3.23 Electrical, Optical, and Magnetic Properties of Materials
Fall 2007

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ANHARMONICITY

Galloping Gertie (Tacoma Narrows Bridge, the old one...)

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Last time

1. Chemical potential as a function of T: intrinsic and extrinsic case
2. Population of impurity levels
3. Equilibrium carrier densities in impure semiconductors, and simplified expressions
4. p-n junction: depletion layer/space charge, built-in voltage, operation under bias and rectification
Study

- Singleton, most appropriately, scattered around.
Carrier concentration in a p-n junction

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What is the built-in voltage $V_{bi}$?

\[ qV_{bi} = \mu_n - \mu_p \]

\[ \mu_p = \mu_i - k_b T \ln \left( \frac{N_a}{n_i} \right) \quad \mu_n = \mu_i + k_b T \ln \left( \frac{N_D}{n_i} \right) \]

\[ \therefore V_{bi} = \frac{k_b T}{q} \ln \left( \frac{N_a N_d}{n_i^2} \right) \]
Qualitative Effect of Bias

- Forward bias (+ to p, - to n) decreases depletion region, increases diffusion current exponentially
- Reverse bias (- to p, + to n) increases depletion region, and no current flows ideally

Forward Bias

Reverse Bias

Solve minority carrier diffusion equations on each side and determine J at depletion edge

\[
J = q \left( \frac{D_e n_i^2}{L_e N_a} + \frac{D_h n_i^2}{L_h N_d} \right) \left( \frac{qV_a}{k_B T} - 1 \right) = J_o \left( \frac{qV_a}{k_B T} - 1 \right)
\]

\[
\frac{D_i}{\mu_i} = \frac{k_B T}{q}, \quad L_i = \sqrt{D_i \tau_i}
\]
Rectification

Semiconductor solar cells

Bipolar Junction Transistor

Field-effect Transistor

Bloch oscillations

Conductivity in semiconductors

\[ j = -n e v \]
\[ v = -\frac{eE\tau}{m} \]
\[ j = \frac{ne^2\tau}{m} E \]

\[ \sigma = n_e e \frac{e\tau_e}{m_e} + n_h e \frac{e\tau_h}{m_h} \]

\[ \mu_e = \frac{e\tau_e}{m_e} \]
\[ \mu_h = \frac{e\tau_h}{m_e} \]

Ohmic to ballistic conductance

What happens when electric field is applied?

- If we reduce the length conductance grows indefinitely!
- Experiment shows limiting value $G_c$.
- This resistance comes from contacts

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Electron transport at the nanoscale

- Short length $\Rightarrow$ Few scattering events $\Rightarrow$ Phase coherency
- Wave character becomes important

Multi-walled carbon nanotubes

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- $\sim_{\mu}m$, room temperature
- 50 % of the theoretical value
- Very high current density $\Rightarrow$ non-dissipative transport

S. Franks et al., Science 280, 1744 (1998)
Electron transport at the nanoscale


Quantum conductance of an ideal ballistic conductor

No scattering, length-independent!

\[ N_{\text{ch}} = 3 \]

\[ I^+ = \frac{e}{L} \sum_k v f^+(E) = \frac{e}{L} \sum_k \frac{\partial E}{\partial k} f^+(E) = \frac{2e}{h} \int_{-\infty}^{+\infty} f^+(E) dE \]

\[ I = I^+ - I^- = \frac{2e}{h} \int_{-\infty}^{+\infty} [f^+(E) - f^-(E)] dE = \frac{2e^2}{h} \frac{(\mu_1 - \mu_2)}{e} = \frac{2e^2}{h} V \]

Conductance quantum

\[ G = \frac{dI}{dV} = \frac{2e^2}{h} N_{\text{ch}} \]
Conductance from transmission

- Predominant “wave” character

➤ Solve the Schrödinger equation

\[ e^{ik_1x} \quad r e^{-ik_1x} \quad t e^{ik_1x} \]

\[ \frac{1}{2} k_1^2 = E \quad , \quad \frac{1}{2} k_2^2 = E + V \]

\[ \mathcal{T} = t^*t = \left[ 1 + \frac{1}{4} \frac{V^2}{E(E+V)} \sin^2(k_2W) \right]^{-1} \]
Quantum transport in CNTs

- Temperature / Length / Phonons ...

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Please see: Fig. 1a in Kong, Jing, et al. "Quantum Interference and Ballistic Transmission in Nanotube Electron Waveguides." *Physical Review Letters* 87 (September 2001): 106801.


- Very short CNT $\Rightarrow$
  conductance independent of *length* and *temperature*

- Longer CNT $\Rightarrow$
  conductance decreases as temperature increases
due to the scattering by phonons

- Estimated mean free path of phonon scattering at R.T. $\Rightarrow \sim 1\mu$m
  (we do not take inelastic scattering into account)

Nanotube electrical interconnects

Problem:
Current saturation at high bias and for long nanotubes

Transport not purely ballistic

Nanotube electrical interconnects

High electric field

Hot electrons
(E > 0.16 eV)

Strong el-ph scattering

Hot phonons
(optical phonons)

Heat dissipation bottleneck

Low energy acoustic phonons

τ^{EP} \sim 0.5 \text{ ps}

τ^{PP} \gg τ^{EP}

Courtesy of Nicola Bonini. Used with permission.
Nanotube electrical interconnects

High electric field

**Strong el-ph scattering**

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$\tau^{EP} \approx 0.5 \text{ ps}$

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$\tau^{PP} \gg \tau^{EP}$

Boltzmann transport equation for electrons and phonons to model nanotubes on substrate [1]

$\tau^{PP} \sim 5 \text{ ps} \gg \tau^{EP} \sim 0.5 \text{ ps}$

(parameter) (ab initio)

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The perfectly harmonic crystal

**Phonon:** lattice vibration of wave-vector \( \mathbf{q} \) and frequency \( \omega_j(\mathbf{q}) \) (\( j \): band index). Frequencies are calculated from the second derivatives of the energy (**interatomic force constants**) versus atomic displacements:

\[
C_{\alpha i, \beta j}(\mathbf{R}_L, \mathbf{R}_{L'}) = \frac{\partial^2 E}{\partial u_{\alpha i, L} \partial u_{\beta j, L'}} \bigg|_{equilibrium} = C_{\alpha i, \beta j}(\mathbf{R}_L - \mathbf{R}_{L'})
\]

Precisely, phonon frequencies are the eigenvalues of the **dynamical matrix** \( \tilde{D}_{\alpha i, \beta j}(\mathbf{q}) \), Fourier transform of \( C_{\alpha i, \beta j}(\mathbf{R}_L) \):

\[
\tilde{D}_{\alpha i, \beta j}(\mathbf{q}) = \sum_L C_{\alpha i, \beta j}(\mathbf{R}_L) e^{-i\mathbf{q}\cdot\mathbf{R}_L}
\]

\[
\omega^2 u_{\alpha i} = \sum_{\beta j} u_{\beta j} \tilde{D}_{\alpha i, \beta j}(\mathbf{q})
\]

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Phonon dispersions in diamond

Phonon dispersions in graphite

Harmonic crystal’s free energy

Quantization of phonons’ energy:

\[ E_j(q) = h \omega_j(q) n + \frac{1}{2} \]

Partition function of one phonon (microcanonical ensemble - T & V constant):

\[ Z_{q,j} = \sum_n \exp\left(-\frac{h \omega_j(q)}{k_B T} \left(n + \frac{1}{2}\right)\right) = \frac{1}{2 \sinh \left(\frac{h \omega_j(q)}{k_B T}\right)} \]

Total partition function:

\[ Z_{\text{total}} = \prod_{q,j} Z_{q,j} = \frac{1}{\prod_{q,j} 2 \sinh \left(\frac{h \omega_j(q)}{k_B T}\right)} \]

Free energy: (\(\{a_i\}\) = lattice parameters)

\[ F(\{a_i\}, T) = E(\{a_i\}) + F_{\text{vib}} \]

\[ = E(\{a_i\}) - k_B T \ln Z_{\text{total}} \]

\[ = E(\{a_i\}) + \sum_{q,j} \frac{h \omega_{q,j}}{2} + k_B T \sum_{q,j} \ln(1 - \exp(-\frac{h \omega_{q,j}}{k_B T})) \]

Courtesy of Nicolas Mounet. Used with permission.
The quasi-harmonic approximation: principle

\[ F(\{a_i\}, T) = E(\{a_i\}) + \sum_{q,j} \frac{\hbar \omega_{q,j}}{2} + k_B T \sum_{q,j} \ln(1 - \exp(-\frac{\hbar \omega_{q,j}}{k_B T})) \]

If phonon frequencies assumed constant (harmonic crystal), no dependence of the vibrational free energy on structure

→ no thermal expansion, no temperature dependence of elastic constants, heat capacity reaching a limit a high temperature, ie. **no anharmonic effects**.

Quasi-harmonic approximation: use harmonic expression of the free energy but add additional dependence of the phonon frequencies on the **lattice parameters** \( \{a_i\} \).

Courtesy of Nicolas Mounet. Used with permission.
Heat capacity

Constant volume heat capacity given by:

\[
C_v = -T \frac{\partial^2 F}{\partial T^2} = \sum_{q,j} c_v(q,j) = k_B \sum_{q,j} \left( \frac{\hbar \omega_{q,j}}{2k_B T} \right) \frac{1}{\sinh^2 \left( \frac{\hbar \omega_{q,j}}{2k_B T} \right)}
\]

Courtesy of Nicolas Mounet. Used with permission.

Figure by MIT OpenCourseWare.

### Thermal expansion

Minimization of quasi-harmonic free energy vs. lattice parameters \( \{a_i\} \):

\[
F(\{a_i\}, T) = E(\{a_i\}) + \sum_{\mathbf{q}, j} \frac{\hbar \omega_{\mathbf{q}, j}(\{a_i\})}{2} + k_B T \sum_{\mathbf{q}, j} \ln(1 - \exp(-\frac{\hbar \omega_{\mathbf{q}, j}(\{a_i\})}{k_B T}))
\]

Equilibrium lattice parameters given by that minimization change with temperature → **Thermal expansion** (or contraction):

\[
\alpha_i = \frac{1}{a_i} \frac{\partial a_i}{\partial T}
\]
Grüneisen parameters

General definition:

\[ \gamma_k(q, j) = \frac{-a_{0,k}}{\omega_{0,q,j}} \frac{\partial \omega_{q,j}}{\partial a_k} \bigg|_0 \]

So that:

\[ \alpha_i = \sum_{q,j} c_v(q, j) \sum_k \frac{S_{ik}}{V_0} \gamma_k(q, j) \]

Grüneisen parameters are usually positive (phonon frequencies decreasing with bonding distance) but low frequency modes can exhibit strongly negative Grüneisen parameters, leading to an overall negative thermal expansion.

One can calculate the frequency derivatives by interpolation of the phonon dispersions vs. lattice parameters.
Thermal Contraction in 2-d and 1-d Carbon

Grüneisen parameters

\[ \gamma_k(q, j) = \left. \frac{-a_{0,k}}{\omega_{0,q,j}} \frac{\partial \omega_{q,j}}{\partial a_k} \right|_0 \]
Grüneisen parameters for SWNT

(8,0) SWNT: Grüneisen parameters

“Pinch” mode

TA bending mode

Radial breathing mode

ZA bending mode of graphite

Courtesy of Nicola Bonini. Used with permission.
Phonon linewidth

\[ \gamma = \gamma^{EP} + \gamma^{PP} \]

(intrinsic linewidth)

**Electron-phonon interactions**

- Phonon emission
  - \( k, \varepsilon_k \rightarrow k - q, \varepsilon_k - \hbar \omega \)
  - \( q, \hbar \omega \)
- Phonon absorption
  - \( k, \varepsilon_k \rightarrow k + q, \varepsilon_k + \hbar \omega \)
  - \( q, \hbar \omega \)

**Phonon-phonon interactions**

- Phonon decay
  - \( q, \omega \rightarrow q', \omega' \)
  - \( q - q' \pm \mathbf{G}, \omega - \omega' \)
- Phonon absorption
  - \( q, \omega \rightarrow q + q' \pm \mathbf{G}, \omega + \omega' \)
  - \( q', \omega' \)
Anharmonic decay channels of $E_{2g}$ mode in graphene

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Please see Fig. 4b in Bonini, Nicola, et al. "Phonon Anharmonicities in Graphite and Graphene." arXiv:0708.4259v2 [cond-mat.mtrl-sci], 2007.
Phonon decay channels of $E_{2g}$ and $A'_1$ modes

Strong $T$-dependence of $A'_1$ mode due to TA-LA and LO-LA decay channels.

Importance of the acoustic phonon population for the transport properties.

Image removed due to copyright restrictions.
Please see: Fig. 4c, d in Bonini, Nicola, et al. "Phonon Anharmonicities in Graphite and Graphene." arXiv:0708.4259v2 [cond-mat.mtrl-sci], 2007.
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