

Regional School on Physics at the Nanoscale: Theoretical and Computational Aspects 14-25 December 2009, Hanoi, Vietnam

Lecture 1

Raman spectroscopy of few-layer graphene:

- counting the number of layers*
- determining the doping charge*

Lecture 2

High current transport: carbon-nanotubes and graphene, materials for future interconnects?

Lecture 3

Cutting graphene into ribbons for device applications: atomic, electronic and chemical structure of (cut) edges.

Raman spectroscopy in graphene (and layered metals)

Theory:

M. Lazzeri, A.M. Saitta, M. Calandra, F. Mauri
IMPMC, Université Pierre et Marie Curie-Paris 6, CNRS

Experiment:

S. Pisana, C. Casiraghi, S. Piscanec, A. C. Ferrari
Engineering Department, Cambridge University,

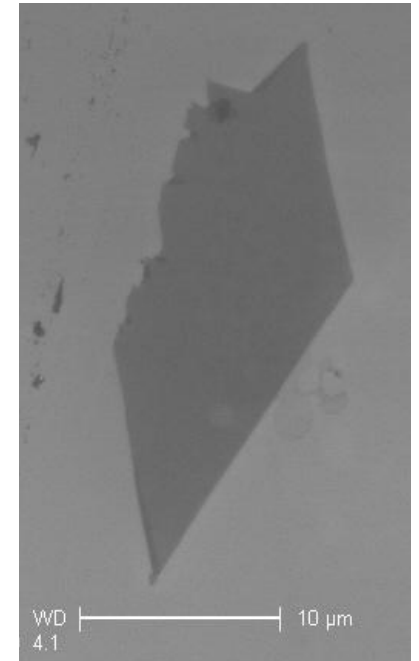
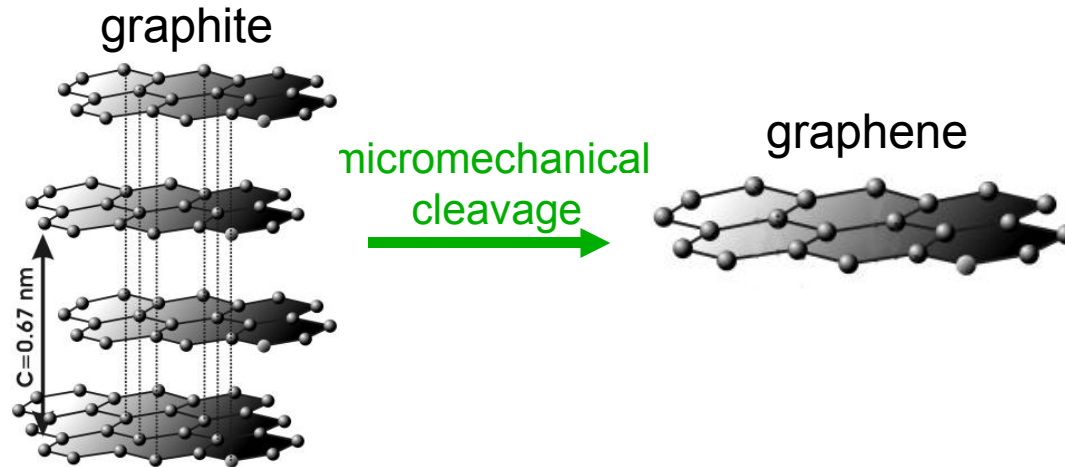
J.C. Meyer, S. Roth

Max Planck Institute for Solid State Research, Stuttgart 70569, Germany

D. Jiang, K.S. Novoselov, A.K. Geim,

Dep. of Physics and Astronomy, University of Manchester

Motivation



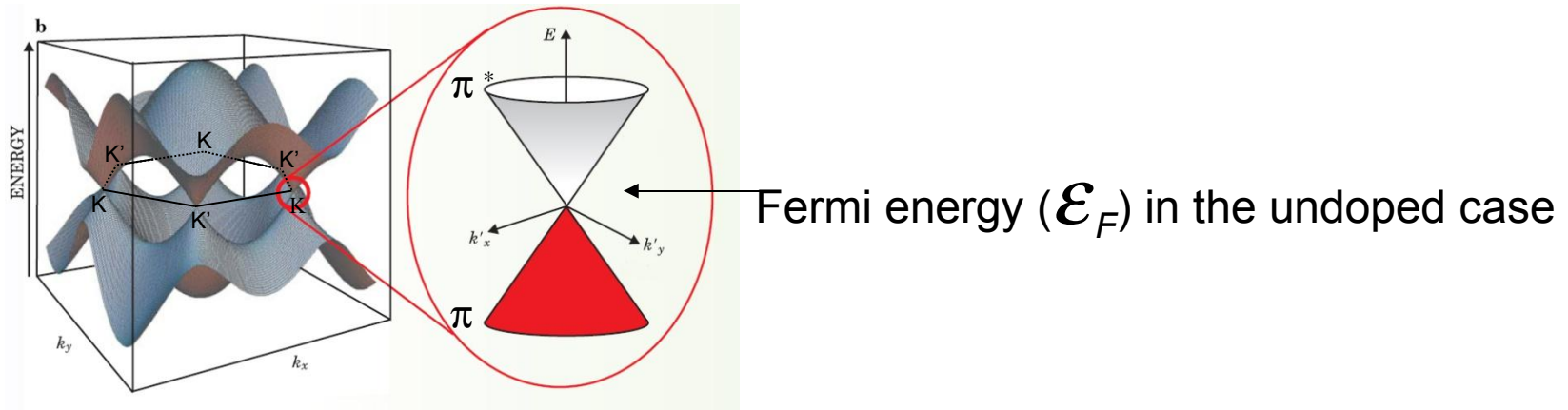
Graphene: material for tomorrow electronic

- Large mobility
- Nano-ribbons or bi-layers can be semiconducting
- Lithography can be used to prepare devices

Motivation

graphene: peculiar electronic structure

π bands = conic at the K and K' points of Brillouin Zone



Dirac cones: linearized bands
(relativistic massless particles)

$$\mathcal{E}_{\mathbf{k}+\mathbf{K}} = \pm v_F k \quad v_F = \text{Fermi velocity}$$

Efficient methods for the characterization?

Raman vibrational spectroscopy

Outline

- Counting the number of layer in a graphene flake
 - Graphene Raman spectra as a function of the number of layers
 - Theoretical explanation
- Non adiabatic vibrations in doped graphene, i.e. how to measure the charge doping with Raman
 - Graphene as one-atom-thick capacitor plate
 - Raman in graphene as a function of the doping
 - Adiabatic Born-Oppenheimer theory (static perturbation)
 - Non-adiabatic theory (dynamic perturbation)
- Raman in layered metals: huge non-adiabatic effects and role of the electron lifetime

How many layer in a flake? with a TEM

[Ferrari, Meyer, Scardaci, Casiraghi, Lazzeri, Mauri, Piscanec, Jiang, Novoselov, Roth, Geim PRL 97, 187401 (2006)]

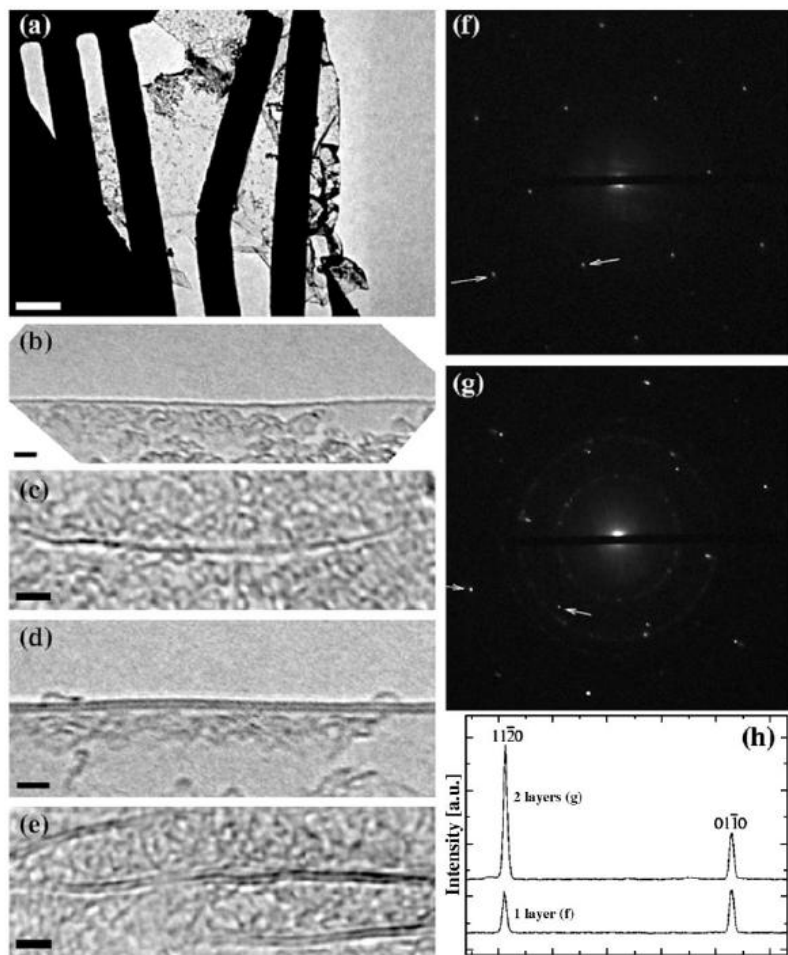


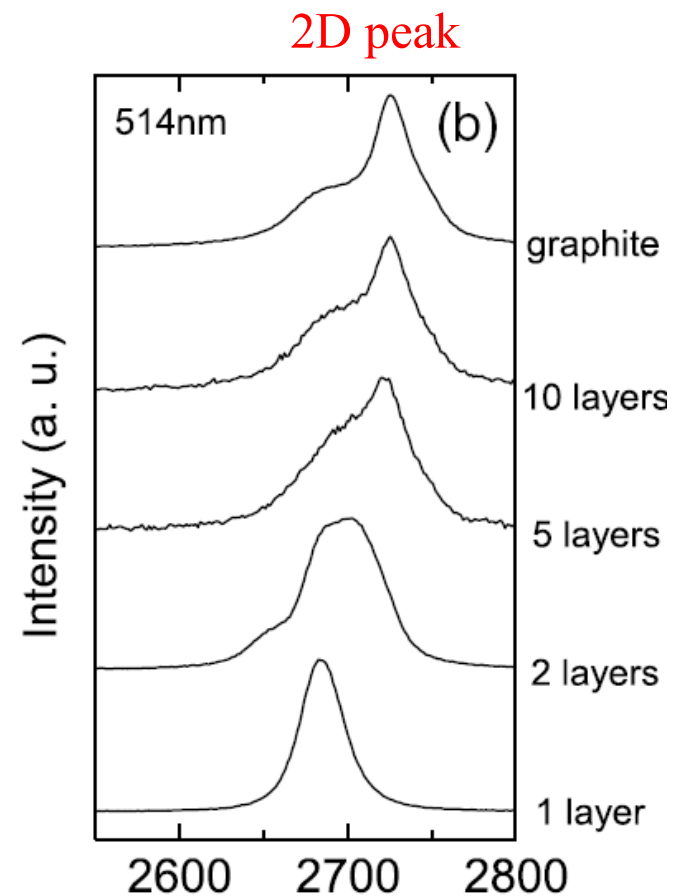
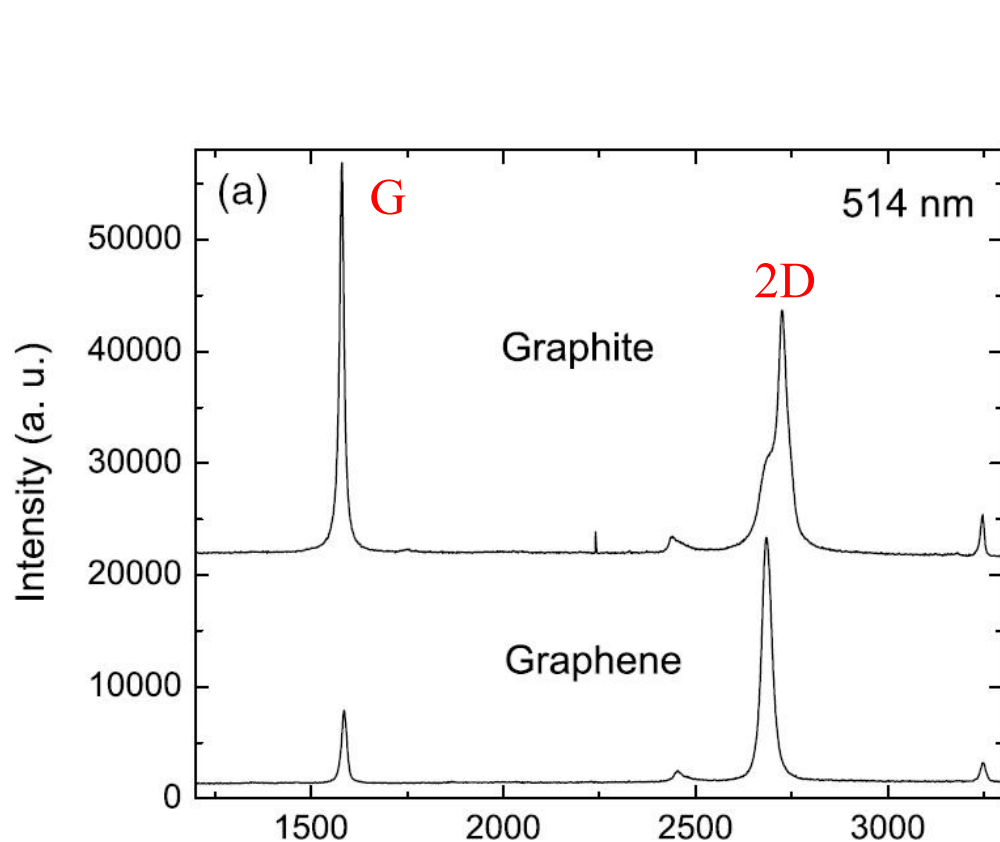
FIG. 1. (a) TEM of suspended graphene. The grid is also visible in optical microscopy. (b) High-resolution image of a folded edge of a single layer and (c) a wrinkle within the layer. (d) Folded edge of a two layer, and (e) internal foldings of the two layer. The amorphous contrast on the sheets is most likely due to hydrocarbon adsorbates on the samples that were cracked by the electron beam. (f) Electron diffraction pattern for close to normal incidence from single layer and (g) from two layers. Weak diffraction peaks from the supporting metal structure are also present. (h) Intensity profile plot along the line indicated by the arrows in (f),(g). The relative intensities of the spots in the two layer are consistent only with *A-B* (and not *A-A*) stacking. Scale bars: (a) 500 nm; (b–e) 2 nm.

Part 1

How to measure how many layers of graphene there are in a flake

How many layer in a flake? with Raman

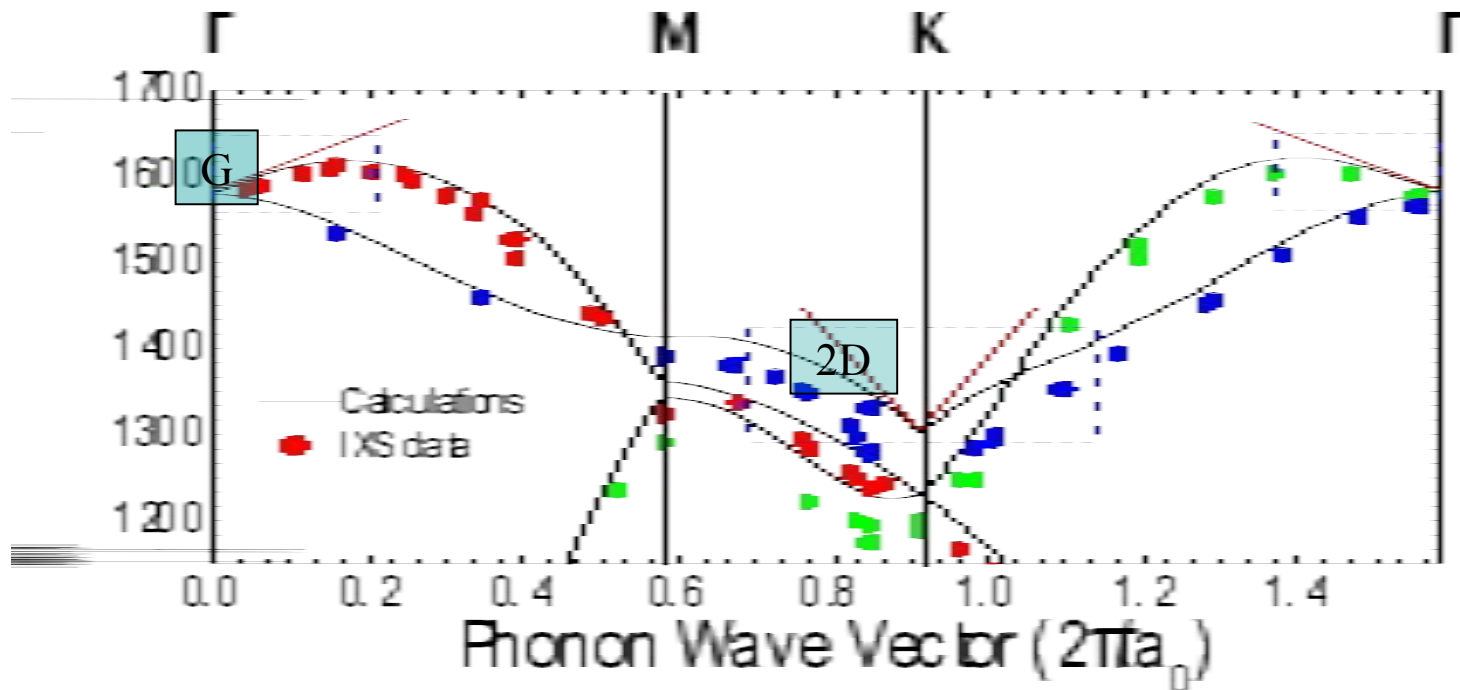
[Ferrari, Meyer, Scardaci, Casiraghi, Lazzeri, Mauri, Piscanec, Jiang, Novoselov, Roth, Geim PRL 97, 187401 (2006)]



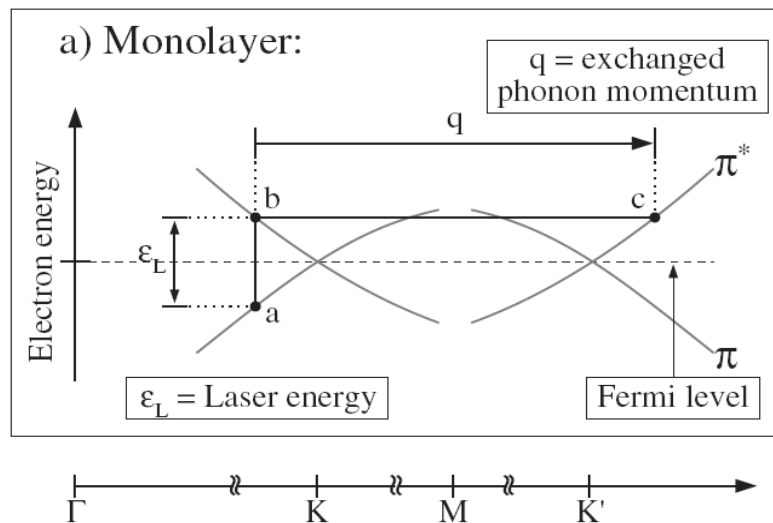
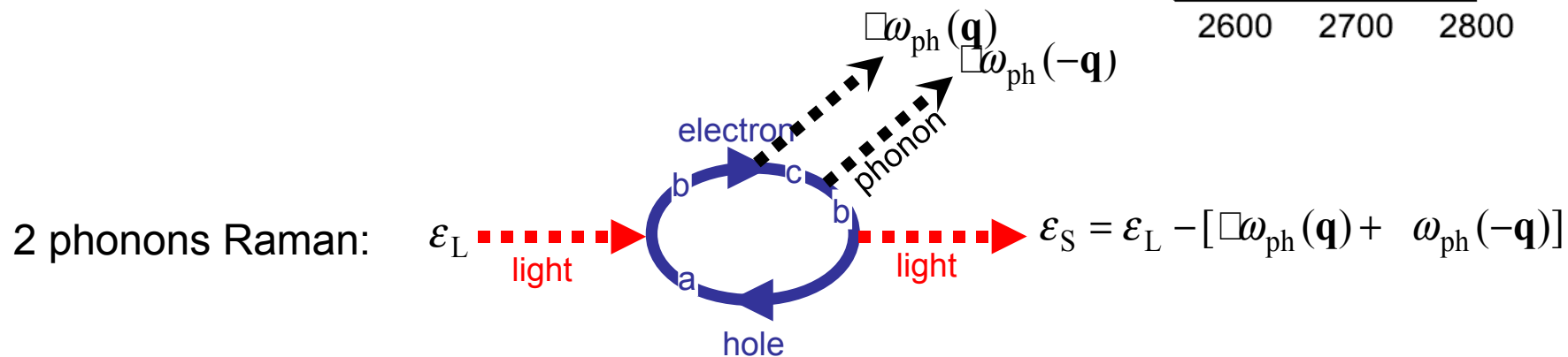
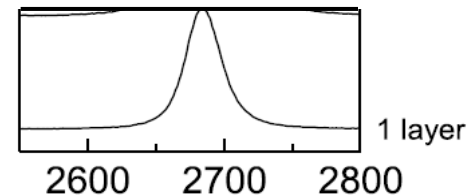
What are the G and 2D peaks?

G peak: zone center G- E_{2g} phonon

2D peak: 2 phonons with momentum q and $-q$ (q between M and K)



2D single layer, one single peak:

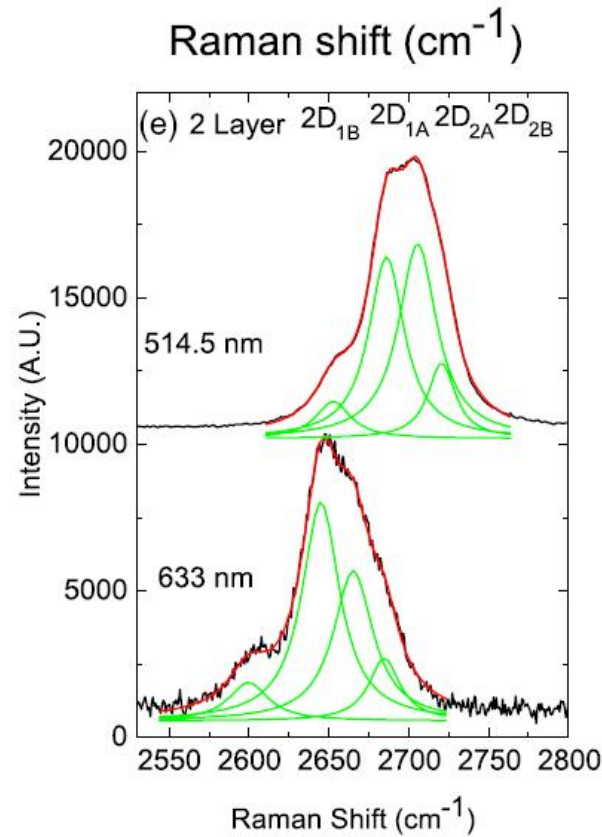


The phonon momentum q is determined by the double resonance condition:

$$E(b) - E(a) = E(c) - E(a) = \epsilon_L$$

intermediate virtual states b and c become real

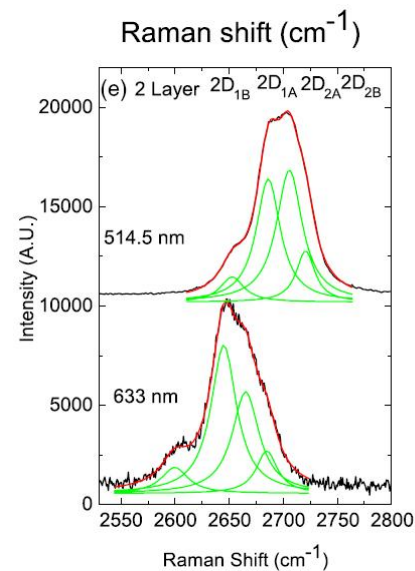
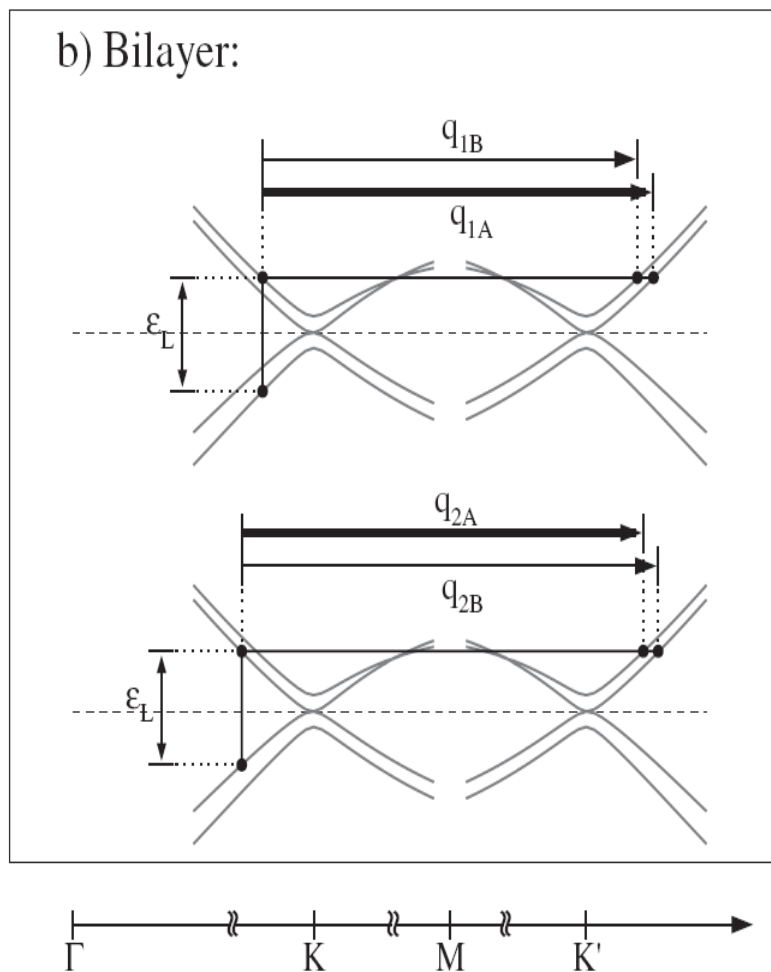
2D bilayer: four peaks



Two possible explanations:

- splitting of the phonon branches due to interlayer coupling: **excluded by our DFT calculations**
- splitting of the electronic bands: **confirmed by our DFT calculations**

2D bilayer: splitting from the electronic bands



positions of the 4 peaks (cm⁻¹)

514.5 nm

Experimental	-44	-10	+10	+25
Theory	-44	-11	+11	+41

633 nm

Experimental	-55	-10	+10	+30
Theory	-44	-9	+9	+41

shape of the 2D peak probes the electronic structure
not the vibrational structure

Part 2

Non adiabatic vibrations in doped graphene

How to measure the charge doping with Raman

Outline

- Failure of the adiabatic approximation in phonons, requirements
- Non-adiabatic effects with DFT in absence of electron relaxation:
 - result for doped graphene
 - interpretation of the violation

Adiabatic approximation for phonons

- Dynamical matrix computed from forces resulting from the static displacement of the atoms from equilibrium:
 - by a frozen phonon calculation
 - or by time-independent perturbation theory
- Standard approximation used in first-principles calculations for phonons both in **insulators** and in **metals**
- Justified in **insulators** if $\omega \ll E_{gap}$

Adiabatic approximation for phonons

Engelsberg, Schrieffer Phys. Rev. (1963), Ipatova, Subashiev Sov. Phys. JETP (1974)

- Can fail in **metals** for phonon with momentum q if:

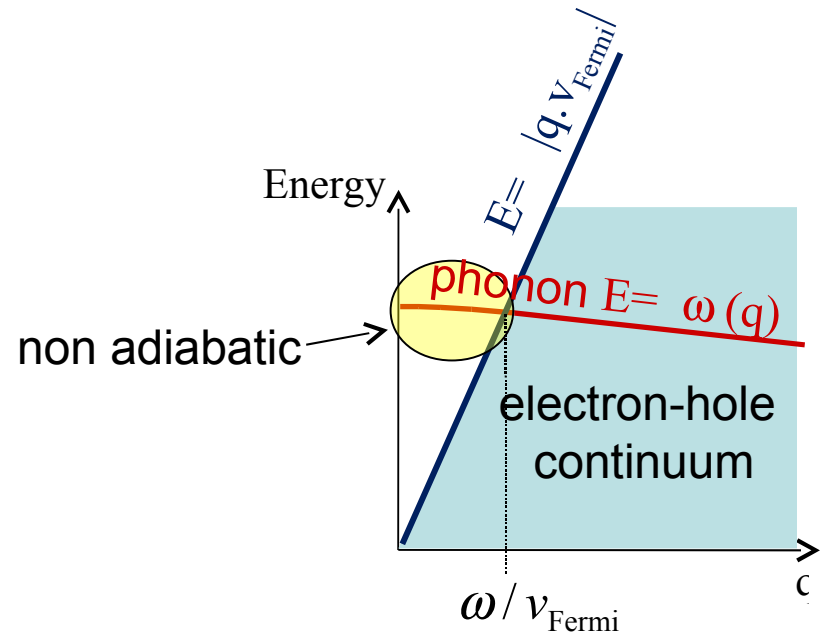
$$\tau_m \gg 1/\omega$$

↑
Electron momentum
relaxation time

- Relaxation of electrons is slower than the ionic motion
- Broadening of electronic bands smaller than phonon energy

$$q \ll \omega / v_{\text{Fermi}}$$

↑
Electron Fermi velocity
in the direction of q



Adiabatic approximation for phonons

Engelsberg, Schrieffer Phys. Rev. (1963), Ipatova, Subashiev Sov. Phys. JETP (1974)

- Can fail in **metals** for phonon with momentum q if:

$$\tau_m \gg 1/\omega$$

↑
Electron momentum
relaxation time

- Easy in a clean metal at low temp.
(in absence of very strong electron-phonon coupling)

$$q \ll \omega / v_{\text{Fermi}}$$

↑
Electron Fermi velocity
in the direction of q

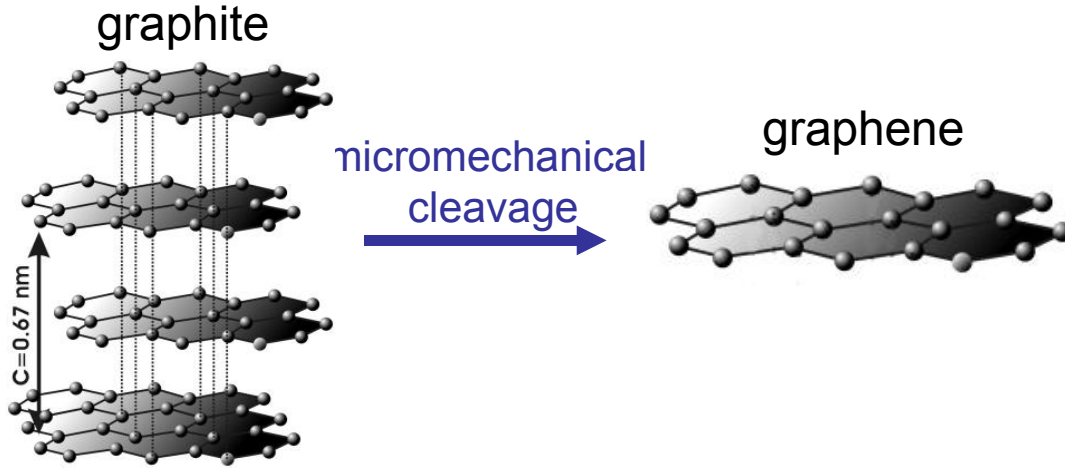
- Difficult in a 3D metal (in Raman minimum q limited by light penetration depth)
- Easy in a **layered metals** (**graphene**)
 v_{Fermi} perp. to the plane is low (zero)

Weak evidence experiments in hcp metals because of condition on q

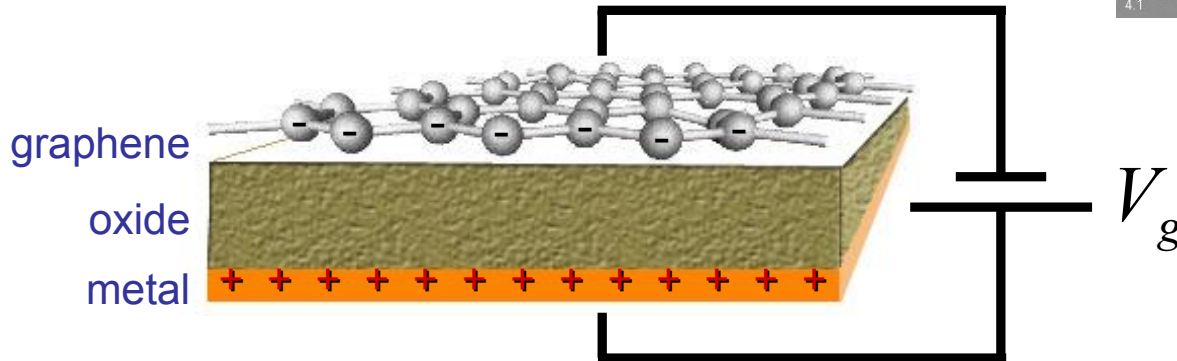
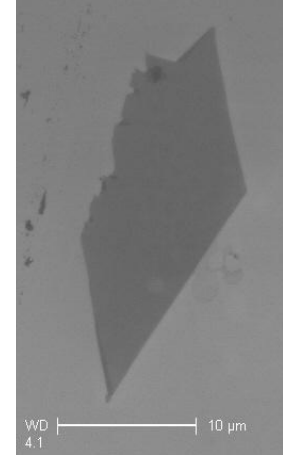
Grant, Schultz, Hufner, Pelzl Phys. Status. Solidi (1973), Ponosov, Bolotin, Sov. Phys. Solid State (1985), Ponosov, Bolotin, Thomsen, Cardona Phys. Stat. Sol. (1998)

Failure proportional to density of states at the Fermi energy: **we need to dope graphene**

Graphene capacitor



10 μm wide
single layer flake



$$\sigma = \text{graphene excess-electron surface-concentration} = \eta V_g$$

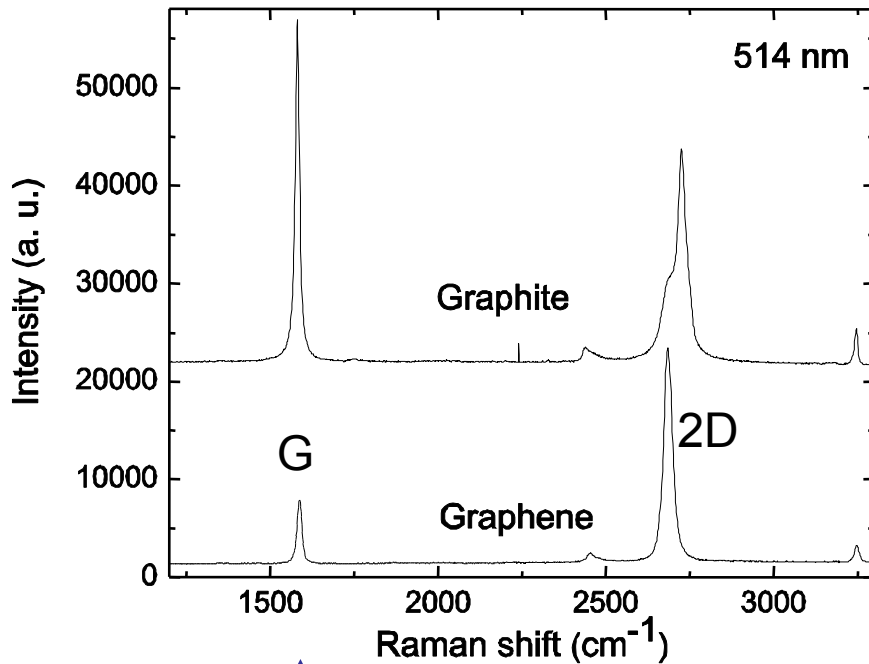
$$\eta \approx 7.2 \times 10^{10} \text{ cm}^2/\text{V}$$

$$V_g = 150 \text{ V}$$

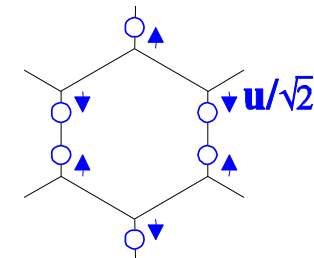
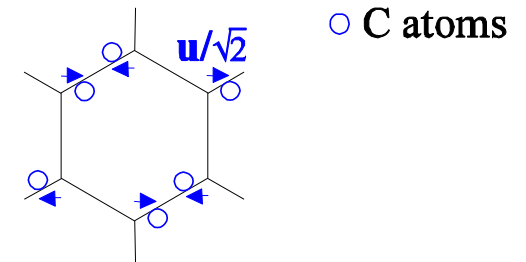
0.003 extra e^- per C
1‰ valence charge

Vibrational Raman

Ferrari, Meyer, Scardaci, Casirgahi, Lazzeri,
Mauri, Piscanec, Jiang, Novoselov, Roth, Geim.
Phys. Rev. Lett. 97, 187401 (2006).

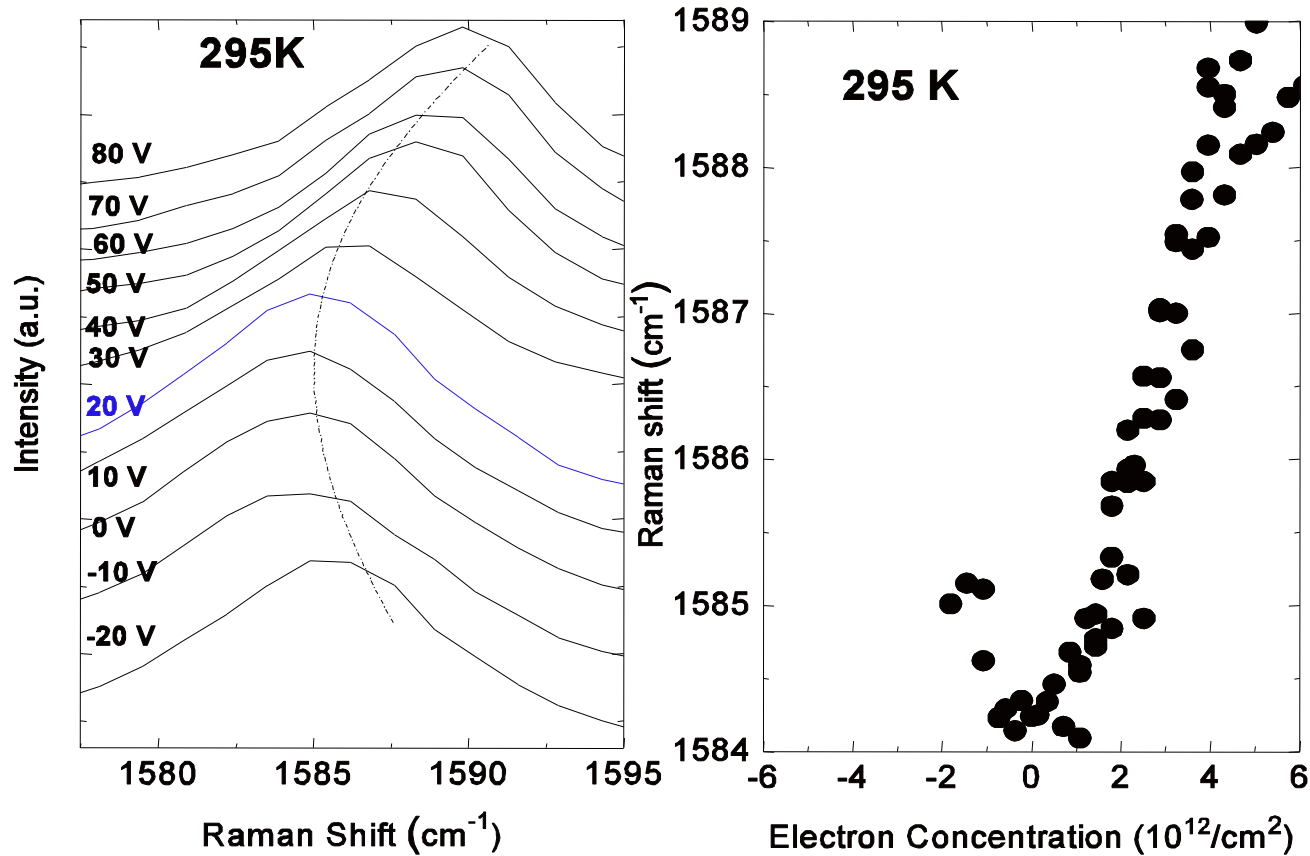


↑
G peak = E_{2g} phonon at Γ =
inplane antiparallel displacement of the 2 atoms



Graphene: Raman G-peak as a function of σ (Vg)

Pisana, Lazzeri, Casiraghi, Novoselov, Geim, Ferrari, Mauri, Nature Materials 6, 198 (2007)



similar results in: Yan, Zhang, Kim, Pinczuk, PRL 98, 166802 (2007)

DFT ab-initio calculations:

- PBE functional, pseudopotentials, PW basis
- New implementation for non-adiabatic calculations in Quantum-espresso gnu package
- Non-adiabatic and adiabatic DFT calculations considering an **infinite electron relaxation time:**

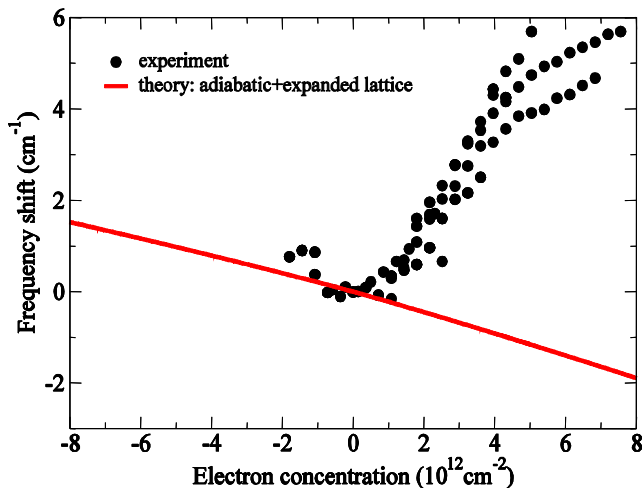
$$\tau_m \gg 1/\omega$$

DFT phonon calculation

M. Lazzeri, F. Mauri, Phys. Rev. Lett., 266407 (2006)

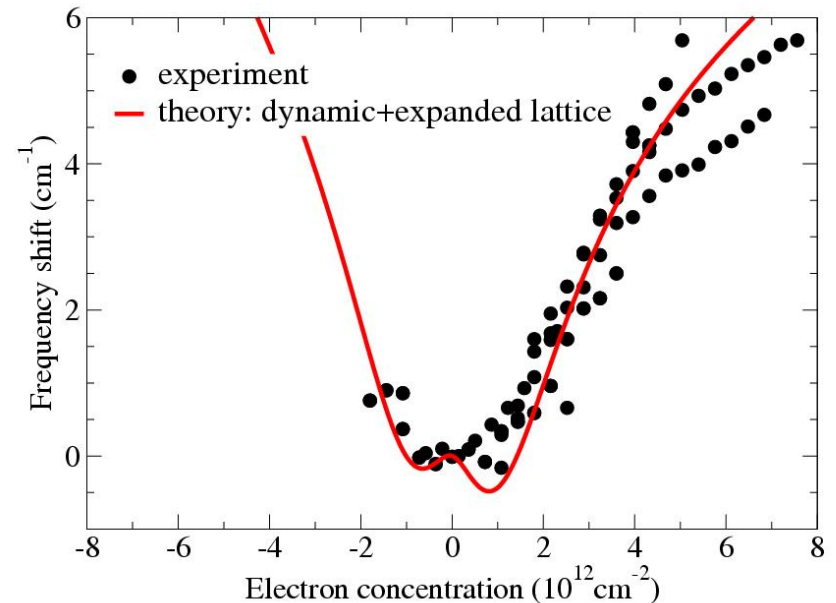
ADIABATIC

- phonon from forces resulting from the *static* displacement of the atoms from equilibrium (by *time-independent* perturbation theory)



NON-ADIABATIC

- the phonon is a dynamic periodic perturbation oscillating at finite frequency ($\sim 1580 \text{cm}^{-1}$): phonon by *time-dependent* perturbation theory with periodic perturbation



Interpreting the results

Shaking the Dirac cones

Pisana, Lazzeri, Casiraghi, Novoselov, Geim, Ferrari, Mauri, Nature Materials 6, 198 (2007)

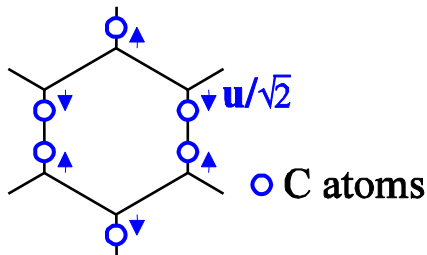
-from the DFT electron-phonon coupling matrix-elements, in presence of a E_{2g} lattice distortion of amplitude u

$$\varepsilon_{\mathbf{k}+\mathbf{K}} = \pm \hbar v_F |\mathbf{k} - \mathbf{s}(\mathbf{u})| \quad \mathbf{u} \cdot \mathbf{s} = 0 \quad s = u \sqrt{2 \langle D_{\Gamma}^2 \rangle_F} / (\hbar v_F)$$

$$\langle D_{\Gamma}^2 \rangle_F = 45.6 (\text{eV} / \text{\AA})^2$$

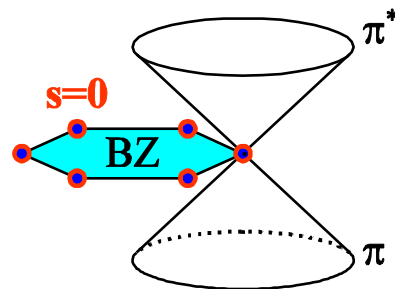
real space

perturbed (finite u)

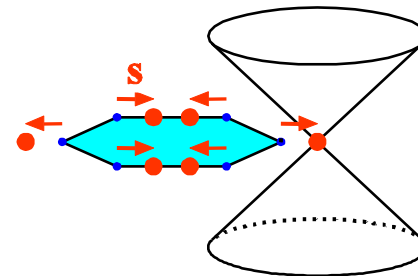


reciprocal space

unperturbed ($u=0$)



perturbed (finite u)



BZ: Brillouin zone
 ● Dirac points
 • K points

Shaking a filled Martini glass

Adiabatic



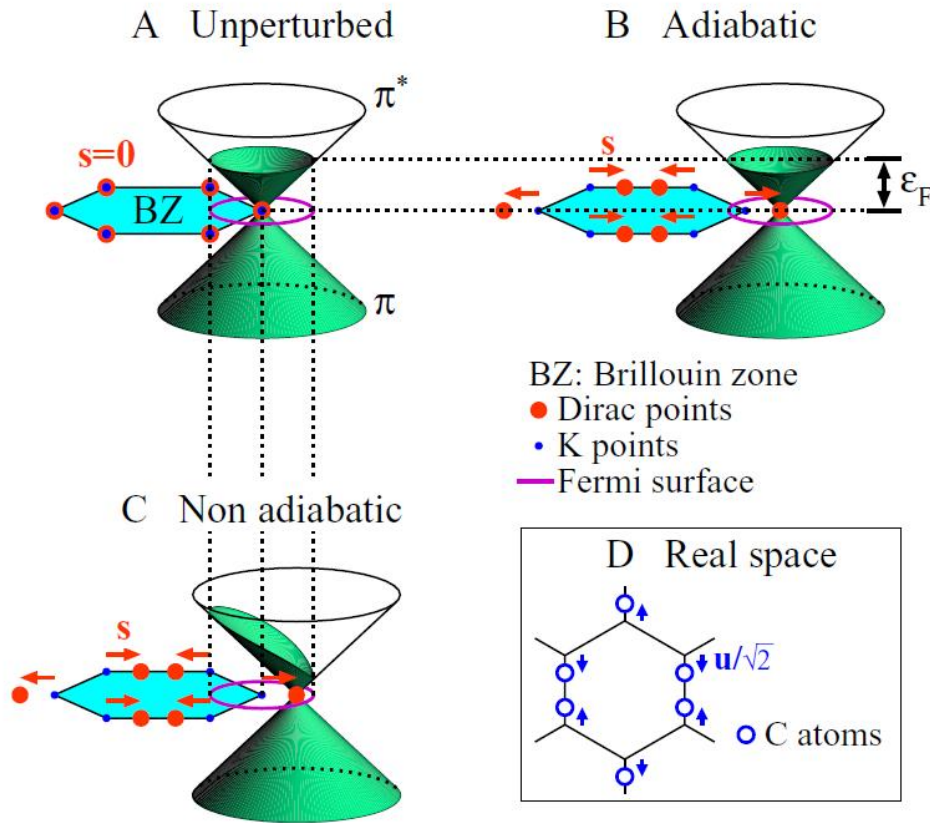
Non adiabatic



...shaken, not stirred (J. Bond)

Shaking a filled Dirac cone

Pisana, Lazzeri, Casiraghi, Novoselov, Geim, Ferrari, Mauri, Nature Materials 6, 198 (2007)



Adiabatic or non-adiabatic?

From transport measurements and fs-spectroscopy:

Electron momentum relaxation time:

$$\tau_m = 100-300 \text{ fs}$$

Phonon period:

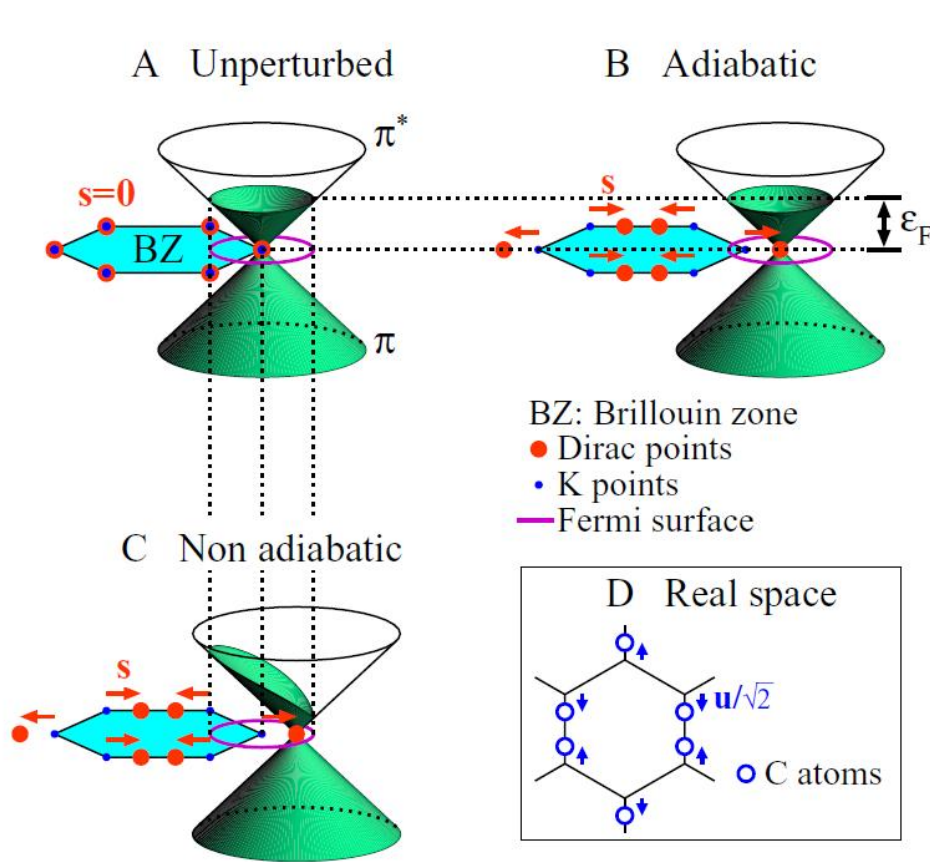
$$T = 21 \text{ fs}$$

$$2\pi \tau_m \gg T$$

the electrons do not have time to relax to the adiabatic ground state:
non-adiabatic electron dynamics

Shaking a filled Dirac cone

Pisana, Lazzeri, Casiraghi, Novoselov, Geim, Ferrari, Mauri, Nature Materials 6, 198 (2007)



$$\omega = \sqrt{\frac{1}{M} \frac{d^2 E(u)}{du^2}}$$

$M = C$ mass $E =$ electronic energy

Adiabatic case: the π -band energy does not depend on u .

ω independent of ε_F .

Non-adiabatic case: the π -band energy increases with u .

$$\omega = \alpha |\varepsilon_F| + \omega_0$$

$$\alpha = \frac{A \langle D_{\Gamma}^2 \rangle_F}{\pi M \omega_0 (v_F)^2} \quad A = \text{unit cell area}$$

Interpreting the results

perturbation-theory point of view

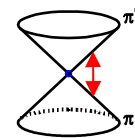
Perturbation theory

M. Lazzeri, F. Mauri, Phys. Rev. Lett., 266407 (2006)

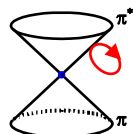
$$\omega_{\mathbf{q}} = \sqrt{\frac{F_{\mathbf{q}}(\omega_0)}{M} + \dots} \quad F_{\mathbf{q}}(\omega_0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{n,m} \frac{f(\epsilon_{m\mathbf{k}} - \epsilon_F) - f(\epsilon_{n\mathbf{k}+\mathbf{q}} - \epsilon_F)}{\epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}+\mathbf{q}} + \omega_0 + i\delta} |D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}}|^2 \quad D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}} = \langle m\mathbf{k} | \frac{dV_{ks}(\mathbf{r})}{du_{\mathbf{q}}} | n\mathbf{k} + \mathbf{q} \rangle$$

For an optical zone-center phonon ($\mathbf{q} \rightarrow 0$)

static case, adiabatic: ($\omega_0 + i\delta$)=0

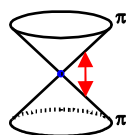
$$F_0(0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{m,n \neq m} \frac{f(\epsilon_{m\mathbf{k}} - \epsilon_F) - f(\epsilon_{n\mathbf{k}} - \epsilon_F)}{\epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}}} |D_{m\mathbf{k},n\mathbf{k}}|^2$$


inter-band contribution

$$- \frac{2}{N_k} \sum_{\mathbf{k}} \sum_m \delta(\epsilon_{m\mathbf{k}} - \epsilon_F) |D_{m\mathbf{k},m\mathbf{k}}|^2$$


intra-band contribution
(phonon-induced variation of the Fermi surface)

dynamic case, non-adiabatic

$$F_0(\omega_0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{m,n \neq m} \frac{f(\epsilon_{m\mathbf{k}} - \epsilon_F) - f(\epsilon_{n\mathbf{k}} - \epsilon_F)}{\epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}} + \omega_0 + i\delta} |D_{m\mathbf{k},n\mathbf{k}}|^2$$


inter-band contribution

Perturbation theory

M. Lazzeri, F. Mauri, Phys. Rev. Lett., 266407 (2006)

$$\omega_{\mathbf{q}} = \sqrt{\frac{F_{\mathbf{q}}(\omega_0)}{M} + \dots} \quad F_{\mathbf{q}}(\omega_0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{n,m} \frac{f(\epsilon_{m\mathbf{k}} - \epsilon_F) - f(\epsilon_{n\mathbf{k}+\mathbf{q}} - \epsilon_F)}{\epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}+\mathbf{q}} + \omega_0 + i\delta} |D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}}|^2 \quad D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}} = \langle m\mathbf{k} | \frac{dV_{ks}(\mathbf{r})}{du_{\mathbf{q}}} | n\mathbf{k} + \mathbf{q} \rangle$$

For an optical zone-center phonon ($\mathbf{q} \rightarrow 0$)

static case, adiabatic

contribution to ω in graphene

$$F_0(0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{m,n \neq m} \frac{f(\epsilon_{m\mathbf{k}} - \epsilon_F) - f(\epsilon_{n\mathbf{k}} - \epsilon_F)}{\epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}}} |D_{m\mathbf{k},n\mathbf{k}}|^2 \leftarrow + \alpha |\epsilon_F|$$

$$- \frac{2}{N_k} \sum_{\mathbf{k}} \sum_m \delta(\epsilon_{m\mathbf{k}} - \epsilon_F) |D_{m\mathbf{k},m\mathbf{k}}|^2 \leftarrow - \alpha |\epsilon_F| \quad (\text{Fermi-surface variation})$$

dynamic case, non-adiabatic

$$F_0(\omega_0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{m,n \neq m} \frac{f(\epsilon_{m\mathbf{k}} - \epsilon_F) - f(\epsilon_{n\mathbf{k}} - \epsilon_F)}{\epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}} + \omega_0 + i\delta} |D_{m\mathbf{k},n\mathbf{k}}|^2 \leftarrow + \alpha |\epsilon_F| + \frac{\alpha \omega_0}{4} \ln \left(\frac{2|\epsilon_F| - \omega_0}{2|\epsilon_F| + \omega_0} \right)$$

Perturbation theory

M. Lazzeri, F. Mauri, Phys. Rev. Lett., 266407 (2006)

$$\omega_{\mathbf{q}} = \sqrt{\frac{F_{\mathbf{q}}(\omega_0)}{M} + \dots} \quad F_{\mathbf{q}}(\omega_0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{n,m} \frac{f(\epsilon_{m\mathbf{k}} - \epsilon_F) - f(\epsilon_{n\mathbf{k}+\mathbf{q}} - \epsilon_F)}{\epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}+\mathbf{q}} + \omega_0 + i\delta} |D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}}|^2 \quad D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}} = \langle m\mathbf{k} | \frac{dV_{ks}(\mathbf{r})}{du_{\mathbf{q}}} | n\mathbf{k} + \mathbf{q} \rangle$$

For an optical zone-center phonon ($\mathbf{q} \rightarrow 0$)

static case, adiabatic

contribution to ω in graphene

$$F_0(0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{m,n \neq m} \frac{f(\epsilon_{m\mathbf{k}} - \epsilon_F) - f(\epsilon_{n\mathbf{k}} - \epsilon_F)}{\epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}}} |D_{m\mathbf{k},n\mathbf{k}}|^2 \leftarrow + \alpha |\epsilon_F|$$

$$- \frac{2}{N_k} \sum_{\mathbf{k}} \sum_m \delta(\epsilon_{m\mathbf{k}} - \epsilon_F) |D_{m\mathbf{k},m\mathbf{k}}|^2 \leftarrow - \alpha |\epsilon_F| \quad (\text{Fermi-surface variation})$$

dynamic case, non-adiabatic

for: $2|\epsilon_F| \gg \omega_0$

$$F_0(\omega_0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{m,n \neq m} \frac{f(\epsilon_{m\mathbf{k}} - \epsilon_F) - f(\epsilon_{n\mathbf{k}} - \epsilon_F)}{\epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}} + \omega_0 + i\delta} |D_{m\mathbf{k},n\mathbf{k}}|^2 \leftarrow + \alpha |\epsilon_F| + \frac{\alpha \omega_0}{4} \ln \left(\frac{2|\epsilon_F| - \omega_0}{2|\epsilon_F| + \omega_0} \right)$$

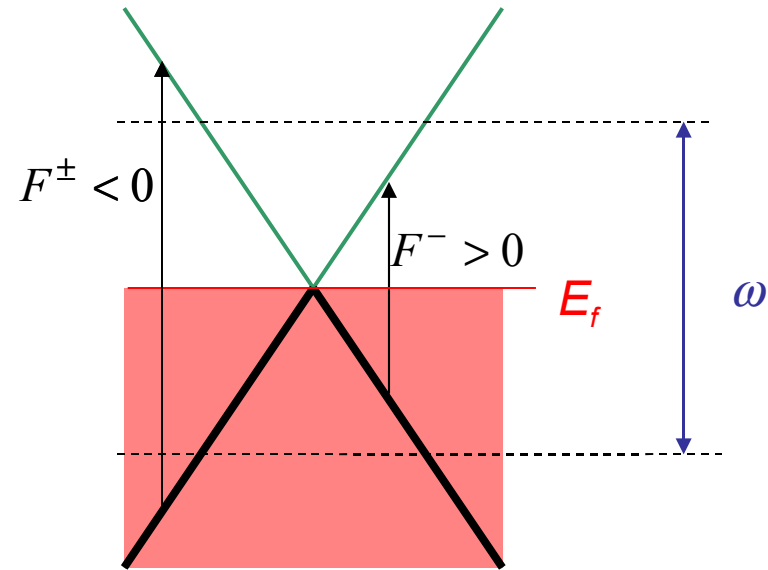
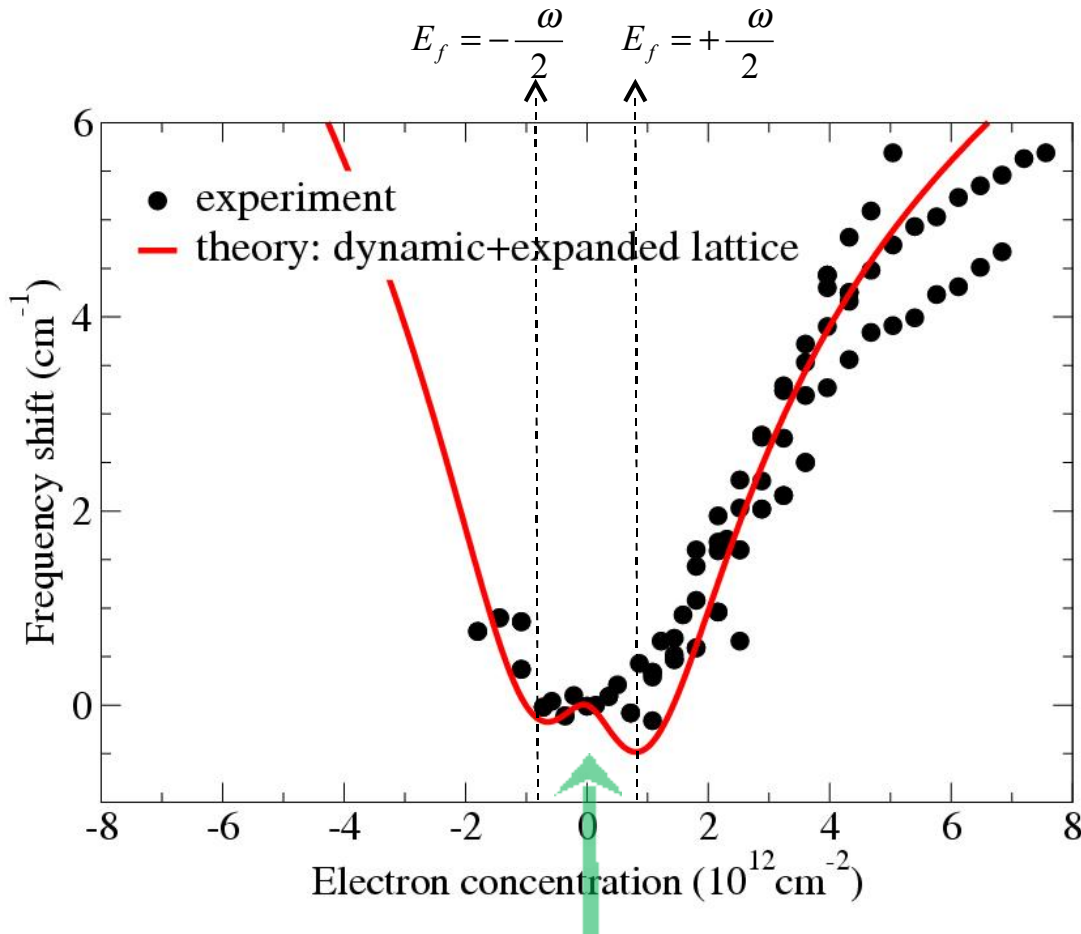
Perturbation theory: non adiabatic

M. Lazzeri, F. Mauri, Phys. Rev. Lett., 266407 (2006)

$$\omega = \sqrt{\frac{F^+}{M} + \frac{F^-}{M} + \dots}$$

$$F^\pm = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_e^{\text{empty}} \sum_o^{\text{occupied}} - \frac{|D_{o\mathbf{k},e\mathbf{k}}|^2}{\varepsilon_{e\mathbf{k}} - \varepsilon_{o\mathbf{k}} \pm \omega}$$

$$D_{o\mathbf{k},e\mathbf{k}} = \langle o\mathbf{k} | \frac{dV_{ks}(\mathbf{r})}{du} | e\mathbf{k} \rangle = \text{electron - phonon coupling}$$



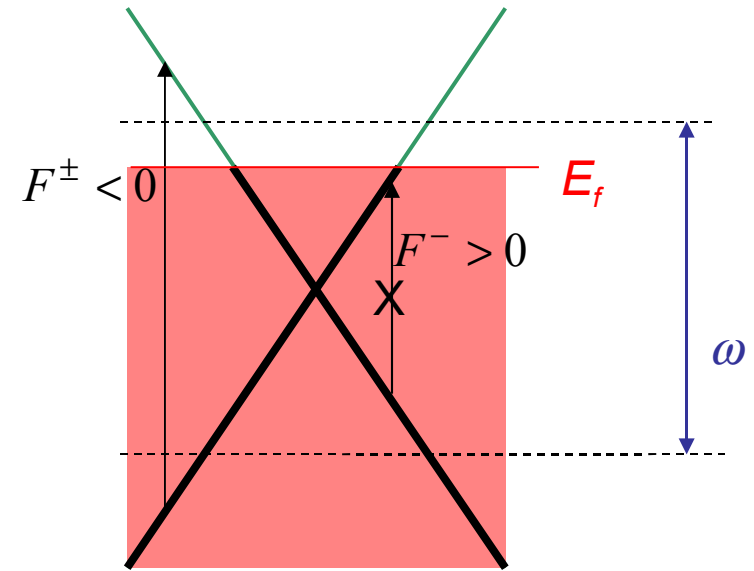
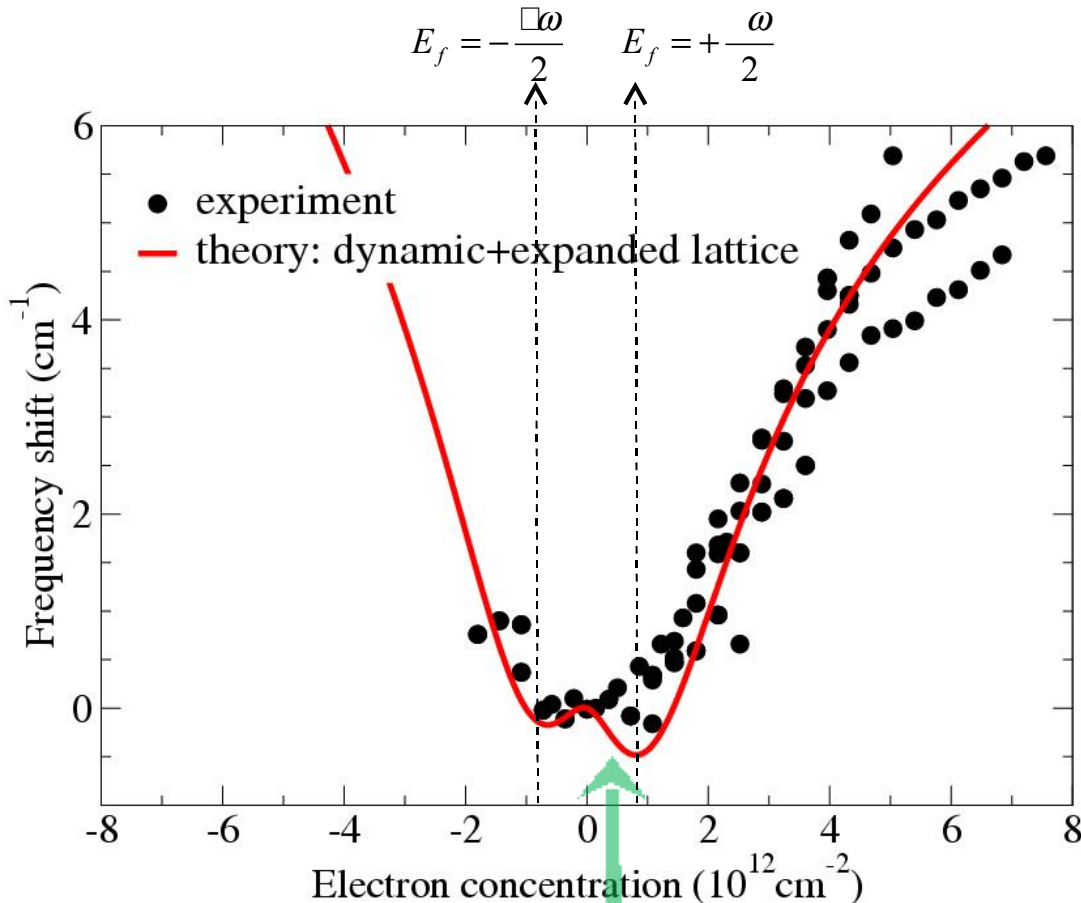
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M. Lazzeri, F. Mauri, Phys. Rev. Lett., 266407 (2006)

$$\omega = \sqrt{\frac{F^+}{M} + \frac{F^-}{M} + \dots}$$

$$F^\pm = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_e^{\text{empty}} \sum_o^{\text{occupied}} - \frac{|D_{o\mathbf{k},e\mathbf{k}}|^2}{\varepsilon_{e\mathbf{k}} - \varepsilon_{o\mathbf{k}} \pm \omega}$$

$$D_{o\mathbf{k},e\mathbf{k}} = \langle o\mathbf{k} | \frac{dV_{ks}(\mathbf{r})}{du} | e\mathbf{k} \rangle = \text{electron - phonon coupling}$$



for $|E_f| < \Delta\omega/2$ ω decreases with E_f

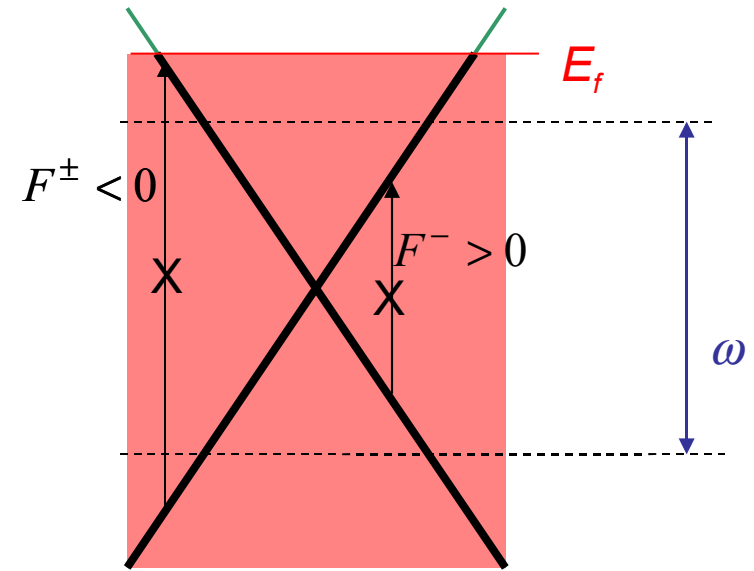
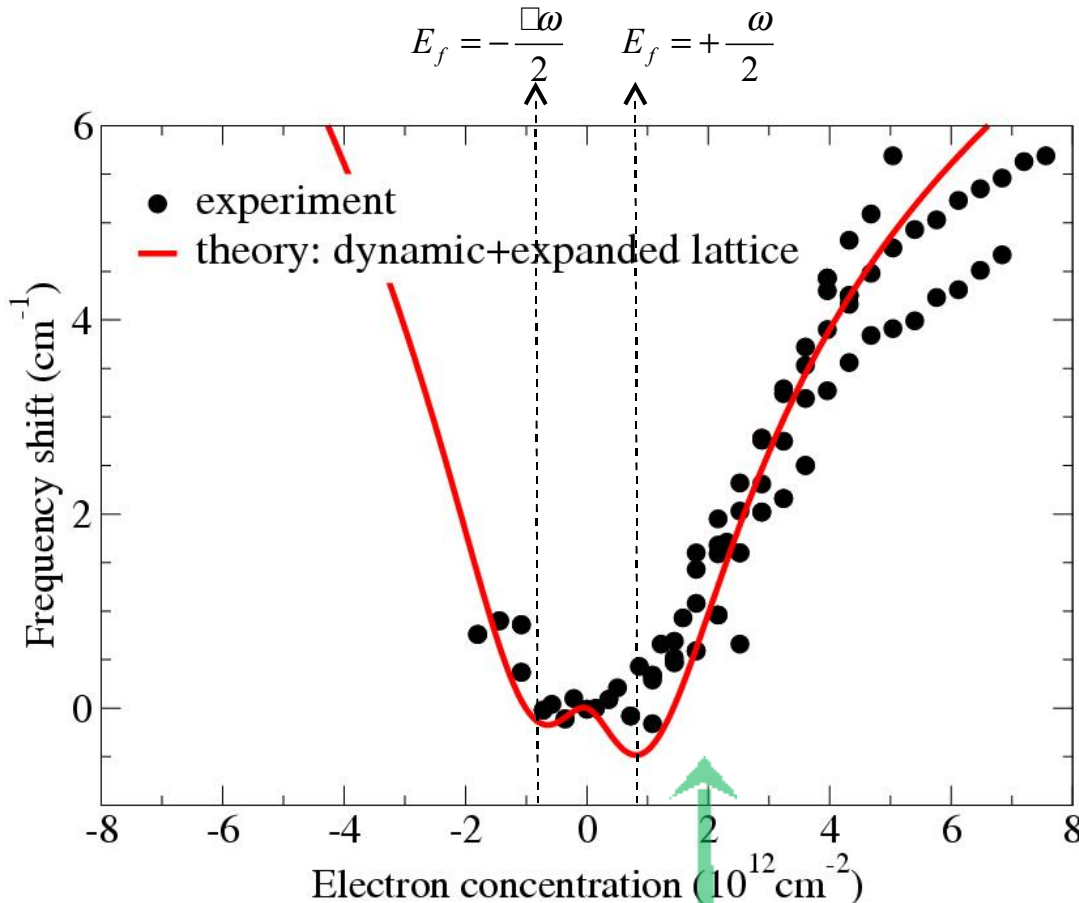
Perturbation theory: non adiabatic

M. Lazzeri, F. Mauri, Phys. Rev. Lett., 266407 (2006)

$$\omega = \sqrt{\frac{F^+}{M} + \frac{F^-}{M} + \dots}$$

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for $|E_f| < \frac{\omega}{2}$ ω decreases with $|E_f|$
 for $|E_f| > \frac{\omega}{2}$ ω increases with $|E_f|$

Conclusions part 1 and 2

Measuring the number of layer

- 2D Raman peak is very sensitive to the number of layer in a flake
- The shape of the 2D peak is an image of the electronic band splitting

Measuring the charge doping in a graphene monolayer

- Graphene: stiffening of the zone-center phonon with electron and hole doping
- Adiabatic calculation fails, dynamic calculation reproduces the stiffening
- The adiabatic phonon energy has two contributions:
 - the distortion of the electronic bands, associated with the phonon displacement,
 - the consequent rearrangement of the Fermi surface
- In graphene these two contributions cancel out exactly
- In general, if $\tau_m \gg 1/\omega$ the correct zone-center phonon treatment should not include the adiabatic Fermi-surface rearrangement
- The $\tau_m \gg 1/\omega$ condition occurs in many metals
- The effect occurs for phonons with $\omega > v_F / \lambda$ Observable in layer compounds

Part 3

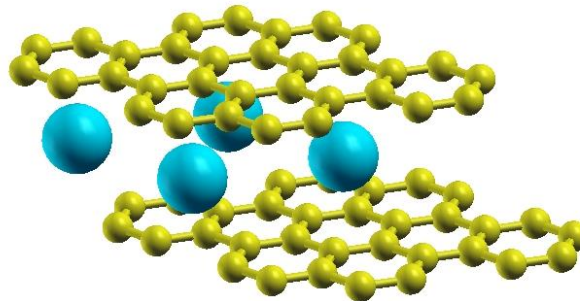
Raman spectra of layered metals
huge non adiabatic effects and
role of electron relaxation

Larger non adiabatic effects?

non-adiabatic adiabatic

$$\frac{\omega^{\text{NA}} - \omega^{\text{A}}}{\omega^{\text{A}}} \cong \text{DOS}(E_{\text{Fermi}}) \langle D_{i\mathbf{k}}^2 \rangle_{\text{Fermi}} \left(2 \frac{d^2 E_{\text{tot}}}{du^2} \right)^{-1} \quad D_{i\mathbf{k}} = \langle i\mathbf{k} | \frac{V_{\text{scf}}}{du} | i\mathbf{k} \rangle$$

- The violation increases with $\text{DOS}(E_{\text{Fermi}})$
- $q \ll \omega / v_{\text{Fermi}}$ to observe with Raman we need a layer metal

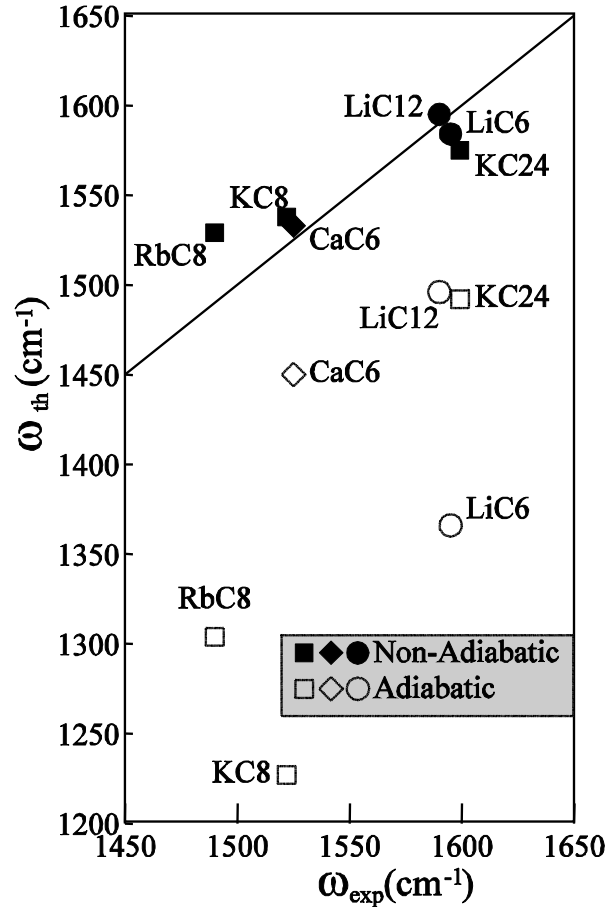


Intercalated graphite, MgB2: layer metals with large $\text{DOS}(E_{\text{Fermi}})$

DFT theory (with $\tau_m = \infty$) vs. expt.

Saitta, Lazzeri, Calandra, Mauri, PRL 100, 226401 (2008)

intercalated graphite: G peak

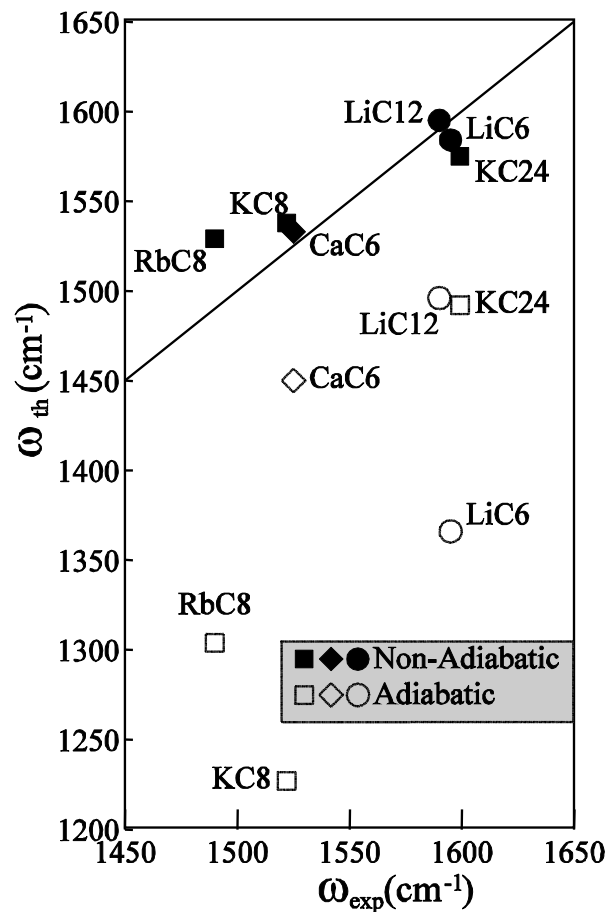


huge nonadiabatic effects
(311 cm^{-1} in KC_8)

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Saitta, Lazzeri, Calandra, Mauri, PRL 100, 226401 (2008)

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hcp metals (ω in cm^{-1})

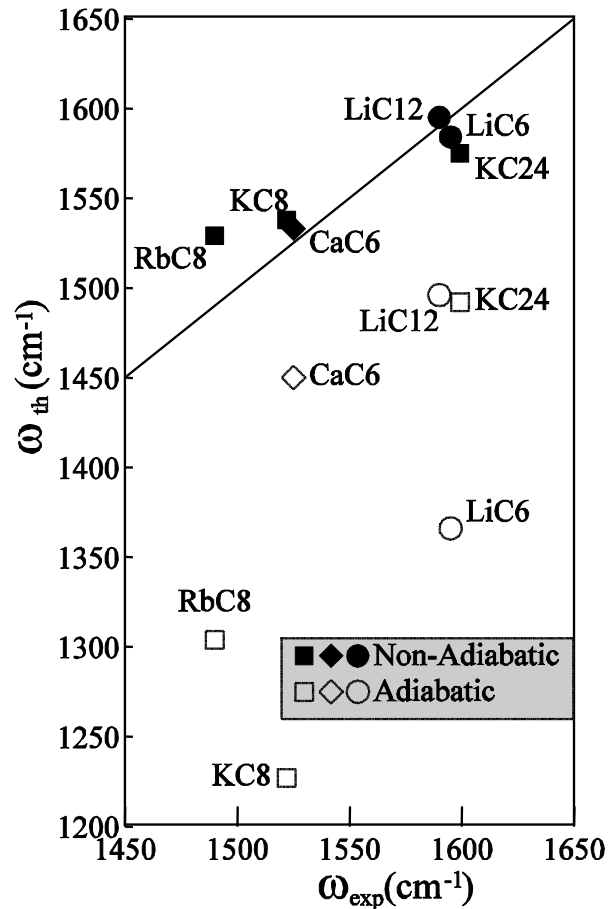
	ω^A	ω^{NA}	ω^{exp}
Mg	122	123	122.5
Ti	139	151	141

nonadiabatic effects 10% in Ti, but measured ω is adiabatic, since: $q \gg \omega / v_{Fermi}$

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MgB_2 (ω in cm^{-1})

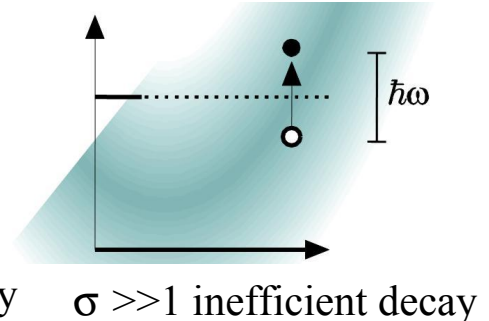
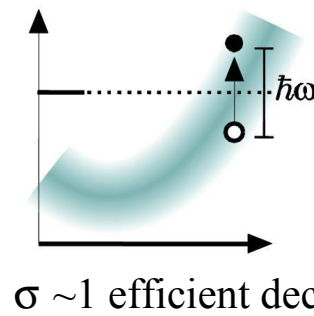
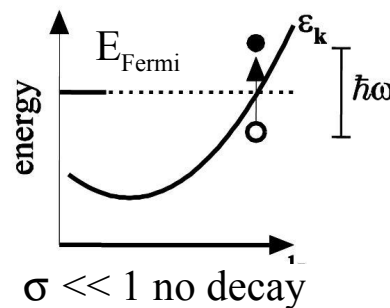
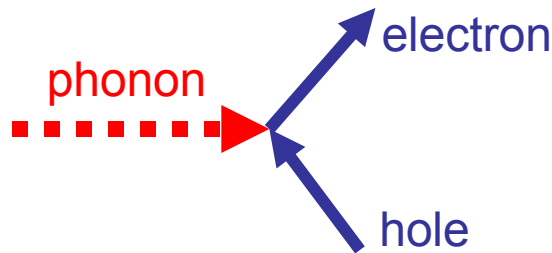
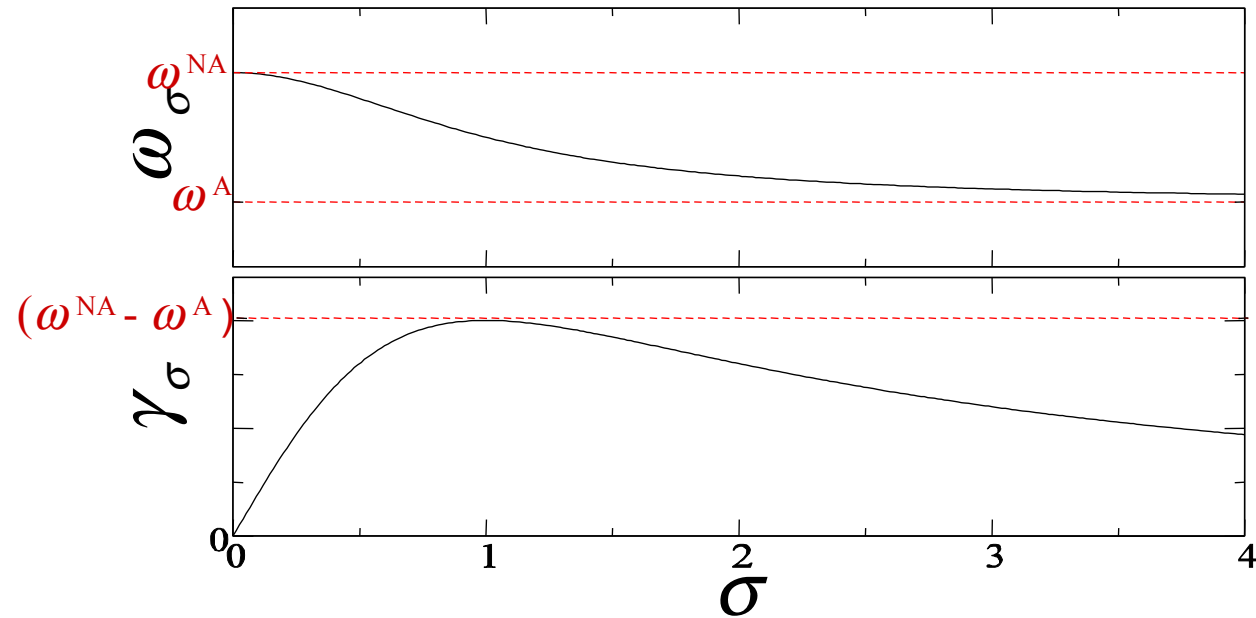
	ω^A	ω^{NA}	ω^{exp}
MgB_2	538	761	600

expt. between adiabatic and non adiabatic, since: $\tau_m \sim 1 / \omega$

Theory with finite electron relaxation time, τ_m

Saitta, Lazzeri, Calandra, Mauri, PRL 100, 226401 (2008)

$$\sigma = \frac{1}{\tau_m \omega^A} \quad \omega_\sigma = \omega^A + \frac{(\omega^{\text{NA}} - \omega^A)}{1 + \sigma^2} \quad \text{FWHM} = \gamma_\sigma = (\omega^{\text{NA}} - \omega^A) \frac{2\sigma}{1 + \sigma^2}$$



Theory with finite electron relaxation time, τ_m

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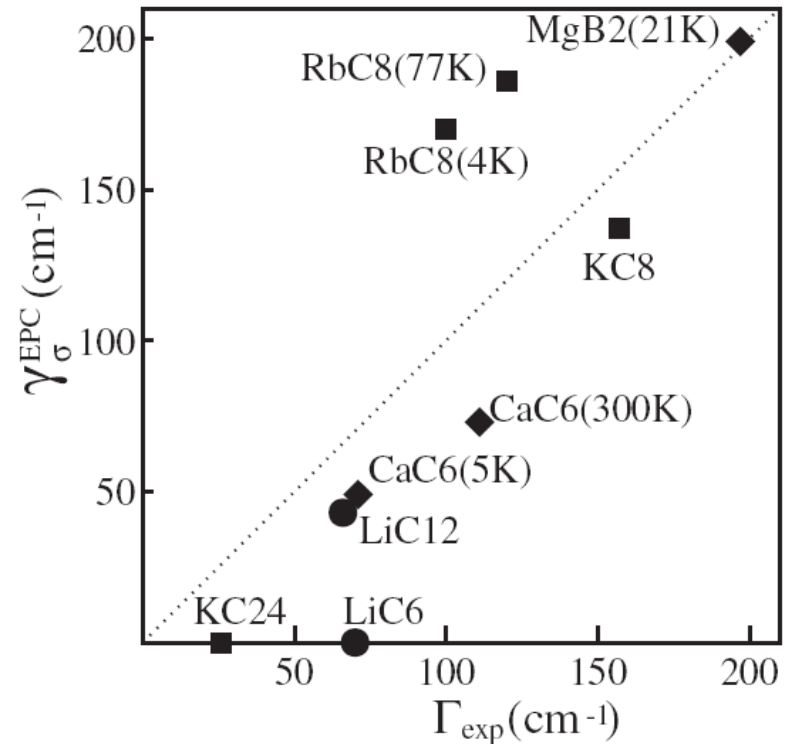
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G peak FWHM theory vs. experiment

• We estimate σ imposing

$$\omega_\sigma = \omega_{\text{exp}}$$

• We compute the linewidth γ_σ
with this σ



Infinite mass limit

With negligible electron relaxation, i.e. for: $\sigma = \frac{1}{\tau_m \omega^A} \ll 1$

$$\frac{\omega_\sigma - \omega^A}{\omega^A} \cong \text{DOS}(E_{\text{Fermi}}) \langle D_{i\mathbf{k}}^2 \rangle_{\text{Fermi}} \left(2 \frac{d^2 E_{\text{tot}}}{du^2} \right)^{-1} \quad D_{i\mathbf{k}} = \langle i\mathbf{k} | \frac{V_{\text{scf}}}{du} | i\mathbf{k} \rangle$$

the non-adiabatic effect are mass independent



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the non-adiabatic effect are mass independent

However for $M \rightarrow \infty$, $\omega^A \rightarrow 0$, $\sigma = \frac{1}{\tau_m \omega^A} \gg 1$ and:

$$\frac{\omega_\sigma - \omega^A}{\omega^A} \cong \text{DOS}(E_{\text{Fermi}}) \langle D_{i\mathbf{k}}^2 \rangle_{\text{Fermi}} \frac{\tau_m^2}{2M} = O\left(\frac{1}{M}\right) \rightarrow 0$$

In the infinite mass limit the adiabatic frequency is recovered

Conclusions

- Failure of the adiabatic approximation in phonons if:

$$\tau_m \gg 1/\omega \qquad q \ll \omega/v_{\text{Fermi}}$$

- **First non-adiabatic DFT** calculations of phonons
- At $q=0$, the **violation** can be **huge** (10%-30%) in both normal and layered metals, but only in layered metals Raman measures $q=0$
- **Non adiabatic** effects are **crucial** to reproduce the experimental Raman spectra of all layered metals
- From the experimental Raman frequency and linewidth is possible to extract the **electron relaxation time**

Momentum relaxation time in metals

from Ashcroft and Mermin

Metal	momentum-relaxation-time (fs)		phonon-period/(2π) (fs) [from ν Debye]
	77K	273K	
Li*	73	8.8	19
Na*	170	32	51
K*	180	41	76
Cu*	210	27	24
Ag*	200	40	36
Au*	120	30	45
Mg*	67	11	24
Fe*	32	2.4	18
Zn	24	4.9	33
Cd	24	5.6	64
Hg	7.1		76
Al*	65	8	19
Ga	8.4	1.7	32
In	17	3.8	59
Tl	9.1	2.2	80
Sn	11	2.3	45-29
Pb	5.7	1.4	87
Bi	0.72	0.23	64
Sb	2.7	0.55	38

XX* = $2\pi\tau_m > T$ at low temperature (non-adiabatic effect expected)