

Electron-phonon coupling in graphene

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Outline

1. **Electron-Phonon coupling**
2. **Lifetime broadening - Theory**
3. **Electrons in graphene**
4. **Phonons in graphene**
5. **Lifetime broadening of Graphene bands**
6. **Master thesis projects**

http://fy.chalmers.se/~hellsing/student_projects/EPC_seminars_2019.2.pdf

1. Electron-Phonon coupling

Electron-Phonon Coupling (EPC)

- ▶ Fundamental interest
- ▶ Damping of vibrational excitations and electronic friction
- ▶ Lifetime of electronic excitations
- ▶ Photoinduced surface reactions
- ▶ Superconductivity
(BCS theory: I. Eremin, Max-Planck Institut
[<https://www.pks.mpg.de/ieremin/teaching/wroclaw1.pdf>])

Fundamentals

Many important chemical and physical phenomena are influenced by inherent dissipative processes which involve energy transfer between the electrons (electron-electron scattering) and between the electrons and the ionic motion (electron-phonon scattering) - EPC.

Non-adiabatic interaction between the valence electrons and the ion motion in a solid reveals the break down of the Born-Oppenheimer approximation – Electrons are not infinitely fast !

$$\frac{\omega_{plasmon}}{\omega_{phonon}} \approx 10^3$$

Electron-phonon coupling influences e.g vibrational damping of adsorbates and lifetime of excited surface states.

Several experimental techniques, e.g. HREELS, IR and ARPES are able to give information about the importance of EPC

Combined with advanced theoretical calculations it is possible to sort out the relative importance of EPC and to point out key parameters.

Graphene has recently surprised us with a strong electron-phonon coupling. Utilizing this property to modify graphene to become a superconductor is a challenge.

Calculations within Density functional theory (DFT)

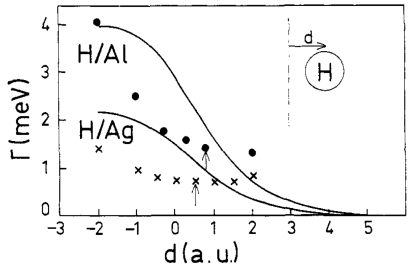
Damping of a vibrationally excited H atom near a metal

► **H/Jellium:**

..... Al ($r_s = 2.07$)

x x x Ag ($r_s = 3.00$)

——- “Local density approximation”



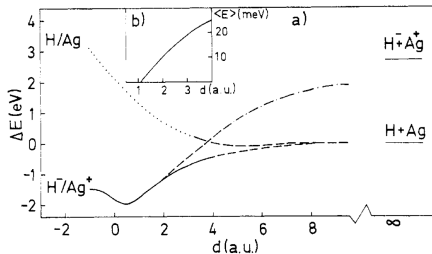
B.Helsing and M. Persson, Physica Scripta. Vol. 29. 360-371, 1984

Electronic friction at surfaces

- ▶ The friction coefficient in terms of the stochastic force

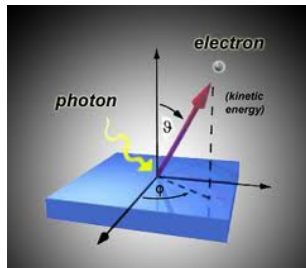
$$\eta = \frac{1}{k_B} \text{Re} \int_0^\infty dt \langle F^{st}(t) F^{st}(0) \rangle = \frac{M}{\hbar} \Gamma$$

A thermal H atom approaching a Jellium surface



Lifetimes of surface states

- ▶ **Photo emission experiment** - photo electron and photo hole created

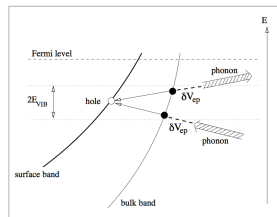


- ▶ **EPC** - phonon absorption and emission

A. Eiguren, B. Hellsing et al., Phys. Rev. Lett. 88(2002)066805-1

A. Eiguren, B. Hellsing et al., Phys. Rev. B 67(2003)235423

B. Hellsing, A. Eiguren et al., J. Phys. Cond. Mat. 14(2002)5959



Experiment and Calculations

Cu(111) and Ag(111):

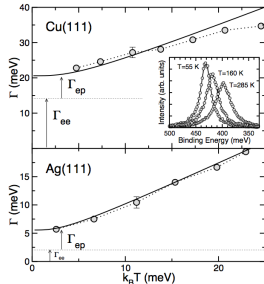
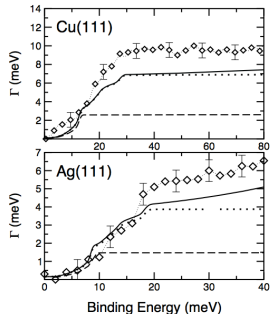
- ▶ $T = 0$: ($\Rightarrow n_B = 0$)

$$\Gamma_{n\mathbf{k}} = 2\pi \int_0^{\omega_{max}} \alpha^2 F_{\mathbf{k}_i}(\omega) d\omega$$

- ▶ **high T** : $k_B T \gg \hbar\omega_{max}$

$$\Gamma_{n\mathbf{k}}(T) = 2\pi \lambda_{n\mathbf{k}} k_B T$$

A. Eiguren, B. Hellsing, F. Reinert et al.,
 Phys. Rev. Lett. 88(2002)066805-1



Mini many-body course

The Greens' function related to a state $|a\rangle$ is written

$$G_a(\varepsilon) = \frac{1}{\varepsilon - \varepsilon_a - i\delta}$$

With this construction of the Greens' function the imaginary part will give the spectrum

$$\frac{1}{\pi} \text{Im}G_a(\varepsilon) = \frac{1}{\pi} \frac{\delta}{(\varepsilon - \varepsilon_a)^2 + \delta^2} = \delta(\varepsilon - \varepsilon_a)$$

Now if we consider this pure state coupled to some other degrees of freedom, e.g. phonons we replace the $i\delta$ in the denominator of the Greens' function of the pure state $|a\rangle$ by a complex so called self-energy $\Sigma_a(\varepsilon)$.

$$G_a(\varepsilon) = \frac{1}{\varepsilon - \varepsilon_a - \Sigma_a(\varepsilon)}$$

where

$$\Sigma_a(\varepsilon) = \text{Re}\Sigma_a(\varepsilon) + i\text{Im}\Sigma_a(\varepsilon)$$

Taking again the imaginary part of the Greens' function we get the spectrum or what is also called the Spectral function $A_a(\varepsilon)$.

$$A_a(\varepsilon) = \frac{1}{\pi} \text{Im}G_a$$

In the band picture we label the states with n and \mathbf{k} and we get

$$A_n(\varepsilon, \mathbf{k}) = \frac{1}{\pi} \frac{\text{Im}\Sigma_n(\varepsilon, \mathbf{k})}{(\varepsilon - \varepsilon_n(\mathbf{k}) - \text{Re}\Sigma_n(\varepsilon, \mathbf{k}))^2 + (\text{Im}\Sigma_n(\varepsilon, \mathbf{k}))^2}$$

$$\text{Im}\Sigma_n(\varepsilon, \mathbf{k}) \sim \text{Im}\Sigma(\varepsilon_n(\mathbf{k}), \mathbf{k}) \sim \Delta_{n\mathbf{k}}$$

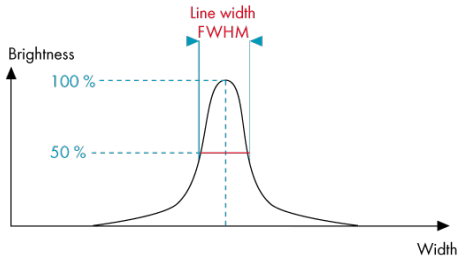
$$\text{Re}\Sigma_n(\varepsilon, \mathbf{k}) \sim \text{Re}\Sigma(\varepsilon_n(\mathbf{k}), \mathbf{k}) \sim \Lambda_{n\mathbf{k}}$$

A Lorentzian shaped spectral function:

$$A_n(\varepsilon, \mathbf{k}) = \frac{1}{\pi} \frac{\Delta_{n\mathbf{k}}}{(\varepsilon - \varepsilon_n(\mathbf{k}) - \Lambda_{n\mathbf{k}})^2 + \Delta_{n\mathbf{k}}^2}$$

Spectral function - Photo Emission Spectroscopy (EPS)

In the sudden approximation the spectral function $A_n(\varepsilon, \mathbf{k})$ corresponds to the photoemission peak.



Line width = Lifetime broadening (FWHM): $\Gamma_{n\mathbf{k}} = 2\Delta_{n\mathbf{k}}$

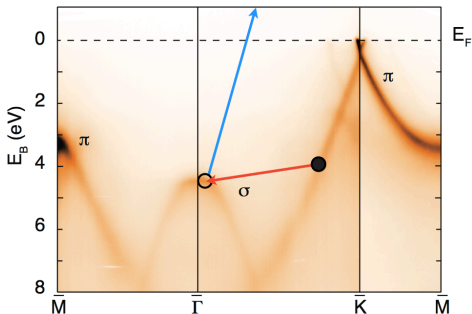
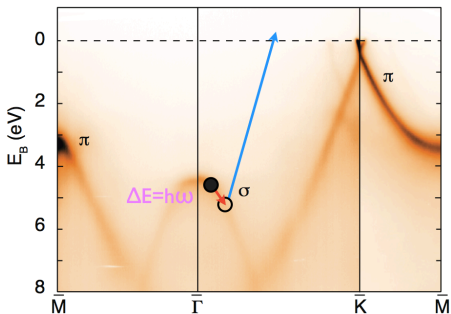
We sum up all phonon induced electron scattering processes from occupied states to the photo-hole ($n\mathbf{k}$), requiring momentum and energy conservation. The temperature is below any characteristic phonon energy \Rightarrow only phonon emission takes place.

$\Gamma_{n\mathbf{k}}$ from ARPES

ARPES = Angular Resolved PhotoEmission Spectroscopy

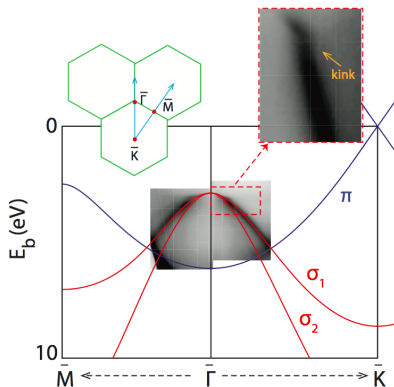
Lindwidth $\Gamma_{n\mathbf{k}} \leftrightarrow$ Hole lifetime $\tau_{n\mathbf{k}}$

$$\text{Heisenberg : } \Delta E \Delta t \geq \hbar \quad \Rightarrow \quad \tau_{n\mathbf{k}} \geq \frac{\hbar}{\Gamma_{n\mathbf{k}}}$$



Experiment - ARPES

- ▶ ARPES investigation of the σ band in graphene [1]

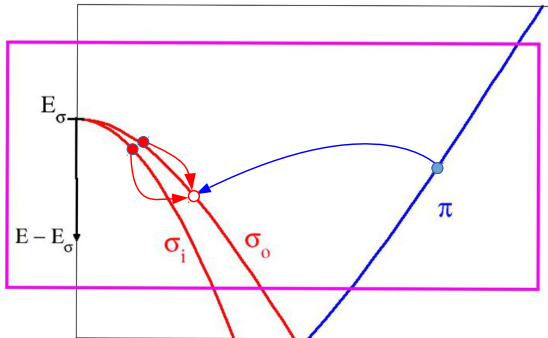


System	$\lambda \pm \Delta\lambda$	T (K)
MLG/SiC	0.96 ± 0.04	100
MLG/SiC	0.97 ± 0.04	300
BLG/SiC	0.75 ± 0.05	100
Graphite	0.97 ± 0.04	100
MLG/ Ir	0.97 ± 0.05	70
QFMLG/Ir	0.96 ± 0.04	70
QFMLG/Rb/Ir	0.96 ± 0.04	70

2. Lifetime broadening

Linewidth of an electronic state ε_{nk}

We consider electron scattering from occupied states to the empty state, the **hole state** ε_{nk} , created in the photoemission experiment. The temperature is below any characteristic phonon energy \Rightarrow only phonon emission takes place.



Electron scattering with phonon emission can take place from electron states $n'\mathbf{k}'$ to the photo hole state $n\mathbf{k}$.

Momentum conservation:

$$\mathbf{k} = \mathbf{k}' + \mathbf{q} \pm \mathbf{G}$$

\mathbf{q} is a phonon wave vector, \mathbf{G} is a reciprocal lattice vector.

Energy conservation (phonon emission):

$$\varepsilon_{n\mathbf{k}} = \varepsilon_{n'\mathbf{k}'} - \hbar\omega_{\nu\mathbf{q}}$$

$\hbar\omega_{\nu\mathbf{q}}$ is a phonon energy of mode ν and momentum \mathbf{q} .

According to the Heisenberg uncertainty relation the decay rate times \hbar gives the so called **lifetime broadening** or **linewidth**.

We are aiming the EPC contribution to the width of the peak (linewidth) of the spectral function recorded in the photoemission experiment.

Applying first order time dependent perturbation theory - Golden Rule - the lifetime broadening can be calculated.

Perturbation theory

Perturbation theory: Q = ion displacement and x = electron coordinate :

$$H(Q, x) \approx H(0, x) + \frac{\delta H}{\delta Q} Q = H(0, x) + \frac{\delta V}{\delta Q} Q$$

V is the one-electron potential. In the harmonic approximation

$$\begin{aligned} \langle I = 1, n | H(Q, x) | I = 0, m \rangle &= \langle 1 | Q | 0 \rangle \langle n | \frac{\delta V}{\delta Q} | m \rangle = \\ &= \sqrt{\frac{\hbar}{2M\Omega}} \langle n | \frac{\delta V}{\delta Q} | m \rangle, \end{aligned} \quad (1)$$

$$\varepsilon_m = \varepsilon_n + \hbar\Omega$$

Fermi Golden Rule

$$\Gamma_{n\mathbf{k}} = 2\pi \sum_{n'\nu\mathbf{q}} |\langle n\mathbf{k} | \delta V_{\mathbf{q}}^{\nu} | n'\mathbf{k} + \mathbf{q} \rangle|^2 \delta(\varepsilon_{n'\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} - \hbar\omega_{\nu\mathbf{q}}) \quad (2)$$

$\delta V = \nabla_{\vec{Q}} V \cdot \vec{Q}$, n is electronic band index, \mathbf{k} electron wave vector, ν vibrational mode index and \mathbf{q} the phonon wave vector.

The delta function takes care of the energy and momentum conservation.

In the harmonic approximation we have

$$\delta V_{\mathbf{q}}^{\nu}(\mathbf{r}) = \sqrt{\frac{\hbar}{2M\omega_{\nu}(\mathbf{q})}} \sum_{\mathbf{R}} [\mathbf{e}^{\nu}(\mathbf{q}) \cdot \mathbf{v}'(\mathbf{R} + \mathbf{r}_s; \mathbf{r})] e^{-i\mathbf{q} \cdot (\mathbf{R} + \mathbf{r}_s)} \quad , \quad (3)$$

\mathbf{R} denotes location of unite cells, $\mathbf{e}^{\nu}(\mathbf{q})$ is a $N_s \times 3$ dimensional polarization vector with components $e_{si}^{\nu}(\mathbf{q})$, where s labels the atoms in the unit cell ($s = 1, 2, 3, \dots, N_s$, where N_s is the number of atoms in the unite cell). Index i refers to the three cartesian coordinates, x , y and z .

$$\mathbf{v}'(\mathbf{R}; \mathbf{r})$$

is the deformation potential with $N_s \times 3$ components

$v'_{si}(\mathbf{R} + \mathbf{r}_s; \mathbf{r}) = \frac{\partial V_s}{\partial Q_i}(\mathbf{r} - (\mathbf{R} + \mathbf{r}_s))$ where index i refers to the displacement vector ($Q_i = \{Q_x, Q_y, Q_z\}$).

One-electron model potential

I chose a spherically symmetric smooth attractive Gaussian shaped effective one-electron potential with two parameters.

$$V(\mathbf{r}) = V(r) = -V_0 e^{-(\frac{r}{\alpha})^2} \quad (4)$$

V_0 and α represents the strength (depth) and the real space extension (screening length), respectively.

The phonon induced perturbation to first order

$$\delta V_\nu = \frac{\partial V}{\partial Q_\nu} Q_\nu,$$

where Q_ν is the ionic displacement coordinate of the vibrational mode ν .

Deformation potential

We apply the Rigid ion approximation (RIA). RIA corresponds to an approximation when the electron potential is rigidly displaced with the ionic displacement. This is a reasonable approximation if the screening is sufficient to yield a perturbation which is not felt by neighboring ions. We then have

$$V(\mathbf{Q}, \mathbf{r}) = V(\mathbf{r} - \mathbf{Q})$$

If we for example consider an ionic displacement along the x-direction, the deformation potential is

$$\delta V_x(\mathbf{r}) = \frac{\partial V}{\partial Q_x} \cdot Q_x = -\frac{\partial V}{\partial x} \cdot Q_x = x \cdot \frac{2V_0}{\alpha^2} e^{-(\frac{r}{\alpha})^2} \cdot Q_x$$

In the harmonic approximation the squared magnitude of the mean ionic displacement is

$$|\langle 0 | Q_\nu(\mathbf{q}) | 1 \rangle|^2 = \frac{\hbar}{2M\omega_\nu(\mathbf{q})}$$

$$\Gamma \iff \lambda$$

At zero temperature ($T=0$) we have

$$\Gamma_{n\mathbf{k}} = 2\pi\hbar \int_0^\infty \alpha^2 F_{n\mathbf{k}}(\omega) d\omega$$

and the local electron-phonon coupling constant $\lambda_{n\mathbf{k}}$

$$\lambda_{n\mathbf{k}} = 2 \int_0^\infty \frac{\alpha^2 F_{n\mathbf{k}}(\omega)}{\omega} d\omega$$

where $\alpha^2 F_{n\mathbf{k}}(\omega)$ is the Eliashberg function. This function can be seen as the phonon density of states weighted by the electron-phonon coupling. The integration is over all phonon frequencies.

$$\lambda(\varepsilon) = \sum_{n\mathbf{k}} \lambda_{n\mathbf{k}} \delta(\varepsilon - \varepsilon_{n\mathbf{k}}) , \quad \lambda = \lambda(\varepsilon_{\mathbf{F}}) \quad (5)$$

3. Electrons in graphene

Electrons in graphene - a Tight Binding Model

In the tight-binding model the one-electron wave function is written

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{js} c_{nsj}(\mathbf{k}) \Phi_{sj}(\mathbf{k}, \mathbf{r}) \quad (6)$$

Bloch orbitals

$$\Phi_{sj}(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \phi_j(\mathbf{r} - (\mathbf{R} + \mathbf{r}_s)) e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{r}_s)}$$

$s = \{A, B\}$ denotes the two non-equivalent sites of the carbon atoms. \mathbf{R} is a lattice vector connecting the unit cells. N is the number of unit cells we sum over. \mathbf{r}_A and \mathbf{r}_B are the position of the A and B atom relative the center of the unit cell.

The local atomic basis hydrogen-atom-like wave functions are

$$\phi_j = \{ \phi_{2s}, \phi_{2p_x}, \phi_{2p_y}, \phi_{2p_z} \}$$

The radial part of the carbon atom basis according to Slater [Slater et al. Physical Review 36, 57 (1930)]

$$R_n = R_2 \sim r e^{-Z^* r/2} \quad , \quad r = \sqrt{x^2 + y^2 + z^2}$$

where $Z^* = 3.25$ a.u. is the screened effective charge seen by the $2s$ and $2p$ electrons in carbon atom.

The normalized basis functions in cartesian coordinates are:

$$\phi_{2s} = \frac{(Z^*)^{5/2}}{\sqrt{96\pi}} r e^{-Z^* r/2} \quad , \quad \phi_{2p_z} = \frac{(Z^*)^{5/2}}{\sqrt{32\pi}} z e^{-Z^* r/2}$$

$$\phi_{2p_x} = \frac{(Z^*)^{5/2}}{\sqrt{32\pi}} x e^{-Z^* r/2} \quad , \quad \phi_{2p_y} = \frac{(Z^*)^{5/2}}{\sqrt{32\pi}} y e^{-Z^* r/2}$$

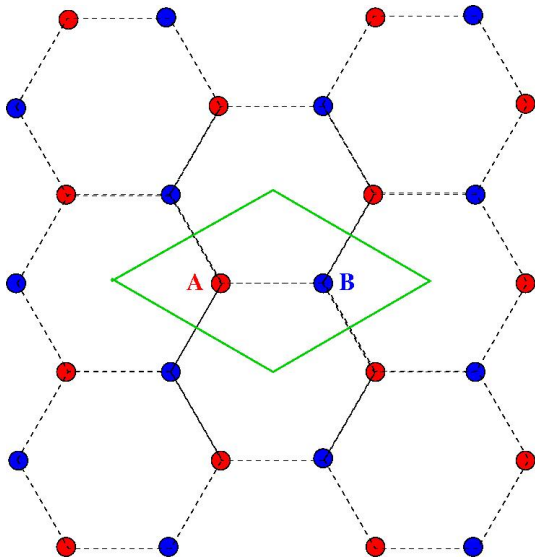


Figure: The unit cell of graphite

The generalized eigenvalue problem:

$$H\vec{\psi} = \varepsilon S\vec{\psi}$$

where H and S is the Hamiltonian and overlap matrix

We have to diagonalize a (8X8) matrix to solve

$$\sum_{s'j'} \langle sj | H - \varepsilon S | s'j' \rangle c_{s'j'} = 0$$

(I do this using the LAPAK subroutine ZHEGV)

$$\Rightarrow (\varepsilon_{n\mathbf{k}}, c_{nsj}(\mathbf{k})) \Rightarrow (\varepsilon_{n\mathbf{k}}, \psi_{n\mathbf{k}})$$

We consider nearest neighbour hopping

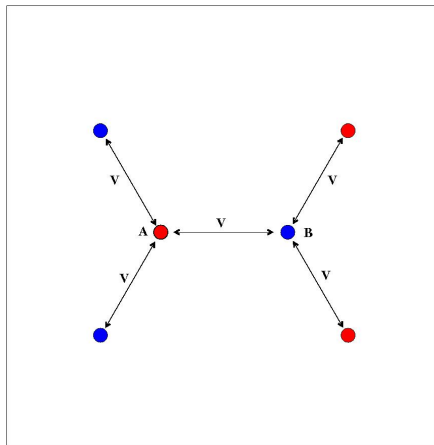


Figure: Nearest neighbour hopping

Details:

For a given electron momentum \mathbf{k} :

$$\langle sj | H - \varepsilon(\mathbf{k}) S | s'j' \rangle =$$

$$c_{sj}^*(\mathbf{k}) c_{s'j'}(\mathbf{k}) \sum_{l=1}^{\infty} \langle \phi_{sj}(\mathbf{r} - \mathbf{R}_0^s) | H - \varepsilon(\mathbf{k}) S | \phi_{s'j'}(\mathbf{r} - (\mathbf{R}_l^{s'} - \mathbf{R}_0^s)) \rangle \times$$

$$e^{i\mathbf{k} \cdot (\mathbf{R}_l^{s'} - \mathbf{R}_0^s)} \approx$$

(Nearest neighbour interaction: A has three B neighbours and B has three A neighbours)

$$c_{sj}^*(\mathbf{k}) c_{s'j'}(\mathbf{k}) \sum_{l=1}^3 \langle \phi_{sj}(\mathbf{r} - \mathbf{R}_0^s) | H - \varepsilon(\mathbf{k}) S | \phi_{s'j'}(\mathbf{r} - (\mathbf{R}_l^{s'} - \mathbf{R}_0^s)) \rangle \times$$

$$e^{i\mathbf{k} \cdot (\mathbf{R}_l^{s'} - \mathbf{R}_0^s)}$$

Parameters:

$$\varepsilon_{2s}, \varepsilon_{2p}, V_{ss\sigma}, V_{sp\sigma}, V_{pp\sigma}, V_{pp\pi} \text{ and } S_{ss\sigma}, S_{sp\sigma}, S_{pp\sigma}, S_{pp\pi}$$

With d = nearest C-C distance. For example:

$$\varepsilon_{2p} = \langle \phi_{2p_x}(\mathbf{r}|H|\phi_{2p_x}(\mathbf{r})) \rangle = \langle \phi_{2p_y}(\mathbf{r}|H|\phi_{2p_y}(\mathbf{r})) \rangle = \langle \phi_{2p_z}(\mathbf{r}|H|\phi_{2p_z}(\mathbf{r})) \rangle$$

$$V_{sp\sigma} = \langle \phi_{2s}(\mathbf{r}|H|\phi_{2p_x}(\mathbf{r} - d\hat{x})) \rangle$$

$$V_{pp\sigma} = \langle \phi_{2p_x}(\mathbf{r}|H|\phi_{2p_x}(\mathbf{r} - d\hat{x})) \rangle$$

$$V_{pp\pi} = \langle \phi_{2p_z}(\mathbf{r}|H|\phi_{2p_z}(d\hat{x} - \mathbf{r})) \rangle$$

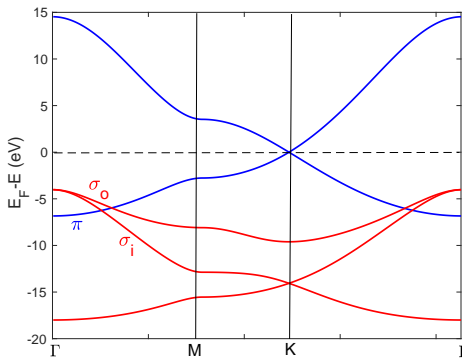


Figure: Tight-binding

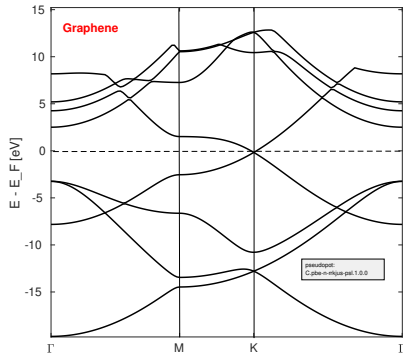


Figure: DFT

Tight binding parameters (*B. Gharekhanlou et al, "Graphene: Properties, Synthesis and Applications", 2011, Editor Zhiping Xu*):.

$$\begin{aligned}\varepsilon_{2s} &= -8.70 \text{ eV}, \quad \varepsilon_{2p} = 0, \quad V_{ss\sigma} = -6.70 \text{ eV}, \\ V_{sp\sigma} &= 5.50 \text{ eV}, \quad V_{pp\sigma} = 5.90(5.10) \text{ eV}, \quad V_{pp\pi} = -3.10 \text{ eV}\end{aligned}$$

The value of $V_{pp\sigma}$ is adjusted to fit DFT (*Mazolla et al. Phys. Rev. B 95, 075430 (2017)*) results.

Parameters of the overlap matrix S :

$$S_{ss\sigma} = 0.20, \quad S_{sp\sigma} = -0.10, \quad S_{pp\sigma} = -0.15, \quad S_{pp\pi} = -0.12$$

4. Phonons in graphene

Phonons in graphene - a Force Constant Model

We consider all six phonon modes, three optical and three acoustic;

The optical phonon modes are: longitudinal optical (LO), transversal optical (TO) and out-of-plane optical (ZO).

The acoustic phonon modes are: longitudinal acoustic (LA), transversal acoustic (TA) and the out-of-plane acoustic (ZA).applying a constant force model.

Setting up the Dynamical matrix we include up to third order nearest neighbor interactions. I apply the nine force constant model by Falkovsky (*L.A. Falkovsky, Phys.Lett. A* **372**, 5189 (2008)) and (*B. Hellsing et al., Phys. Rev. B* **98**, 205428 (2018)).

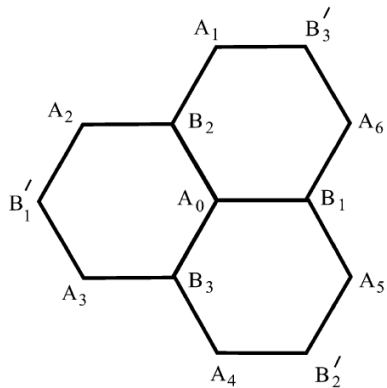


Figure: Third order neighbour interaction

The dynamical matrix D is calculated including up to third order nearest neighbor interactions. The force constants $\Phi_{ll'}^{As}$ are defined by

$$D_{ll'}^{As}(\mathbf{q}) = \sum_{\mathbf{R}_s} \Phi_{ll'}^{As}(\mathbf{R}_s) e^{-i\mathbf{q} \cdot \mathbf{R}_s}, \quad (7)$$

\mathbf{R}_s labels the vectors from a center A atom to the three nearest B atom, the six next-nearest A atoms and the three next-next-nearest B atoms.

l denotes the components of a complex vector (ξ, η) .

$\xi = X + iY$ and $\eta = X - iY$,

$\mathbf{X}_{\parallel} = X\hat{x} + Y\hat{y}$ is the atomic in-plane displacement vector.

We transform the dynamical matrix D from the (ξ, η) representation to the cartesian representation (X, Y) (B. Hellsing, *Phys. Rev. B* **98**, 205428 (2018)) and include also the out-of-plane displacement Z .

$$D_{ll'}^{ss'}(\mathbf{q}) \Rightarrow D_{ii'}^{ss'}(\mathbf{q}),$$

where the subscript i labels the three components X , Y and Z of the Cartesian displacement vector $\mathbf{X} = X\hat{x} + Y\hat{y} + Z\hat{z}$.

The Newtonian equation of motion:

$$M\ddot{x} = -kx$$

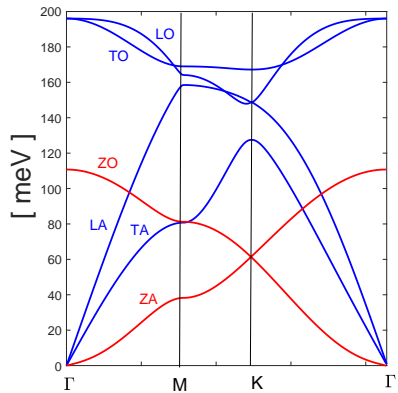
Time Fourier transform: $\tilde{x}(\omega) = x(t)e^{i\omega t}$

$$\left[\frac{k}{M} - \omega^2\right]\tilde{x} \equiv [D - \omega^2]\tilde{x} = 0$$

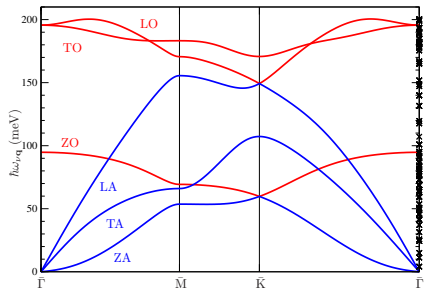
The equation of motion give us an eigenvalue problem to solve:

$$\sum_{s' i'} [D_{ii'}^{ss'}(\mathbf{q}) - \omega_\nu^2(\mathbf{q}) \delta_{ss'} \delta_{ii'}] e_{s' i'}^\nu(\mathbf{q}) = 0 , \quad (8)$$

The solutions give us the dispersion of the six eigen modes $\omega_\nu(\mathbf{q})$. e_ν is the 6-dimensional phonon polarization vector for each vibrational.



Phonon bands: Force constant model



Phonon bands: DFT

Interaction with the substrate

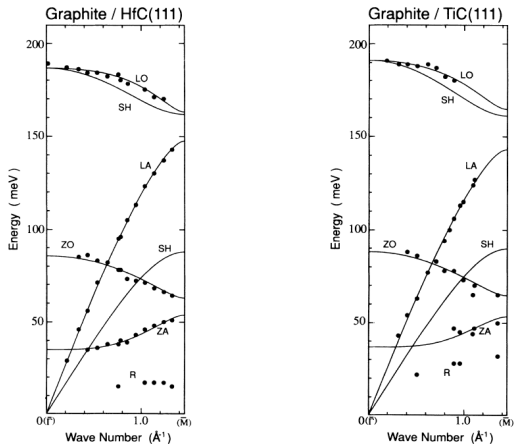


Figure: EELS Experiment [*T. Aizawa et al., PRB 42, 469 (1990)*]

I introduce a spring between all the carbon atoms and a rigid substrate.

The spring constant is set to fit the finite frequency of the ZA model at $\mathbf{q}=0$. According to experiments [*T. Aizawa, R. Souda, S. Otani, Y. Ishizawa, and C. Oshima, Phys. Rev. B 42, 469 (1990)*], $\hbar\omega_{ZA}(\mathbf{q} = 0) \approx 35$ meV for four different transition metal carbide substrates.

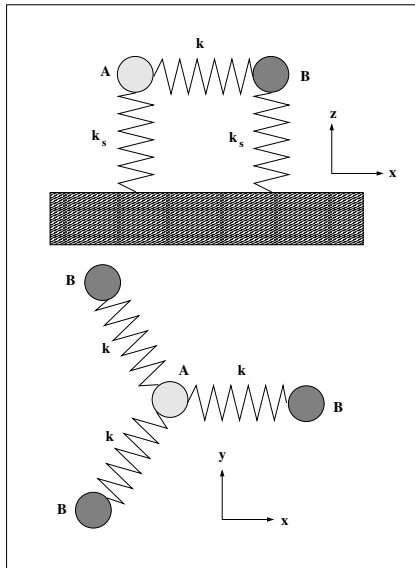


Figure: Graphene attached to a rigid substrate

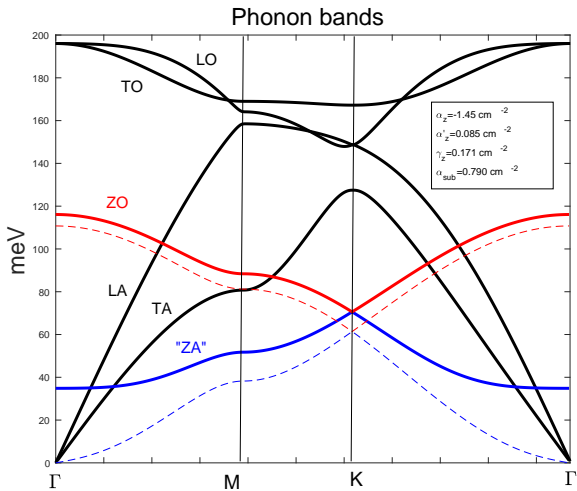


Figure: Phonon band structure including substrate interaction

5. Lifetime broadening of Graphene bands

EPC matrix element

With the wave functions given in Eq. (6) we have that the EPC matrix element is given by

$$\begin{aligned} \langle n\mathbf{k} | \delta V_{\mathbf{q}}^{\nu} | n'\mathbf{k}' \rangle &= \frac{1}{N} \sum_{sj} \sum_{s'j'} c_{nsj}^* c_{n's'j'} \\ &\times \sum_{\mathbf{R}, \mathbf{R}', \mathbf{R}''} \langle \phi_j(\mathbf{x} - (\mathbf{R} + \mathbf{r}_s)) \delta v_{\nu\mathbf{q}}(\mathbf{x} - (\mathbf{R}'' + \mathbf{r}_s'')) \phi_{j'}(\mathbf{x} - (\mathbf{R}' + \mathbf{r}_{s'})) \rangle_{u.c.} \\ &\times e^{-i\mathbf{k} \cdot (\mathbf{R} + \mathbf{r}_s)} e^{-i\mathbf{q} \cdot (\mathbf{R}'' + \mathbf{r}_s'')} e^{i\mathbf{k}' \cdot (\mathbf{R}' + \mathbf{r}_{s'})} , \end{aligned}$$

where

$$\delta v_{\nu\mathbf{q}}(\mathbf{x}) = \sqrt{\frac{\hbar}{2M\omega_{\nu}(\mathbf{q})}} [\mathbf{e}^{\nu}(\mathbf{q}) \cdot \mathbf{v}'(\mathbf{x})] , \quad (9)$$

\mathbf{R} is the lattice vectors connecting the centers of the unit cells and \mathbf{r}_A and \mathbf{r}_B give the position of the A and B atoms relative the center of the unit cell.

N is the number of unit cells summed over and $\langle \dots \rangle_{u.c.}$ denotes real space integration over the unit cell.

In the numerical calculation I consider a cluster of 7 unit cells ($N=7$), one central and the 6 nearest.

The real-space integration is taken over the central unit cell. This corresponds to $\mathbf{R}'' = \mathbf{0}$ and then we multiply with N . This eliminates N in the denominator in the previous equation.

Phase space effects

Consider \vec{k} -space near the Γ point.

The sampling of initial electron states that fulfills momentum and energy conservation results in a very different picture when comparing the intra and inter σ band scattering ($\sigma_o \rightarrow \sigma_o$ and $\sigma_i \rightarrow \sigma_o$) and the interband scattering $\pi \rightarrow \sigma_o$.

In the σ band scattering the electron states are found in a tiny circle around the Γ -point just inside the hole state (see Fig. 9).

For the interband scattering $\pi \rightarrow \sigma_o$ the situation is the opposite, the electron states are sampled in a large region (see Fig. 10).

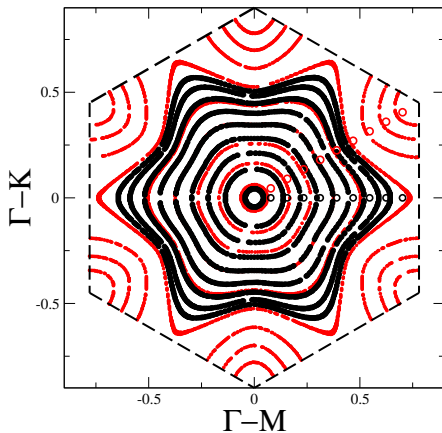


Figure: Intra σ_o band scattering. The open circles are initial hole states, red color ($\Gamma-K$ direction) and black color ($\Gamma-M$ direction). The closed lines (just inside the hole location) are the initial electron states

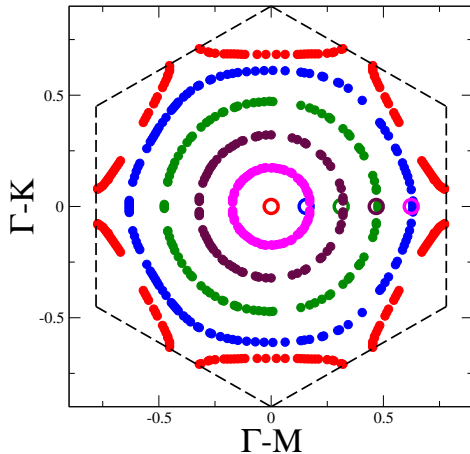
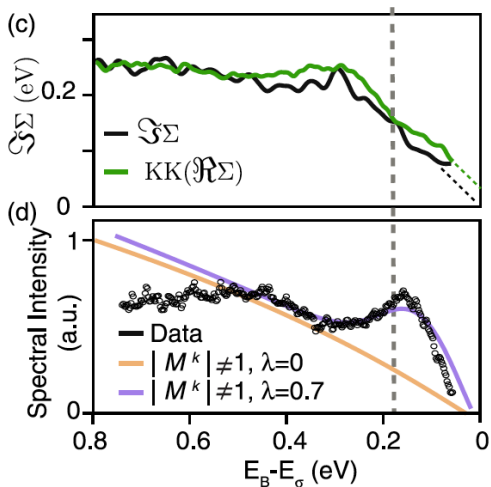


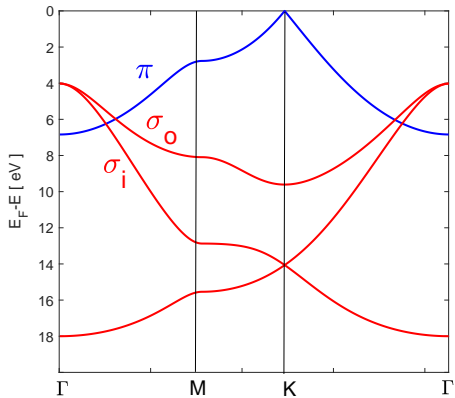
Figure: Phase space describing the initial and final electron states for the inter $\pi \rightarrow \sigma_o$ band scattering

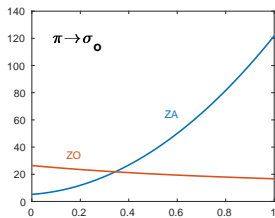
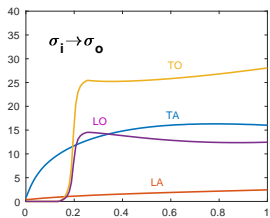
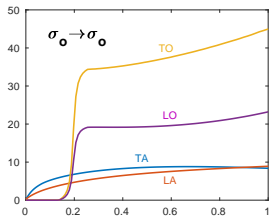
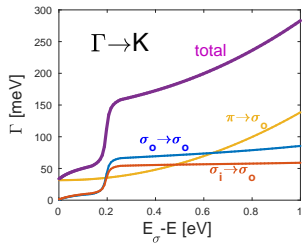
Linewidth Γ - ARPES experiments

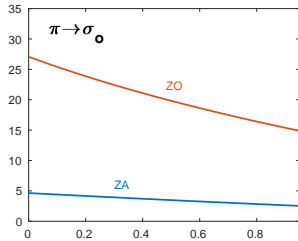
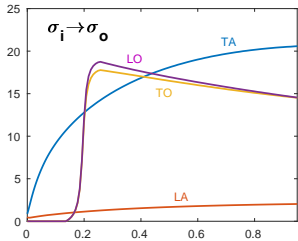
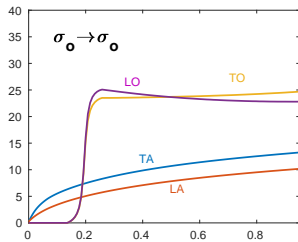
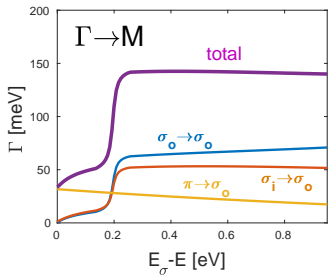


Linewidth Γ - calculation

σ_o - band







$$\Gamma \rightarrow K \iff \Gamma \rightarrow M$$

EPC matrix element $\langle \sigma_o | \delta V_{ZA} | \pi \rangle$

$$\bar{\Gamma} \rightarrow \bar{K}: |\sigma_o\rangle \approx \frac{1}{\sqrt{2}}(|2p_x^A\rangle - |2p_x^B\rangle)$$

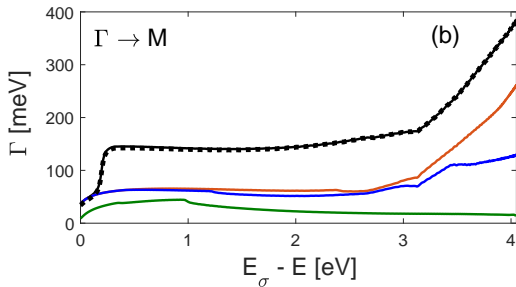
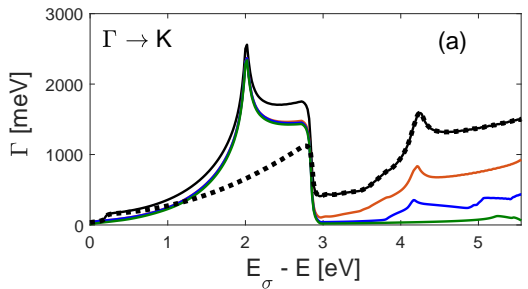
$$\bar{\Gamma} \rightarrow \bar{M}: |\sigma_o\rangle \approx \frac{1}{\sqrt{2}}(|2p_y^A\rangle - |2p_y^B\rangle).$$

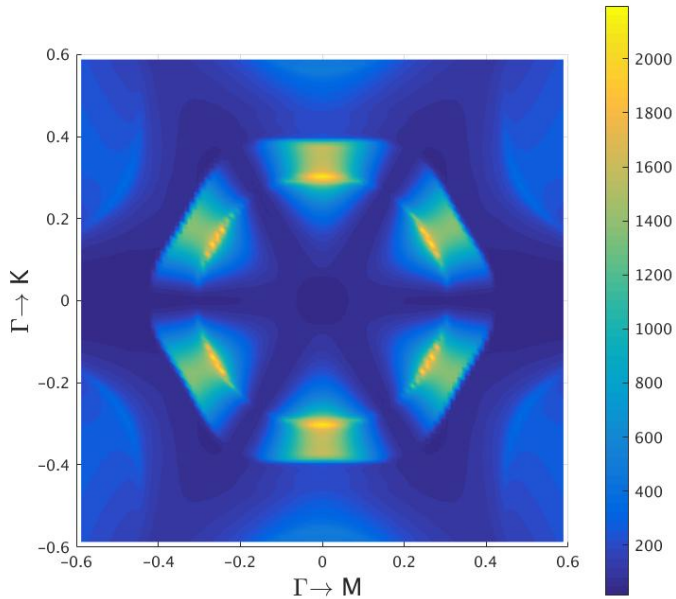
\Rightarrow

$\bar{\Gamma} \rightarrow \bar{K}$: EPC matrix element $\langle \text{even} | \text{odd}_z | \text{odd}_z \rangle$ is large.

$\bar{\Gamma} \rightarrow \bar{M}$: EPC matrix element $\langle \text{odd}_y | \text{odd}_z | \text{odd}_z \rangle$ close to zero.

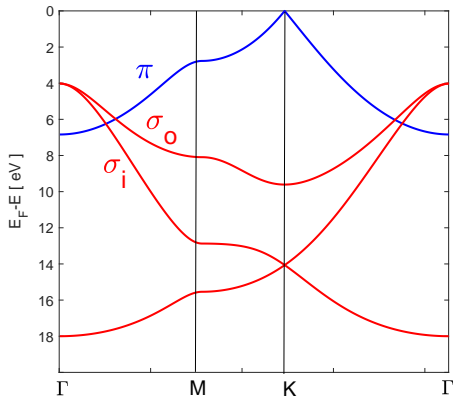
All the way $\bar{\Gamma} \rightarrow \bar{K}$ and $\bar{\Gamma} \rightarrow \bar{M}$



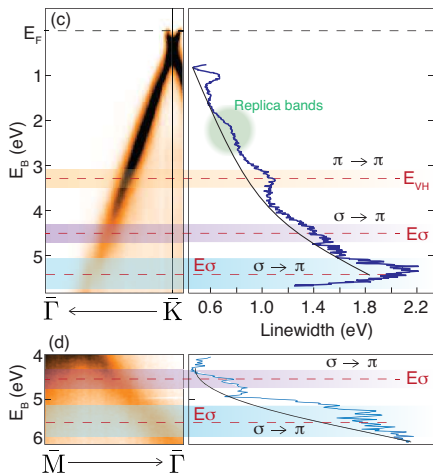
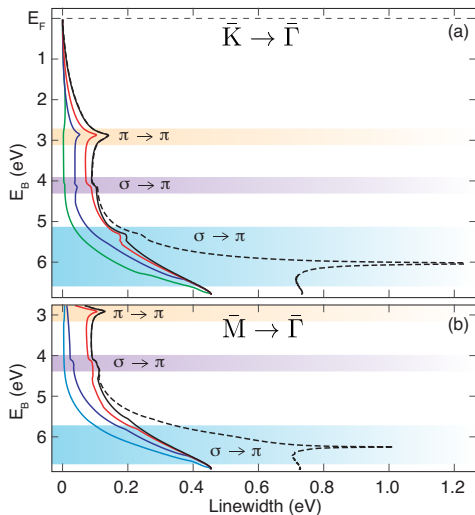


Linewidth Γ - calculation

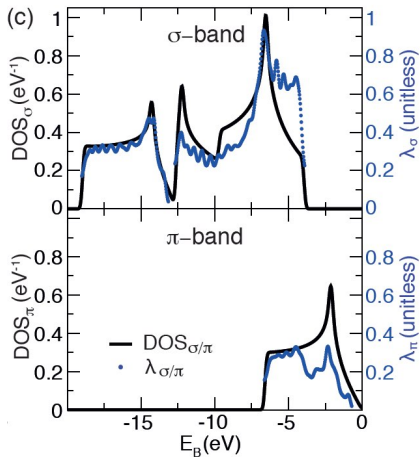
π - band



π band – TB calculation and ARPES



$$\lambda(\varepsilon)$$



Mazzola et al. PRB 95, 075430 (2017)

$$\lambda \implies T_c$$

The σ band lies far from the Fermi level and does not contribute to graphene's transport properties. What would happen if the σ band could be shifted to the Fermi level? McMillan formula (*W. L. McMillan PRB 167, 331 (1968)*), corrected by Allen (*P. B. Allen et al. PRB 12, 905 (1975)*) and valid for $\lambda < 1.5$),

$$T_c = \frac{\hbar\omega_{\log}}{1.20} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right), \quad (10)$$

Effective Coulomb repulsion for s and p band superconductors $\mu^*=0.1$ (*D. M. Gaitonde et al., Bull. Mater. Sci.26, 137 (2003)*), the logarithmically averaged phonon frequency $\omega_{\log} \approx 91$ meV (*Chen Si, et al.Phys. Rev. Lett. 111, 196802 (2013)*) and $0.8 < \lambda < 1.0$, we predict $49 \text{ K} < T_c < 72 \text{ K}$.

Graphene and BC bandstructure (DFT)

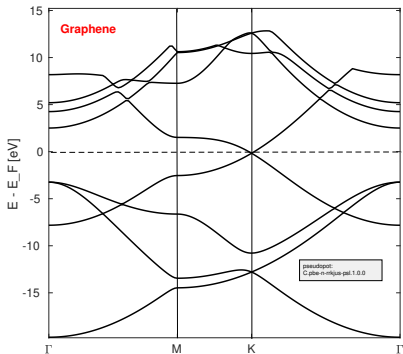


Figure: Graphene band structure

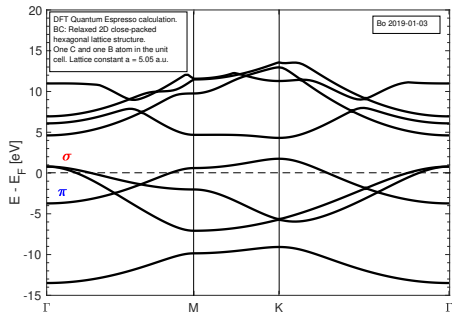


Figure: BC band structure

Remarks

Substrate influence on the electron structure ?

We might expect that the π bands would be most strongly influenced by the presence of a substrate, as their wave functions are built up by the $2p_z$ orbitals pointing towards the substrate. It is well established that a carbon “buffer layer” or “zeroth layer” (which resembles graphene but with a very strong substrate interaction and modified π band) is formed directly on top of SiC during graphene growth. Continued growth (as is relevant for our samples) results in the formation of the first true layer of graphene, which is found to be only weakly bonded to the underlying buffer layer (*Matthaus et al., PRL 99, 076802 (2007)*, *Varchon et al., PRL 99, 126805 (2007)*, *Kageshima et al., Appl. Phys. Express 2, 065502 (2009)*).

The weak substrate interaction may rigidly shift the electronic structure of graphene (i.e. as a result of charge transfer), and the new periodicities present can also create “replica bands” (*Nakatsuji et al., PRB 82, 045428 (2010)*).

First principles band structure calculations show no significant deviations in comparison with calculated band structure for unsupported graphene. (*Varchon et al., PRL 99, 126805 (2007)*). Finally, it is worth noting that even in the case of graphene-on metal, where the substrate interaction can be relatively strong, the graphene band structure deviates very little from the rigidly shifted bandstructure of unsupported graphene (*Sutter et al., PRB 80, 245411 (2009), Sutter et al., AM. Chem. Soc. 132, 8175 (2010)*). For these reasons we consider the electron structure for unsupported graphene to be a reasonable first approximation.

Is the parameter setting of the model potential (V_0 and α) robust ?

Master thesis projects

- ▶ Graphene: Find a scheme to optimize the choice of model one-electron potential and its parameters (presently a Gaussian: V_0 and α) based on the TB parameters from the literature or determined from DFT based calculations. Minimize the error $|(H_{nm}(V_0, \alpha) - H_{nm}^0)/H_{nm}^0|$, where H_{nm} and H_{nm}^0 are the calculated and reference two center Hamiltonian integral, respectively. EPC linewidth calculations. Collaboration with T. Frederiksen, DIPC, San Sebastian.

- ▶ BC: Investigate Boron carbide BC, (every second C atom in graphene is replaced by a Bohr atom). Find out how the TB parameters and force constants of graphene should be changed. Calculate the Lifetime broadening. Collaboration with T. Frederiksen, DIPC, San Sebastian.

Requirements: Quantum mechanics, Solid State Physics (electron structure and phonons), Tight binding (TB) method for electron structure and Force constant model for phonons, some experience with DFT calculation, some skill in coding; Python, Fortran, Matlab etc