)**

\[ E - E_c = \frac{\hbar^2}{2} \left( \frac{k_x^2}{m_{11}} + \frac{k_y^2}{m_{22}} + \frac{k_z^2}{m_{33}} \right) \]

Effective mass

\[ m_{ij} = \frac{\hbar^2}{\left( \partial^2 E / \partial k_i \partial k_j \right)} \]
Constant Energy Surface
Statistical Distributions

Average Number of Particles in a Quantum State

Fermi-Dirac

\[ f = \frac{1}{\exp \left( \frac{E - \mu}{k_B T} \right) + 1} \]

Bose-Einstein

\[ f = \frac{1}{\exp \left( \frac{E - \mu}{k_B T} \right) - 1} \]
Electron Density

\[ E - E_c = \frac{\hbar^2 \left( k_x^2 + k_y^2 + k_z^2 \right)}{2m} \]

\[ N = 2 \sum_{-N_x/2}^{N_x/2} \sum_{-N_y/2}^{N_y/2} \sum_{-N_z/2}^{N_z/2} f(E, T) \]

\[ = 2 \int_{-\pi/a}^{\pi/a} \frac{dk_x}{(2\pi/L_x)} \int_{-\pi/a}^{\pi/a} \frac{dk_y}{(2\pi/L_y)} \int_{-\pi/a}^{\pi/a} \frac{dk_z}{(2\pi/L_z)} f(E, T) \]

\[ = \frac{2V}{8\pi^3} \int_{-\pi/a}^{\pi/a} \int_{-\pi/a}^{\pi/a} \int_{-\pi/a}^{\pi/a} dk_x dk_y dk_z \exp \left( -\frac{E - \mu}{k_B T} \right) \]
Electron Density

\[ n = \frac{N}{V} = \frac{2V}{8\pi^3} \int_{E_c}^{\infty} 4\pi k^2 dk \exp \left[ -\frac{E - \mu}{k_B T} \right] \]

\[ = \frac{1}{\pi^2} \int_{E_c}^{\infty} \left( \frac{2m(E - E_c)}{\hbar^2} \right) \sqrt{\frac{2m(E - E_c)}{\hbar^2}} \exp \left[ -\frac{E - \mu}{k_B T} \right] dE = \int_{E_c}^{\infty} \frac{\sqrt{2m^{3/2} \sqrt{E - E_c}}}{\pi^2 \hbar^3} \exp \left[ -\frac{E - \mu}{k_B T} \right] dE = \int_{E_c}^{\infty} D(E) \exp \left[ -\frac{E - \mu}{k_B T} \right] dE \]

\[ = 2 \left( \frac{2\pi m^* \kappa_B T}{\hbar^2} \right)^{3/2} \exp \left( -\frac{E_c - \mu}{k_B T} \right) \]

\[ = N_c \exp \left( -\frac{E_c - \mu}{k_B T} \right) \]

Density of States \( D(E) \):
Number of quantum states per unit volume and per energy interval

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Nanoengineering Group

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Electron Density

**General:**

\[ n = \int_{E_c}^{\infty} D(E) f(E, \mu, T) dE \]

\[ n = 2 \left( \frac{2 \pi m^* \kappa_B T}{\hbar^2} \right)^{3/2} \exp\left( -\frac{E_c - \mu}{k_B T} \right) = N_c \exp\left( -\frac{E_c - \mu}{k_B T} \right) \]

**Under Boltzmann Statistics**

\[ D(E) = \frac{\sqrt{2m^{3/2}} \sqrt{E - E_c}}{\pi^2 \hbar^3} \]

- Conduction Band
- Valence Band
- Chemical Potential \( \mu \)
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