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Non adiabatic vibrations in doped graphene

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Non adiabatic vibrations in doped graphene

Theory:

M. Lazzeri, F. Mauri

IMPMC, Université Pierre et Marie Curie-Paris 6, CNRS

Experiment:

S. Pisana, C. Casiraghi, A. C. Ferrari

Engineering Department, Cambridge University,

K.S. Novoselov, A.K. Geim,

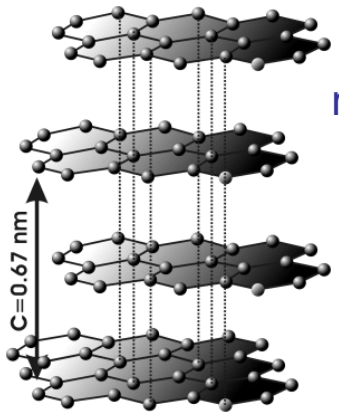
Dep. of Physics and Astronomy, University of Manchester

Outline

-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)
-Discussion

Graphene capacitor

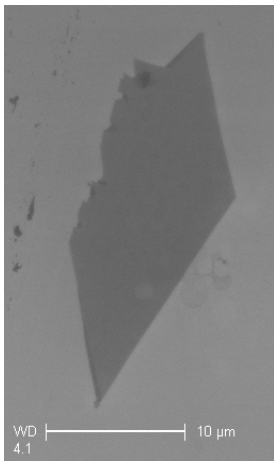
graphite

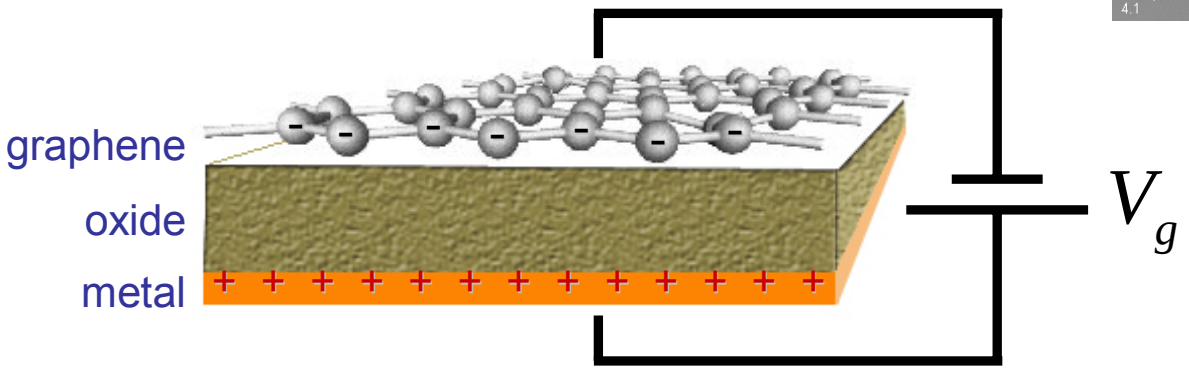


micromechanical cleavage

graphene

10 μm wide single layer flake





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

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

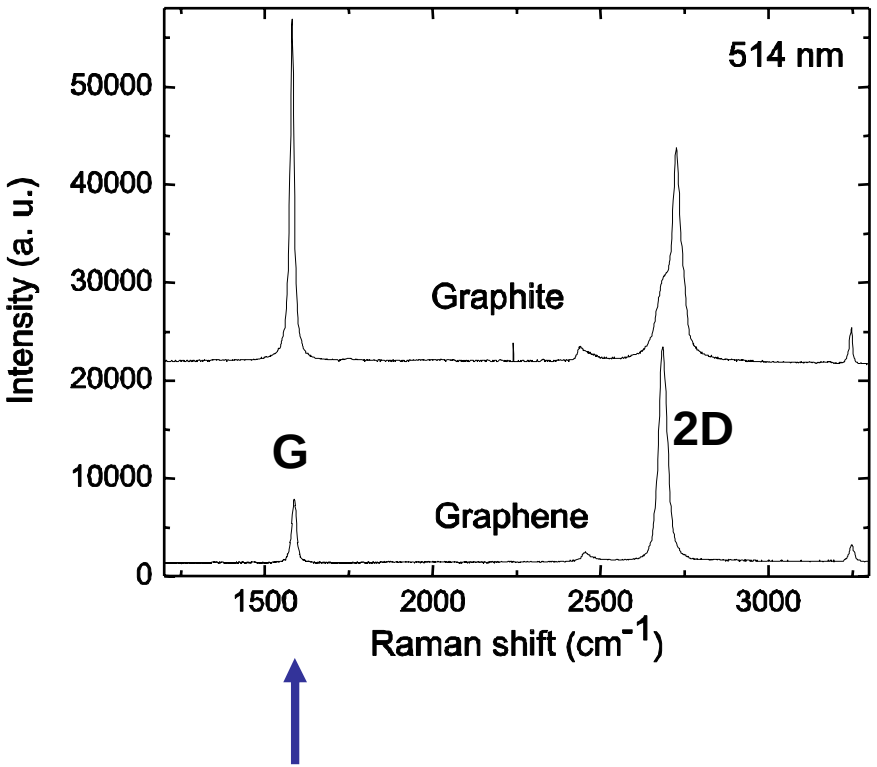
$$V_g = 150\ \text{V}$$

$$0.003\ \text{extra e}^-\ \text{per C}$$

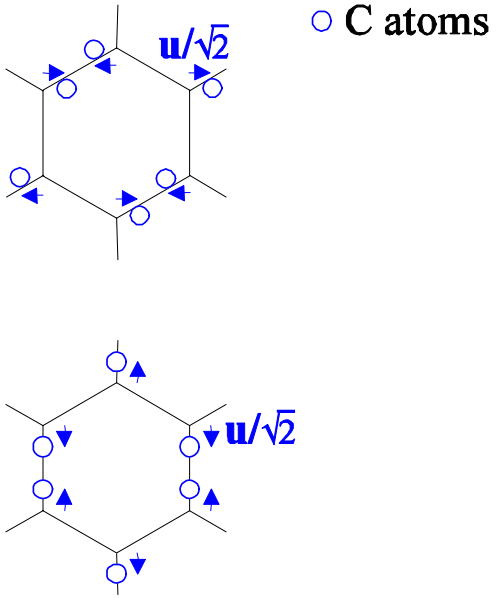
$$1‰\ \text{valence charge}$$

Vibrational Raman

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

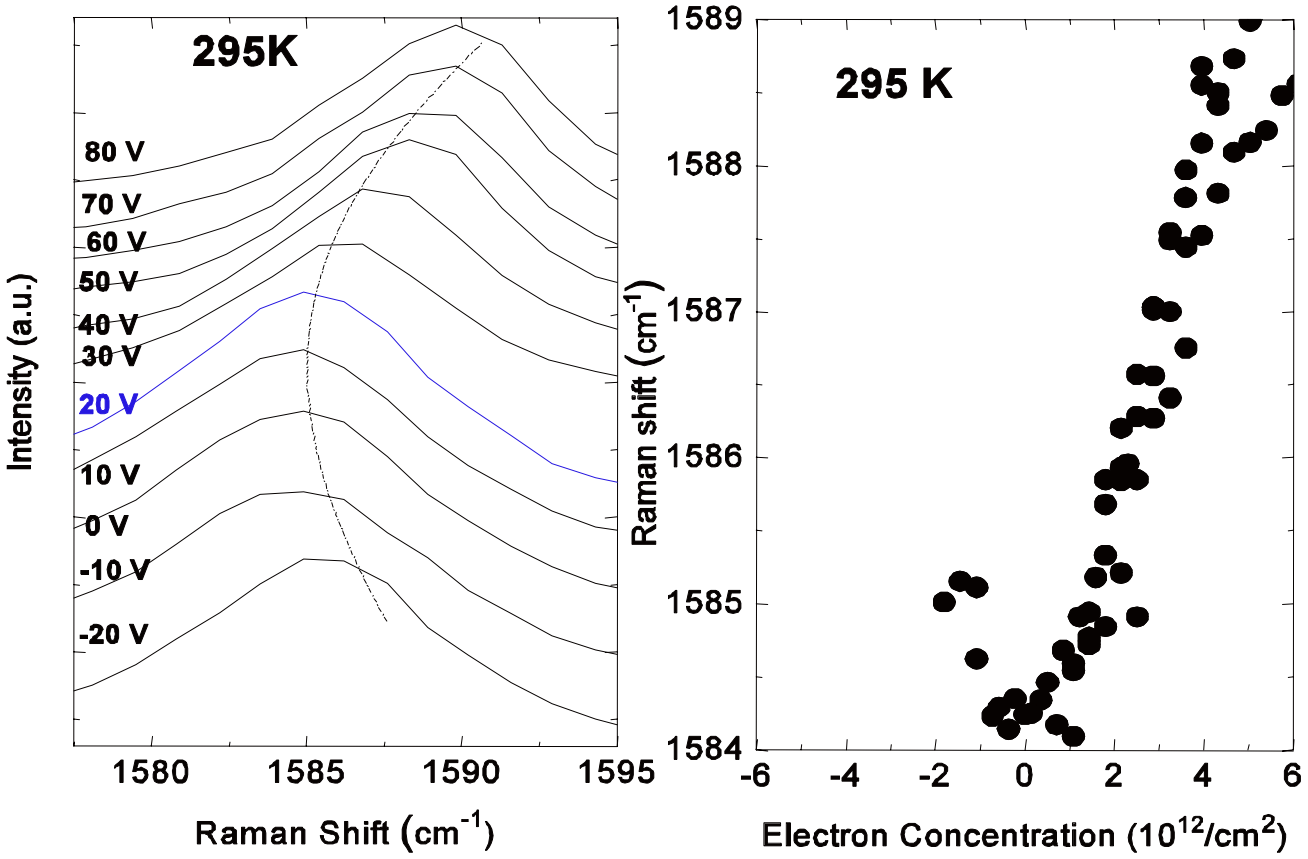


G peak = E_{2g} phonon at Γ =
inplane antiparallel displacement of the 2 atoms



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

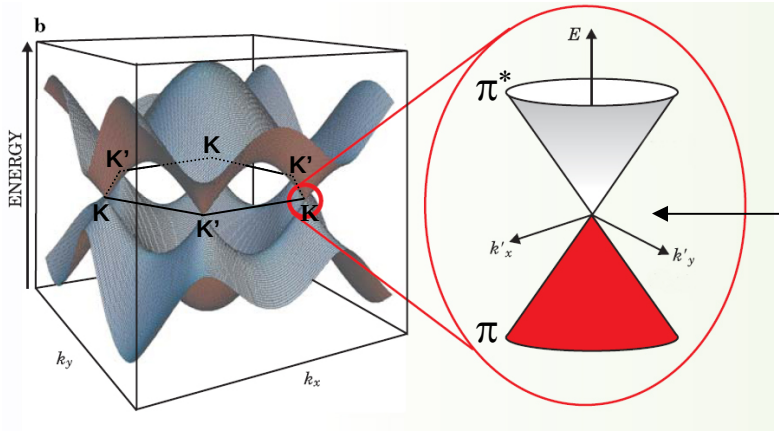
Pisana, Lazzeri, Casiraghi, Novoselov, Geim, Ferrari, Mauri, cond-mat/0611714



similar results in: Yan, Zhang, Kim, Pinczuk, unpublished

Graphene electronic structure

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



Fermi energy ($\mathcal{E}_F$) in the undoped case

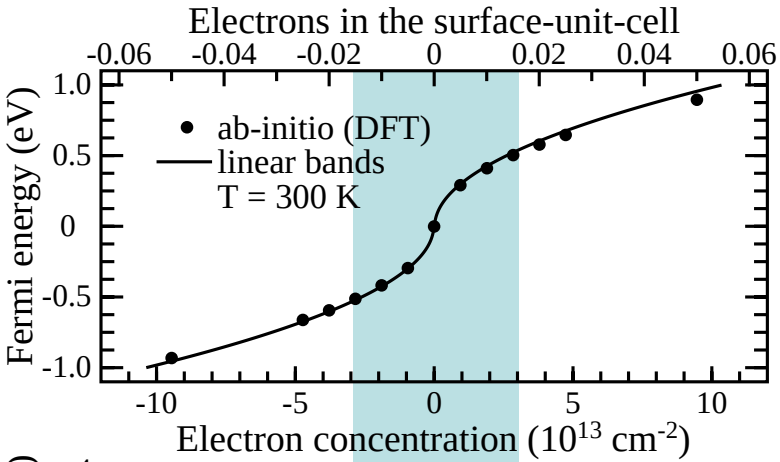
Dirac cones: linearized bands

$$\varepsilon_{\mathbf{k}+\mathbf{K}} = \pm\hbar v_F k \qquad v_F = \text{Fermi velocity}$$

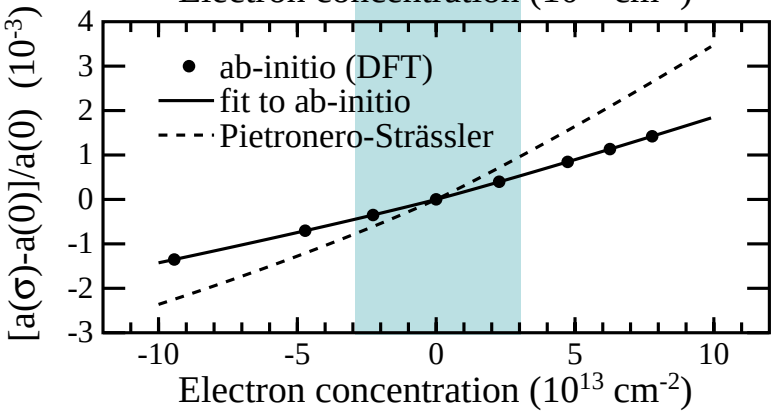
DFT ab-initio calculations:

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

-PBE functional, Fermi-Dirac electronic distribution, charged cell with uniform neutralizing background
-pseudopotentials, PW basis, 64x64 k-point mesh
-Quantum-espresso gnu package



Variation of ε_F with doping



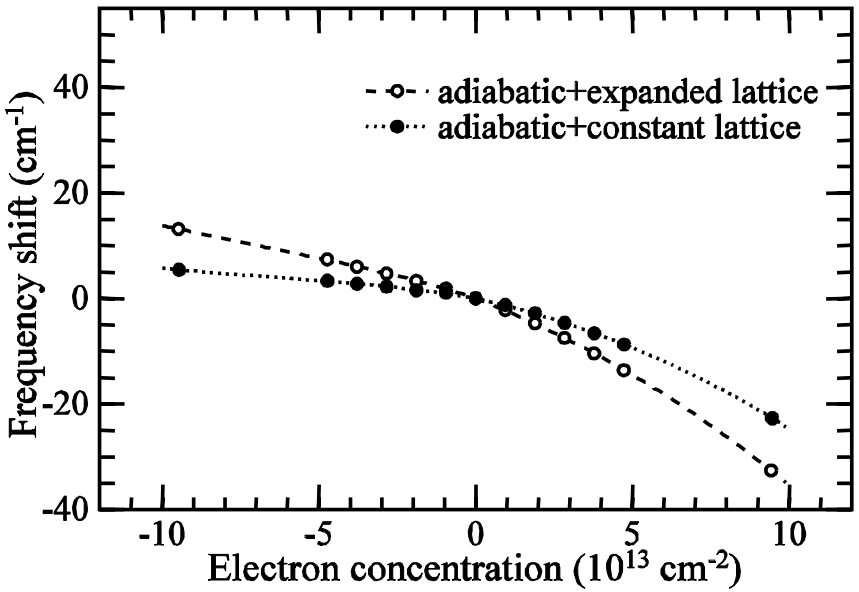
Variation of the lattice parameter (‰)

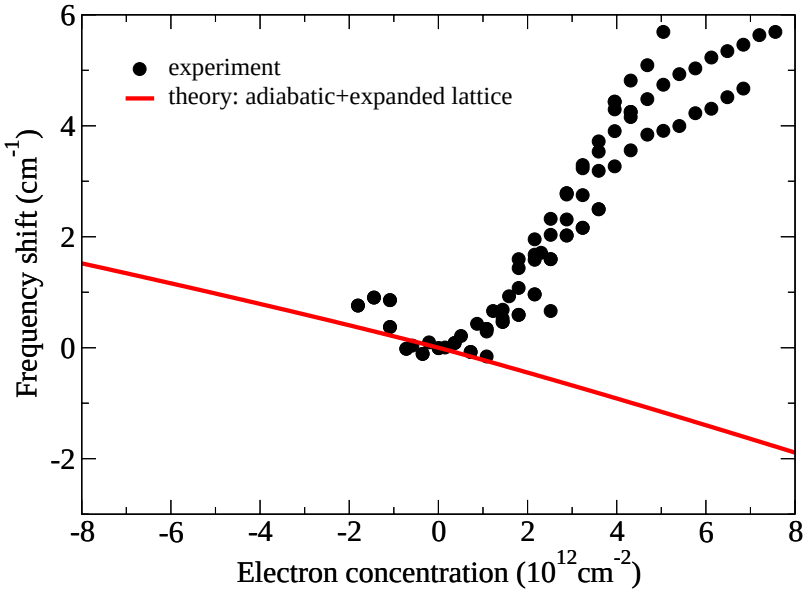
Adiabatic DFT phonon calculation

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

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

-undoped theoretical frequency = 1554 cm^{-1}, (expt. 1584 cm^{-1})



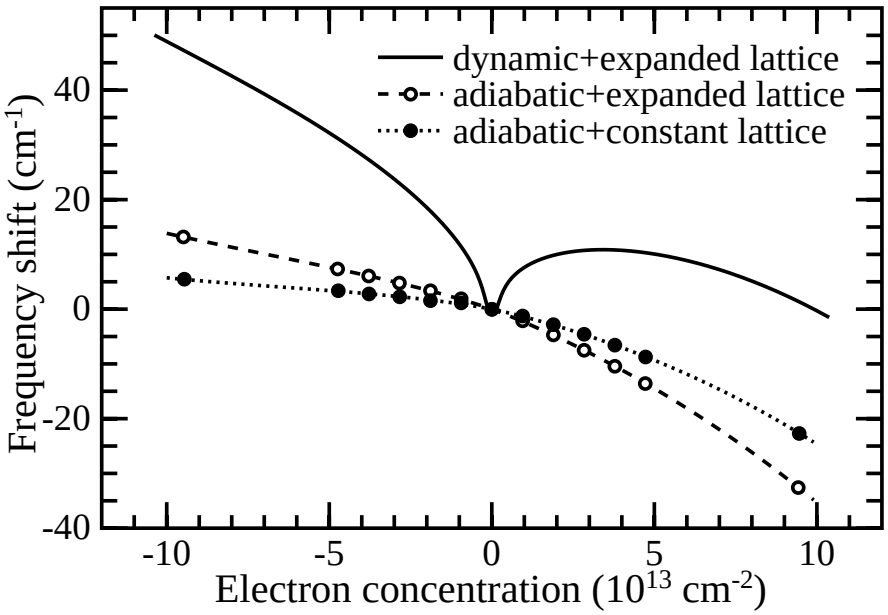


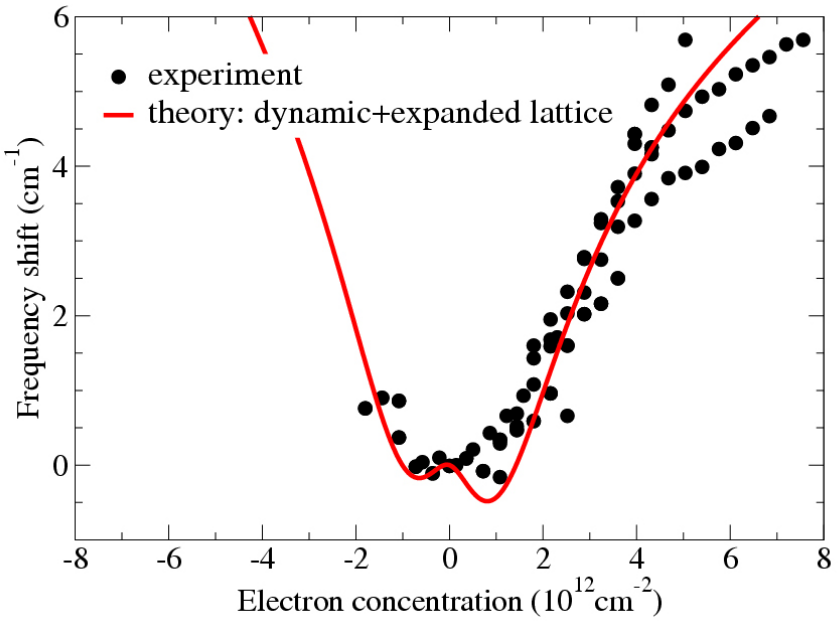
Non-adiabatic DFT phonon calculation

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

-the phonon is a dynamic perturbation oscillating at finite frequency

-the dynamical matrix is computed by *time-dependent* perturbation theory considering a periodic perturbation with a frequency of 1584 cm^{-1}





Interpreting the results

frozen-phonon point of view

Shaking the Dirac cones

Pisana, Lazzeri, Casiraghi, Novoselov, Geim, Ferrari, Mauri, cond-mat/0611714

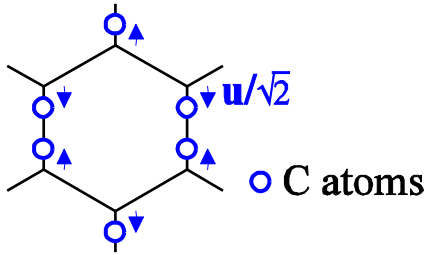
-from the DFT electron-phonon coupling matrix-elements, in presence of a E_{2g} lattice distortion of amplitude **u**

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

$$\left\langle D_\Gamma^2 \right\rangle_F = 45.6(\mathrm{eV}/\mathring{\mathrm{A}})^2$$

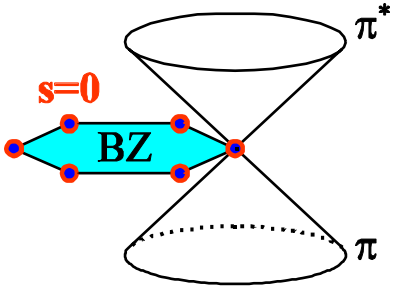
real space

perturbed (finite **u**)

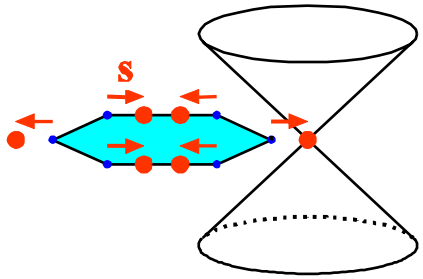


reciprocal space

unperturbed (**u=0**)



perturbed (finite **u**)



BZ: Brillouin zone
● Dirac points
• K points

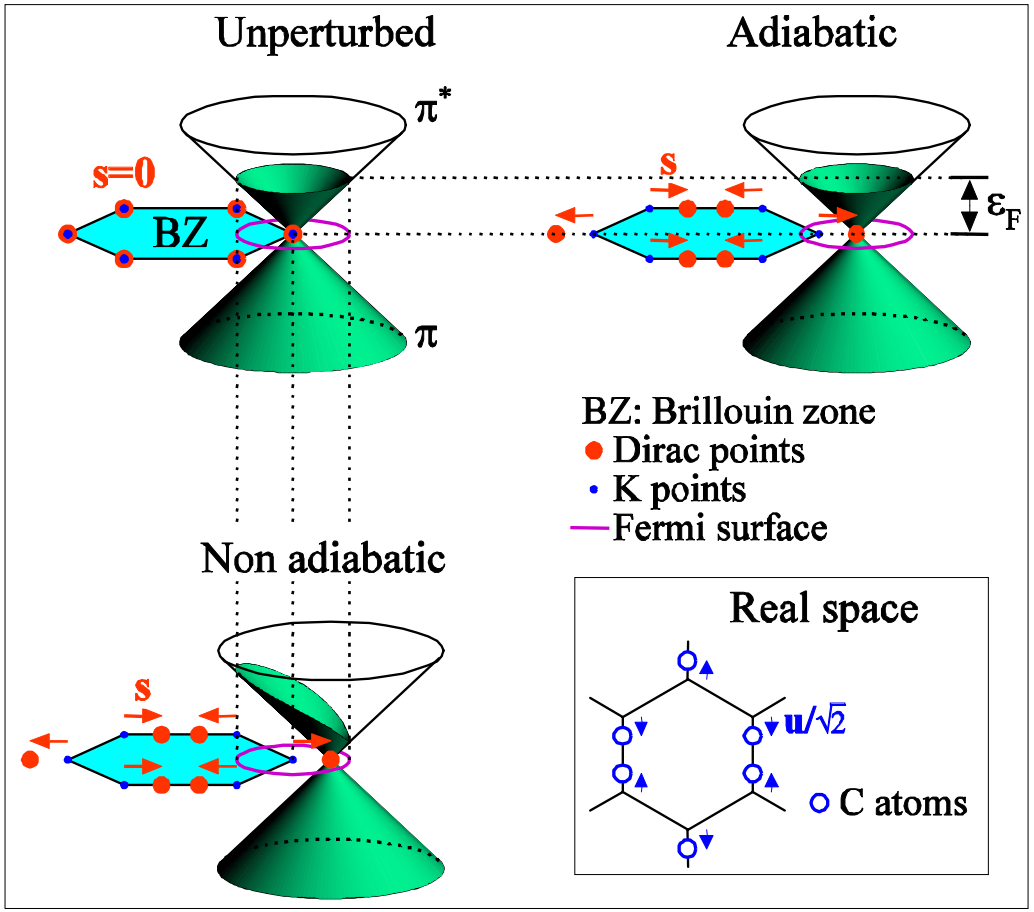
Shaking a filled Martini glass

Adiabatic

Non adiabatic

Shaking a filled Dirac cone

Pisana, Lazzeri, Casiraghi, Novoselov, Geim, Ferrari, Mauri, cond-mat/0611714



Adiabatic or non-adiabatic?

From transport measurements and fs-spectroscopy:

Electron mometum relaxation time:

τ_m =100-300 fs

Phonon period:

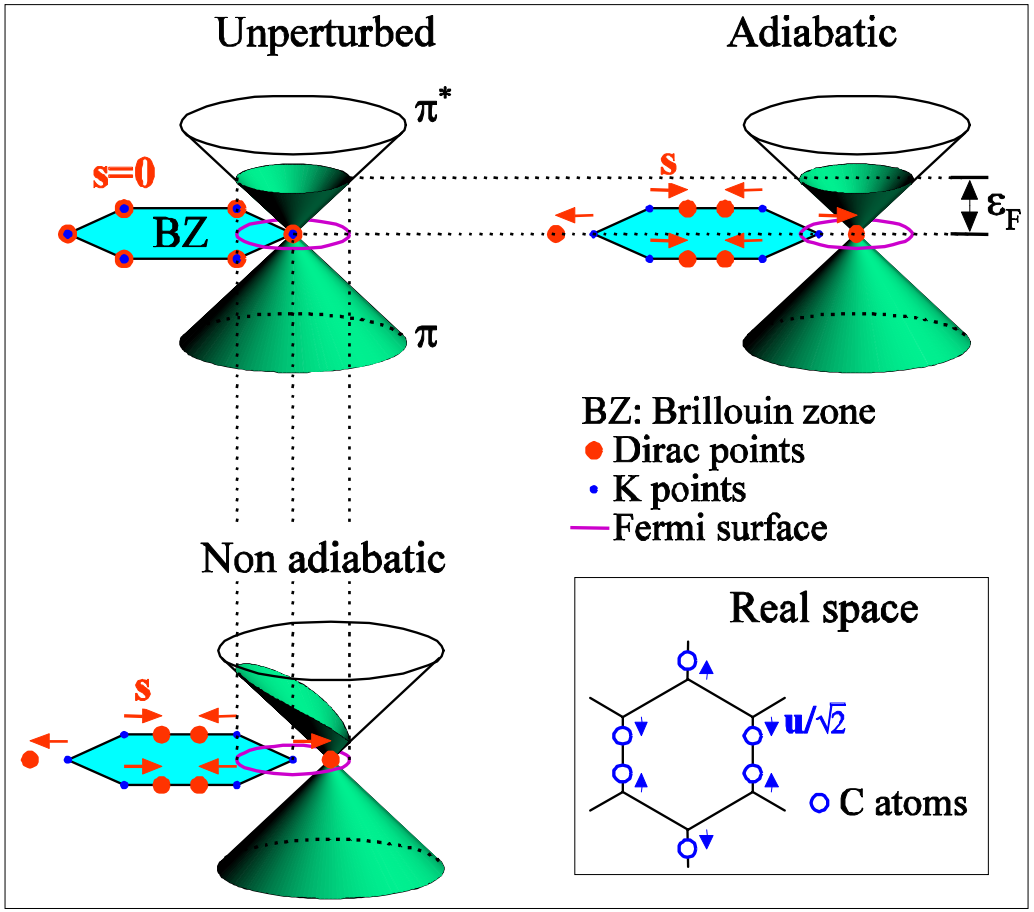
T= 21 fs

$2\pi\tau_m >> T$

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, cond-mat/0611714



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

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*.

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

$$\alpha = \frac{A\left\langle D_\Gamma^2 \right\rangle_F}{\pi M \omega_0 (\hbar v_F)^2}$$

A = unit cell area

Interpreting the results

perturbation-theory point of view

Perturbation theory

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

$$\omega_{\mathbf{q}} = \sqrt{\frac{F_{\mathbf{q}}(\omega_0)}{M} + \ldots} \qquad F_{\mathbf{q}}(\omega_0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{n,m} \frac{f(\varepsilon_{m\mathbf{k}} - \varepsilon_F) - f(\varepsilon_{n\mathbf{k}+\mathbf{q}} - \varepsilon_F)}{\varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}+\mathbf{q}} + \hbar\omega_0 + i\delta} \left| D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}} \right|^2 \qquad D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}} = \left\langle m\mathbf{k} \left| \frac{dV_{ks}(\mathbf{r})}{du_{\mathbf{q}}} \right| n\mathbf{k}+\mathbf{q} \right\rangle$$

For an optical zone-center phonon (**q**->**0**)

static case (adiabatic)

$$F_{\mathbf{0}}(0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{m,n\neq m} \frac{f(\varepsilon_{m\mathbf{k}} - \varepsilon_F) - f(\varepsilon_{n\mathbf{k}} - \varepsilon_F)}{\varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}}} \left| D_{m\mathbf{k},n\mathbf{k}} \right|^2$$

← inter-band contribution

$$-\frac{2}{N_k} \sum_{\mathbf{k}} \sum_{m} \delta(\varepsilon_{m\mathbf{k}} - \varepsilon_F) \left| D_{m\mathbf{k},m\mathbf{k}} \right|^2$$

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

dynamic case (non-adiabatic)

$$F_{\mathbf{0}}(\omega_0) = \frac{2}{N_k} \sum_{\mathbf{k}} \sum_{m,n\neq m} \frac{f(\varepsilon_{m\mathbf{k}} - \varepsilon_F) - f(\varepsilon_{n\mathbf{k}} - \varepsilon_F)}{\varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}} + \hbar\omega_0 + i\delta} \left| D_{m\mathbf{k},n\mathbf{k}} \right|^2$$

← inter-band contribution

Perturbation theory

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

$$\omega_{\mathbf{q}} = \sqrt{\frac{F_{\mathbf{q}}(\omega_0)}{M} + \ldots} \qquad F_{\mathbf{q}}(\omega_0) = \frac{2}{N_k}\sum_{\mathbf{k}}\sum_{n,m}\frac{f(\varepsilon_{m\mathbf{k}}-\varepsilon_F)-f(\varepsilon_{n\mathbf{k}+\mathbf{q}}-\varepsilon_F)}{\varepsilon_{m\mathbf{k}}-\varepsilon_{n\mathbf{k}+\mathbf{q}}+\hbar\omega_0+i\delta}\left|D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}}\right|^2 \qquad D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}} = \left\langle m\mathbf{k}\left|\frac{dV_{ks}(\mathbf{r})}{du_{\mathbf{q}}}\right|n\mathbf{k}+\mathbf{q}\right\rangle$$

For an optical zone-center phonon (**q**->**0**)

static case (adiabatic)

contribution to ω in graphene

$$F_{\mathbf{0}}(0) = \frac{2}{N_k}\sum_{\mathbf{k}}\sum_{m,n\neq m}\frac{f(\varepsilon_{m\mathbf{k}}-\varepsilon_F)-f(\varepsilon_{n\mathbf{k}}-\varepsilon_F)}{\varepsilon_{m\mathbf{k}}-\varepsilon_{n\mathbf{k}}}\left|D_{m\mathbf{k},n\mathbf{k}}\right|^2 \quad \leftarrow \quad +\alpha\left|\varepsilon_F\right|$$

$$-\frac{2}{N_k}\sum_{\mathbf{k}}\sum_{m}\delta(\varepsilon_{m\mathbf{k}}-\varepsilon_F)\left|D_{m\mathbf{k},m\mathbf{k}}\right|^2 \quad \leftarrow \quad -\alpha\left|\varepsilon_F\right|$$

(Fermi-surface variation)

dynamic case (non-adiabatic)

$$F_{\mathbf{0}}(\omega_0) = \frac{2}{N_k}\sum_{\mathbf{k}}\sum_{m,n\neq m}\frac{f(\varepsilon_{m\mathbf{k}}-\varepsilon_F)-f(\varepsilon_{n\mathbf{k}}-\varepsilon_F)}{\varepsilon_{m\mathbf{k}}-\varepsilon_{n\mathbf{k}}+\hbar\omega_0+i\delta}\left|D_{m\mathbf{k},n\mathbf{k}}\right|^2 \quad \leftarrow \quad +\alpha\left|\varepsilon_F\right| + \frac{\alpha\hbar\omega_0}{4}\ln\left(\left|\frac{2\left|\varepsilon_F\right|-\hbar\omega_0}{2\left|\varepsilon_F\right|+\hbar\omega_0}\right|\right)$$

Perturbation theory

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

$$\omega_{\mathbf{q}} = \sqrt{\frac{F_{\mathbf{q}}(\omega_0)}{M} + \ldots} \qquad F_{\mathbf{q}}(\omega_0) = \frac{2}{N_k}\sum_{\mathbf{k}}\sum_{n,m}\frac{f(\varepsilon_{m\mathbf{k}}-\varepsilon_F)-f(\varepsilon_{n\mathbf{k}+\mathbf{q}}-\varepsilon_F)}{\varepsilon_{m\mathbf{k}}-\varepsilon_{n\mathbf{k}+\mathbf{q}}+\hbar\omega_0+i\delta}\left|D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}}\right|^2 \qquad D_{m\mathbf{k},n\mathbf{k}+\mathbf{q}} = \left\langle m\mathbf{k}\left|\frac{dV_{ks}(\mathbf{r})}{du_{\mathbf{q}}}\right|n\mathbf{k}+\mathbf{q}\right\rangle$$

For an optical zone-center phonon (**q**->**0**)

static case (adiabatic)

contribution to ω in graphene

$$F_{\mathbf{0}}(0) = \frac{2}{N_k}\sum_{\mathbf{k}}\sum_{m,n\neq m}\frac{f(\varepsilon_{m\mathbf{k}}-\varepsilon_F)-f(\varepsilon_{n\mathbf{k}}-\varepsilon_F)}{\varepsilon_{m\mathbf{k}}-\varepsilon_{n\mathbf{k}}}\left|D_{m\mathbf{k},n\mathbf{k}}\right|^2 \quad \leftarrow \quad +\alpha\left|\varepsilon_F\right|$$

$$-\frac{2}{N_k}\sum_{\mathbf{k}}\sum_{m}\delta(\varepsilon_{m\mathbf{k}}-\varepsilon_F)\left|D_{m\mathbf{k},m\mathbf{k}}\right|^2 \quad \leftarrow \quad -\alpha\left|\varepsilon_F\right| \qquad \text{(Fermi-surface variation)}$$

dynamic case (non-adiabatic)

for: $2\left|\varepsilon_F\right| >> \omega_0$

$$F_{\mathbf{0}}(\omega_0) = \frac{2}{N_k}\sum_{\mathbf{k}}\sum_{m,n\neq m}\frac{f(\varepsilon_{m\mathbf{k}}-\varepsilon_F)-f(\varepsilon_{n\mathbf{k}}-\varepsilon_F)}{\varepsilon_{m\mathbf{k}}-\varepsilon_{n\mathbf{k}}+\hbar\omega_0+i\delta}\left|D_{m\mathbf{k},n\mathbf{k}}\right|^2 \quad \leftarrow \quad +\alpha\left|\varepsilon_F\right| + \frac{\alpha\hbar\omega_0}{4}\ln\left(\left|\frac{2\left|\varepsilon_F\right|-\hbar\omega_0}{2\left|\varepsilon_F\right|+\hbar\omega_0}\right|\right)$$

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)

Conclusions

- We measure a stiffening of the G peak with both electron and hole doping
- The DFT adiabatic calculation, which is the standard tool for the phonon determination, miserably fails
- The dynamic DFT calculation closely reproduces the observed stiffening

- In the adiabatic approximation the energy of a zone-center phonon is determined by 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, whenever $2\pi\tau_m >> T$ the correct phonon treatment should not include the adiabatic Fermi-surface rearrangement
- The $2\pi\tau_m >> T$ condition occurs in many metals