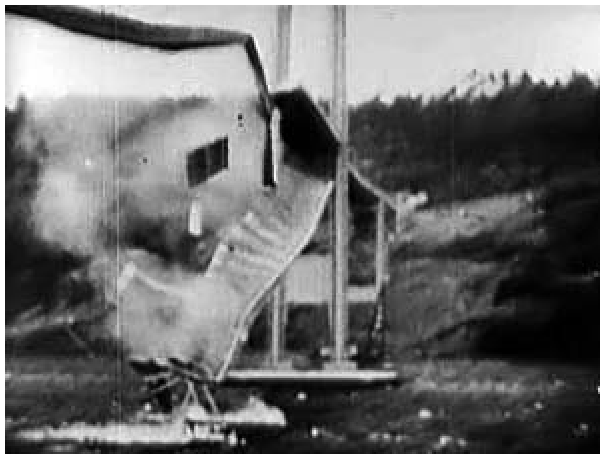
3.23 Electrical, Optical, and Magnetic Properties of Materials
Fall 2007

3.23 Fall 2007 – Lecture 15

ANHARMONICITY



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

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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Please see http://commons.wikimedia.org/wiki/Image:Pn-junction-equilibrium.svg

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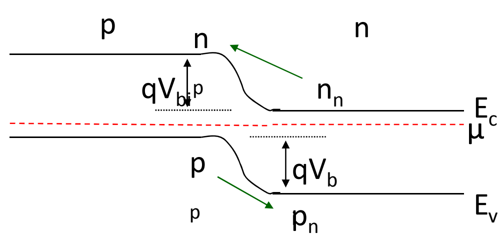
What is the built-in voltage V_{bi}?



$$qV_{bi} = \mu_n - \mu_p$$

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

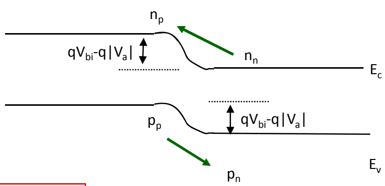
$$\boxed{\therefore V_{bi} = \frac{k_b T}{q} \ln\left(\frac{N_a N_d}{n_i^2}\right)}$$

NERNST

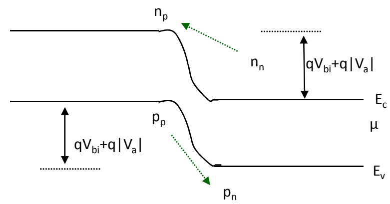
Qualitative Effect of Bias

- 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

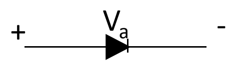
Forward Bias



Reverse Bias

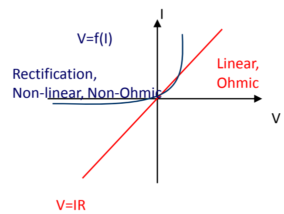


Solve minority carrier diffusion equations on each side and determine J at depletion edge



$$J = q\left(\frac{D_e}{L_e}\frac{n_i^2}{N_a} + \frac{D_h}{L_h}\frac{n_i^2}{N_d}\right)\left(e^{\frac{qV_a}{k_bT}} - 1\right) = J_o\left(e^{\frac{qV_a}{k_bT}} - 1\right)$$

$$\frac{D_i}{\mu_i} = \frac{k_bT}{q} \qquad L_i = \sqrt{D_i\tau_i}$$



Rectification

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Please see: Fig. 29.5 in Ashcroft, Neil W., and Mermin, N. David.
Solid State Physics. Belmont, CA: Brooks/Cole, 1976.

Semiconductor solar cells

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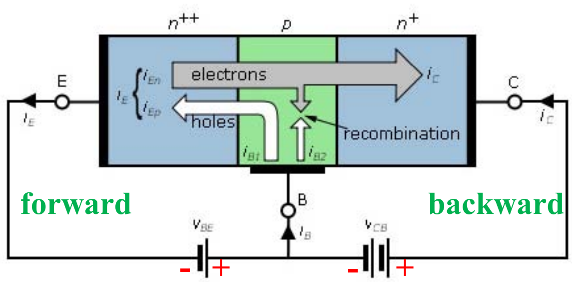
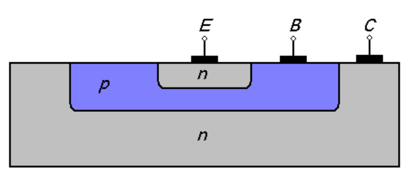
Please see http://commons.wikimedia.org/wiki/Image:Pn-junction-equilibrium.svg

Bipolar Junction Transistor





Field-effect Transistor

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Please see http://commons.wikimedia.org/wiki/Image:Lateral_mosfet.svg

Bloch oscillations

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Please see: Fig. 9.1 in Singleton, John. *Band Theory and Electronic Properties of Solids.* Oxford, England: Oxford University Press, 2001.

Conductivity in semiconductors

$$j = -nev$$

$$v = -\frac{eE\tau}{m}$$

$$j = \frac{ne^2\tau}{m}E$$

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

$$\mu_e = \frac{e\tau_e}{m_e}$$

$$\mu_h = \frac{e\tau_h}{m_h}$$

Text removed due to copyright restrictions.

Please see: Table 3 in Kittel, Charles. "Introduction to Solid State Physics." Chapter 8 in *Semiconductor Crystals.* New York, NY: John Wiley & Sons, 2004.

Ohmic to ballistic conductance

What happens when electric field is applied?

Image removed due to copyright restrictions. Please see Fig. 1.7.2 in
Datta, Supriyo. *Electronic Transport in Mesoscopic Systems*. New York, NY: Cambridge University Press, 1995.

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

Electron transport at the nanoscale

- Short length ⇨ Few scattering events ⇨ Phase coherency
- Wave character becomes important

Multi-walled carbon nanotubes

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Please see: Fig. 1 and 2 in Frank, Stefan, et al. "Carbon Nanotube Quantum Resistors." *Science* 280 (June 1998): 1744-1746.

- ~μm, room temperature
- 50 % of the theoretical value
- Very high current density ⇨ non-dissipative transport

S. Franks et al., Science **280**, 1744 (1998)

Electron transport at the nanoscale

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Please see: Fig. 1 and 3a in Liang, Wenjie, et al. "Fabry-Perot Interference in a Nanotube Electron Waveguide." *Nature* 411 (June 2001): 665-669.

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Ballistic Transport

- Quantum conductance of an ideal ballistic conductor

No scattering, length-independent !

N_{ch}=3

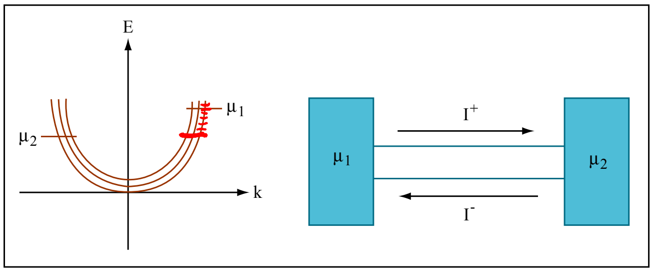

Figure by MIT OpenCourseWare.

$$I^+ = \frac{e}{L}\sum_k v f^+(E) = \frac{e}{L}\sum_k \frac{1}{\hbar}\frac{\partial E}{\partial k} f^+(E) = \frac{2e}{h}\int_{-\infty}^{+\infty} f^+(E)dE$$

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

conductance quantum

$$G = \frac{dI}{dV} = \boxed{\frac{2e^2}{h}} N_{ch}$$

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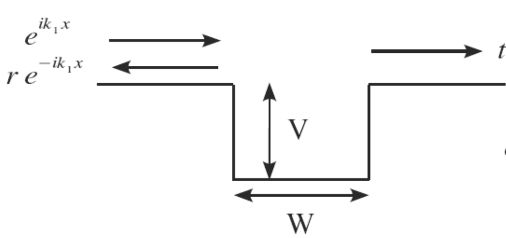
Conductance from transmission

- Predominant "wave" character
  - ➡ Solve the Schrödinger equation



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

$$\mathcal{T} = t^* t = \left[1 + \frac{1}{4}\frac{V^2}{E(E+V)}\sin^2(k_2 W)\right]^{-1}$$

Quantum transport in CNTs

- Temperature / Length / Phonons …

Images removed due to copyright restrictions.

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.

Fig. 3a in Park, Ji-Yong, et al. "Electron-Phonon Scattering in Metallic Single-Walled Carbon Nanotubes." *Nano Letters* 4 (2004): 517-520.

- Very short CNT ⇨
  conductance independent of length and temperature
- Longer CNT ⇨
  conductance decreases as temperature increases
  due to the scattering by phonons
- Estimated mean free path of phonon scattering at R.T. ⇨ ~1μm

(we do not take inelastic scattering into account)

Nanotube electrical interconnects

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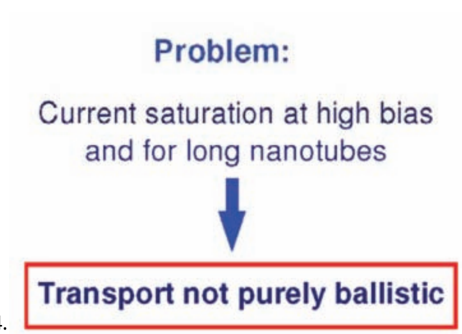
Please see: Fig. 3 in Javey, Ali, et al. "High-Field Quasiballistic Transport in Short Carbon Nanotubes." *Physical Review Letters* 92 (March 2004): 106804.



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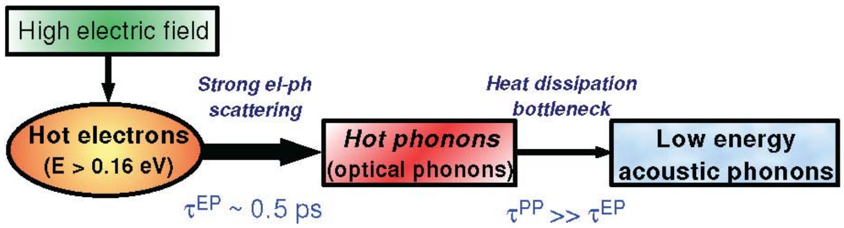
Nanotube electrical interconnects



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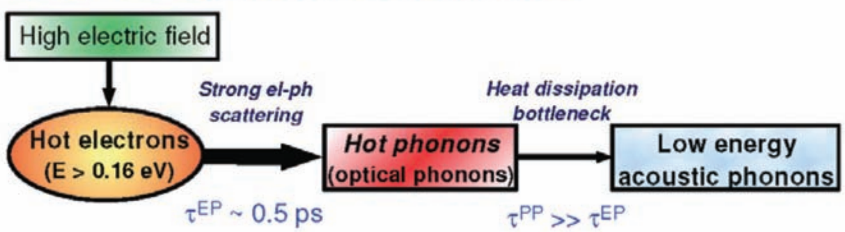
Nanotube electrical interconnects



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Please see: Fig. 2b in Lazzeri, Michele, and Francesco Mauri. "Coupled Dynamics of Electrons and Phonons in Metallic Nanotubes: Current Saturation from Hot-phonon Generation." *Physical Review B* 73 (2006): 165419.

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

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

(parameter) (*ab initio*)

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Phonons 1

The perfectly harmonic crystal

Phonon: lattice vibration of wave-vector **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:

$$C_{\alpha i,\beta j}(\mathbf{R}_L,\mathbf{R}_{L'}) = \left.\frac{\partial^2 E}{\partial u_{\alpha i,L}\partial u_{\beta j,L'}}\right|_{equilibrium} = C_{\alpha i,\beta j}(\mathbf{R}_L - \mathbf{R}_{L'})$$

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

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

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

Phonon dispersions in diamond

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Please see: Fig. 3 in Mounet, Nicolas, and Nicola Marzari. "First-principles Determination of the Structural, Vibrational, and Thermodynamic Properties of Diamond, Graphite, and Derivatives." *Physical Review B* 71 (2005): 205214.

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Phonon dispersions in graphite

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Please see: Fig. 4 in Mounet, Nicolas, and Nicola Marzari. "First-principles Determination of the Structural, Vibrational, and Thermodynamic Properties of Diamond, Graphite, and Derivatives." *Physical Review B* 71 (2005): 205214.

Phonons 2

Harmonic crystal's free energy

Quantization of phonons' energy:

$$E_j(\mathbf{q}) = \hbar\omega_j(\mathbf{q})(n + \frac{1}{2})$$

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

$$Z_{\mathbf{q},j} = \sum_n \exp(-\frac{\hbar\omega_j(\mathbf{q})}{k_B T}(n + \frac{1}{2})) = \frac{1}{2\sinh\frac{\hbar\omega_j(\mathbf{q})}{k_B T}}$$

Total partition function:

$$Z_{total} = \prod_{\mathbf{q},j} Z_{\mathbf{q},j} = \frac{1}{\prod_{\mathbf{q},j} 2\sinh\frac{\hbar\omega_j(\mathbf{q})}{k_B T}}$$

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

$$\begin{aligned} F(\{a_i\}, T) &= E(\{a_i\}) + F_{vib} \\ &= E(\{a_i\}) - k_B T \ln Z_{total} \\ &= E(\{a_i\}) + \sum_{\mathbf{q},j} \frac{\hbar\omega_{\mathbf{q},j}}{2} + k_B T \sum_{\mathbf{q},j} \ln(1 - \exp(-\frac{\hbar\omega_{\mathbf{q},j}}{k_B T})) \end{aligned}$$

Phonons 3

The quasi-harmonic approximation: principle

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

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

$\rightarrow$ 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.

Phonons 4

Heat capacity

Constant volume heat capacity given by:

$$\begin{aligned} C_v &= -T\frac{\partial^2 F}{\partial T^2} \\ &= \sum_{\mathbf{q},j} c_v(\mathbf{q},j) = k_B \sum_{\mathbf{q},j} \left(\frac{\hbar\omega_{\mathbf{q},j}}{2k_B T}\right) \frac{1}{\sinh^2\left(\frac{\hbar\omega_{\mathbf{q},j}}{2k_B T}\right)} \end{aligned}$$

Courtesy of Nicolas Mounet. Used with permission.

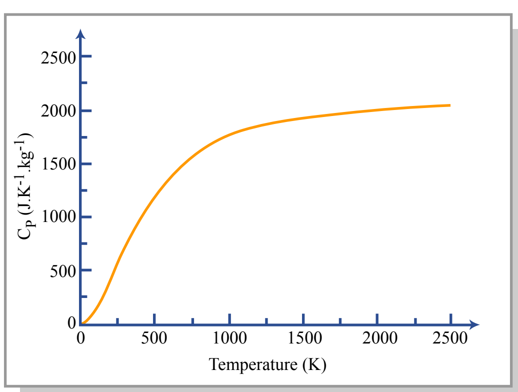

Figure by MIT OpenCourseWare.

Phonons 5

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):

$$\alpha_i = \frac{1}{a_i}\frac{\partial a_i}{\partial T}$$

Phonon 6

Grüneisen parameters

General definition:

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

So that:

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

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

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Please see: Fig. 15 in Mounet, Nicolas, and Nicola Marzari. "First-principles Determination of the Structural, Vibrational, and Thermodynamic Properties of Diamond, Graphite, and Derivatives." *Physical Review B* 71 (2005): 205214.

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

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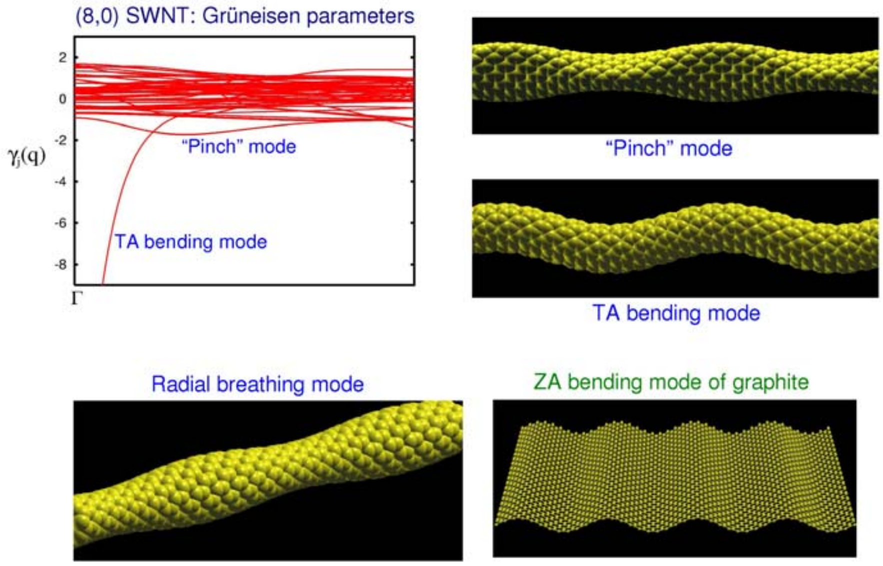
Please see: Fig. 18 and 19 in Mounet, Nicolas, and Marzari, Nicola. "First-principles Determination of the Structural, Vibrational, and Thermodynamic Properties of Diamond, Graphite, and Derivatives." *Physical Review B* 71 (2005): 205214.

Grüneisen parameters for SWNT



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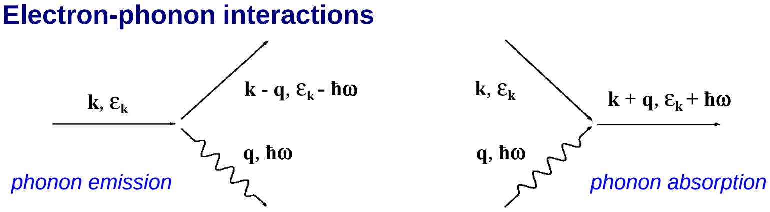
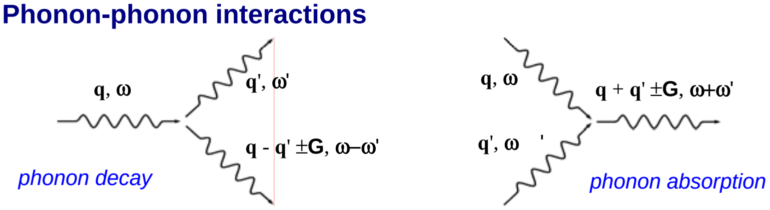
Phonon linewidth

$$\boxed{\gamma = \gamma^{EP} + \gamma^{PP}}$$ (*intrinsic linewidth*)

Electron-phonon interactions



Phonon-phonon interactions



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

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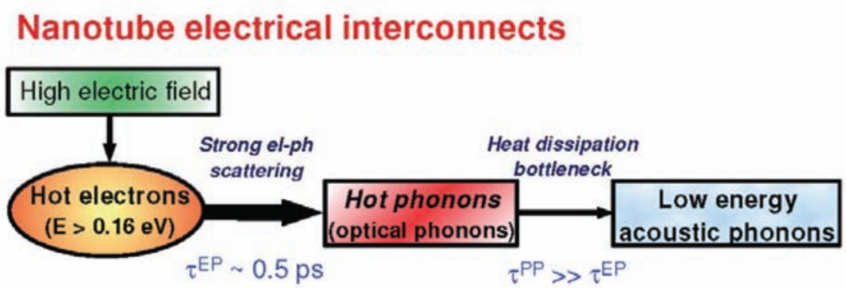
Please see: Fig. 4c, d in Bonini, Nicola, et al. "Phonon Anharmonicities in Graphite and Graphene." arXiv:0708.4259v2 [cond-mat.mtrl-sci], 2007.

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.***



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