A force-constant model of graphene for conductivity calculations

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Motivation

Graphene has some interesting properties:

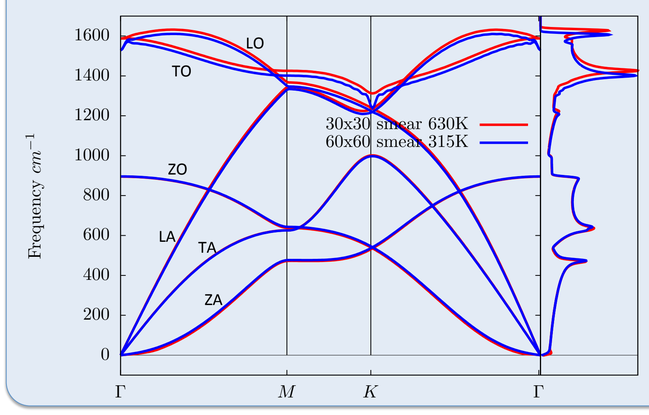
- high charge-carrier mobility (limited by electron-phonon interaction)
- Interesting for high frequency applications (control of mobility is important)

Aim of the project:

- Create a 4 nearest-neighbor (4NN) force-constant model of graphene that reproduces the DFT calculated phonon frequencies and modes.
- The model will be used for calculating the phonon-limited electrical conductivity of graphene and carbon nanotubes.[8]
- Incorporate long-range interactions in the model.

Ab-initio phonon dispersion of graphene

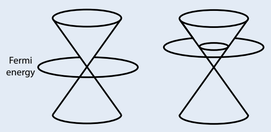
- **Ground-state:** LDA norm-conserving pseudopotential, 35 Ha plane-wave cut-off, 4.65 Bohr lattice constant (relaxed).
- **Phonon dispersion:** DFPT sampling of 30x30 q-points.



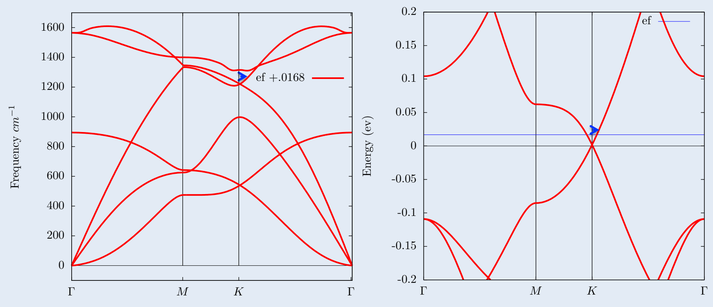
- Kohn anomalies at Γ and K points that connect the Fermi surface (non-analytic phonon dispersion).
- We can't describe the full dispersion with a finite set of force constants (Fourier interpolation fails).
- The electronic temperature changes the slope of the phonon dispersion.

Phonon dispersion of doped graphene

- When doping graphene we change the Fermi energy and the Kohn anomaly is found now on a circle in the Brillouin zone

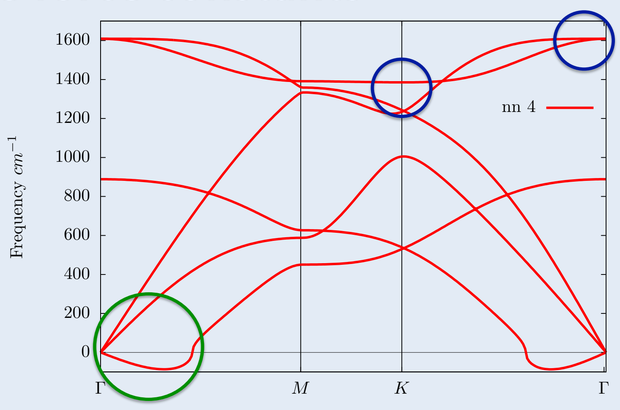


Calculations within the adiabatic approximation



Long-range force constants

- Real space cut-off the force constants up to 4NN.
- Kohn anomalies are suppressed
- Out-of-plane mode frequencies become imaginary (unstable system)
- The 4NN model does not reproduce totally the phonon dispersion.
- Can we add an analytical correction?



Force constant model

The force constants are second derivatives of the total energy with respect to the positions of two atoms:

$$C_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j} \qquad \text{Global reference frame}$$

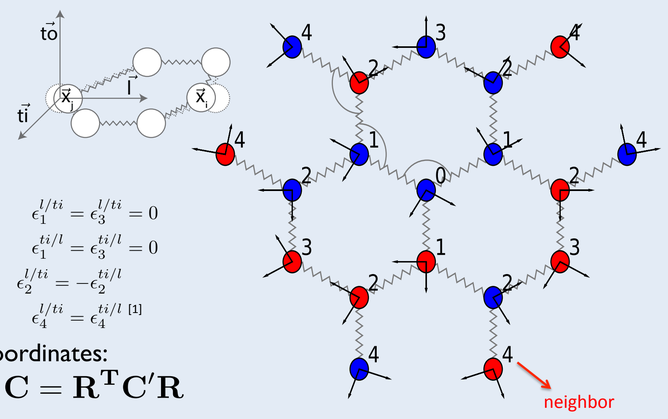
$$C'_{ij} = \frac{\partial^2 E}{\partial x'_i \partial x'_j} \qquad \text{Local reference frame}$$

They depend on:

- Types of atoms interacting
- Relative position vector

Off diagonal terms: often not included [4]

$$\mathbf{C}'_n = \begin{pmatrix} \phi_n^l & \epsilon_n^{l/ti} & 0 \\ \epsilon_n^{ti/l} & \phi_n^{ti} & 0 \\ 0 & 0 & \phi_n^{to} \end{pmatrix}$$



$$\epsilon_1^{l/ti} = \epsilon_3^{l/ti} = 0$$
$$\epsilon_1^{ti/l} = \epsilon_3^{ti/l} = 0$$
$$\epsilon_2^{l/ti} = -\epsilon_2^{ti/l}$$
$$\epsilon_4^{l/ti} = \epsilon_4^{ti/l}$$ [1]

Transformation from local to global coordinates:

$$\mathbf{C} = \mathbf{R}^{\mathbf{T}} \mathbf{C}' \mathbf{R}$$

Build the dynamical matrix:

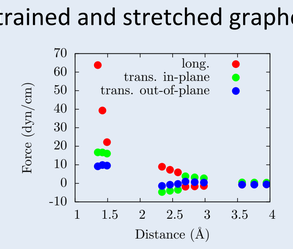
$$\mathbf{D}_{ab}(\vec{q}) = \sum_s \mathbf{C}^s_{ab} e^{i\vec{q}.(\vec{r_a} - \vec{r_s})}$$

Calculate the phonon frequencies:

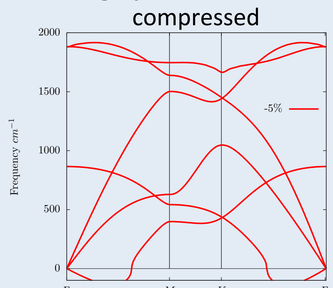
$$\det|\mathbf{D}_{ab}(\vec{q}) - \omega(\vec{q})^2| = 0$$

Phonon dispersion of compressed/stretched graphene

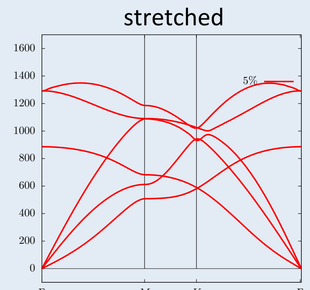
- Fit 4NN force constants to strained and stretched graphene.



compressed



stretched



Phonon displacements

The canonical phonon modes are defined using two rules[2]:

- Eigenvector of a longitudinal (transverse) mode is parallel (perpendicular) to the phonon's momentum
- Phase differences between atoms is $e^{i\vec{q}.(\vec{r_1} - \vec{r_2})}$ for acoustic and $-e^{i\vec{q}.(\vec{r_1} - \vec{r_2})}$ for optical modes.

The DFT calculated phonon modes tend to the canonical ones in the long wavelength limit.
At finite momentum there is an acoustic/optical mixing linear with |q|[2-3].

Canonical modes

$$\mathbf{e}^a_{\mathbf{q},\tilde{LA}} = \frac{1}{\sqrt{2}} e^{i\mathbf{q}\cdot(\mathbf{R}+\mathbf{r_a})} \frac{\mathbf{q}}{|\mathbf{q}|}$$
$$\mathbf{e}^a_{\mathbf{q},\tilde{TA}} = \frac{1}{\sqrt{2}} e^{i\mathbf{q}\cdot(\mathbf{R}+\mathbf{r_a})} \frac{\mathbf{q}\perp}{|\mathbf{q}\perp|}$$
$$\mathbf{e}^a_{\mathbf{q},\tilde{LO}} = \gamma_a \frac{1}{\sqrt{2}} e^{i\mathbf{q}\cdot(\mathbf{R}+\mathbf{r_a})} \frac{\mathbf{q}}{|\mathbf{q}|}$$
$$\mathbf{e}^a_{\mathbf{q},\tilde{TO}} = \gamma_a \frac{1}{\sqrt{2}} e^{i\mathbf{q}\cdot(\mathbf{R}+\mathbf{r_a})} \frac{\mathbf{q}\perp}{|\mathbf{q}\perp|}$$

Modes with Acoustic/Optical mixing

$$\mathbf{e}_{\mathbf{q},LA} = \sqrt{1-\alpha^2|\mathbf{q}|^2}\mathbf{e}_{\mathbf{q},\tilde{LA}} - \delta|\mathbf{q}|[\sin(3\theta_\mathbf{q})\mathbf{e}_{\mathbf{q},\tilde{LO}} + \cos(3\theta_\mathbf{q})\mathbf{e}_{\mathbf{q},\tilde{TO}}]$$
$$\mathbf{e}_{\mathbf{q},TA} = \sqrt{1-\alpha^2|\mathbf{q}|^2}\mathbf{e}_{\mathbf{q},\tilde{TA}} - \delta|\mathbf{q}|[\cos(3\theta_\mathbf{q})\mathbf{e}_{\mathbf{q},\tilde{LO}} - \sin(3\theta_\mathbf{q})\mathbf{e}_{\mathbf{q},\tilde{TO}}]$$
$$\mathbf{e}_{\mathbf{q},LO} = \sqrt{1-\alpha^2|\mathbf{q}|^2}\mathbf{e}_{\mathbf{q},\tilde{LO}} - \delta|\mathbf{q}|[\sin(3\theta_\mathbf{q})\mathbf{e}_{\mathbf{q},\tilde{LA}} + \cos(3\theta_\mathbf{q})\mathbf{e}_{\mathbf{q},\tilde{TA}}]$$
$$\mathbf{e}_{\mathbf{q},TO} = \sqrt{1-\alpha^2|\mathbf{q}|^2}\mathbf{e}_{\mathbf{q},\tilde{TO}} - \delta|\mathbf{q}|[\cos(3\theta_\mathbf{q})\mathbf{e}_{\mathbf{q},\tilde{LA}} - \sin(3\theta_\mathbf{q})\mathbf{e}_{\mathbf{q},\tilde{TA}}]$$

Can we capture this dependence correctly in a 4NN model? Why is it important?

Electron-Phonon coupling

The electron-phonon coupling matrix for graphene has the form[2-3]:

$$H^{\text{e-ph}}_{\mathbf{q}} = i|\mathbf{q}| \begin{bmatrix} 2\alpha(q)Q_{LA} & \beta_A e^{2i\theta_q}(Q_{LA} + iQ_{TA}) \\ \beta_A e^{-2i\theta_q}(Q_{LA} - iQ_{TA}) & 2\alpha(q)Q_{LA} \end{bmatrix} + \quad \text{Acoustic phonons}$$
$$i \begin{bmatrix} 0 & \beta_O e^{i\theta_q}(Q_{LO} + iQ_{TO}) \\ \beta_O e^{-i\theta_q}(Q_{LO} - iQ_{TO}) & 0 \end{bmatrix} \quad \text{Optical phonons}$$

Projection on the canonical modes $Q_\nu = \mathbf{e}_\mathbf{q} \cdot \mathbf{e}_{\mathbf{q},\nu}$

Where β_A and β_O are related to the acoustic-optical mixing in the phonon modes:

$$\beta_A \approx \tilde{\beta_A} - \delta\tilde{\beta_O} \qquad \beta_O = \tilde{\beta_O}$$

Where $\tilde{\beta_A}$ and $\tilde{\beta_O}$ are calculated using the canonical phonon modes.
To get the **correct** electron-phonon coupling the model should reproduce the correct value of δ

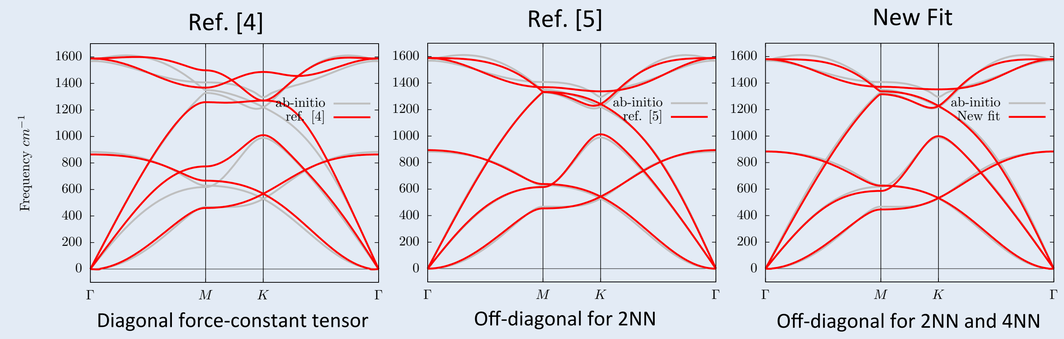
Acoustic-optical mixing

Comparison of 4NN models

- We generate the dynamical matrix using 4NN and compare to the *ab-initio* dynamical matrix and/or the eigenvalues using the quality function and find the best fit using a simplex method:

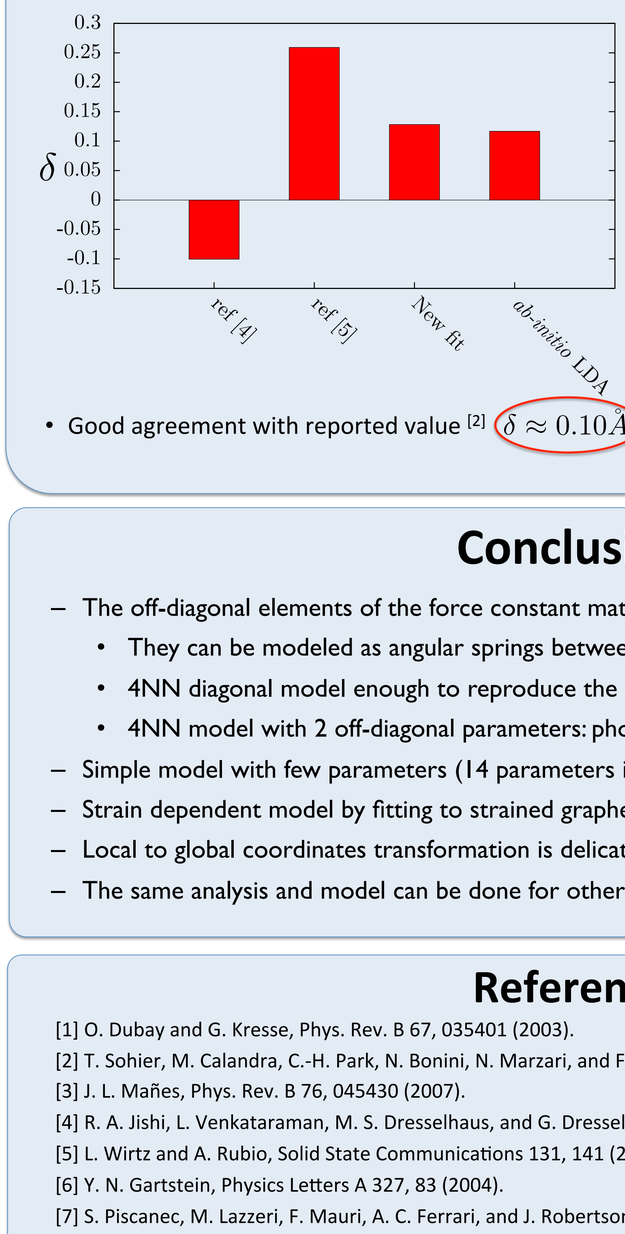
$$\chi = \alpha_{\text{eig}} \sum_{q=N_q} \sum_n \left[\omega_0(\vec{q})_n - \omega(\vec{q})^{ab}_n\right]^2 + \alpha_{\text{dyn}} \sum_{q=N_q} \sum_{ij} \sum_{a,b} \left[\mathbf{D_0}(\vec{q})^{ab}_{ij} - \mathbf{D}(\vec{q})^{ab}_{ij}\right]^2$$

Ref. [4] | Ref. [5] | New Fit



Diagonal force-constant tensor | Off-diagonal for 2NN | Off-diagonal for 2NN and 4NN

- We calculate δ from the phonon eigenvectors calculated with the different models:



- Good agreement with reported value [2] $\delta \approx 0.10\mathring{A}$

Model	Phonon frequencies	Phonon displacements near Γ
Ref [4]	✗	✗
Ref [5]	✓	✗
New Fit	✓	✓

Table 1. Comparison of the different models

n	1	2	3	4
ϕ_n^l	40.905	7.402	-1.643	-0.609
ϕ_n^{ti}	16.685	-4.051	3.267	0.424
ϕ_n^{to}	9.616	-0.841	0.603	-0.501
$\epsilon_n^{l/ti}$	0.000	0.632	0.000	-1.092
$\epsilon_n^{ti/l}$	0.000	-0.632	0.000	-1.092

Table 2. Fitted force constants

Conclusions

- The off-diagonal elements of the force constant matrix are VERY important!
  - They can be modeled as angular springs between the carbon atoms [6].
  - 4NN diagonal model enough to reproduce the dispersion but gives bad phonon eigenvectors
  - 4NN model with 2 off-diagonal parameters: phonon eigenvectors and eigenvalues OK!
- Simple model with few parameters (14 parameters instead of 12).
- Strain dependent model by fitting to strained graphene.
- Local to global coordinates transformation is delicate with off-diagonal terms.
- The same analysis and model can be done for other materials (BN)

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