Workshop on Correlations and Coherence in Quantum Matter

The electronic properties of graphene and its bilayer

Nuno Miguel Peres

peres@fisica.uminho.pt

FCT funded: POCI 2010 via project PTDC/FIS/64404/2006

Graphene pioneers bag Europhysics prize

Outline of the talk

- Introduction to graphene and its properties
- Dynamical conductivity
- Band structure and density states of a BGB
- Gap versus electronic density; screening
- Recent applications

Introduction to graphene

The beginning of a new research area

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1]
Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

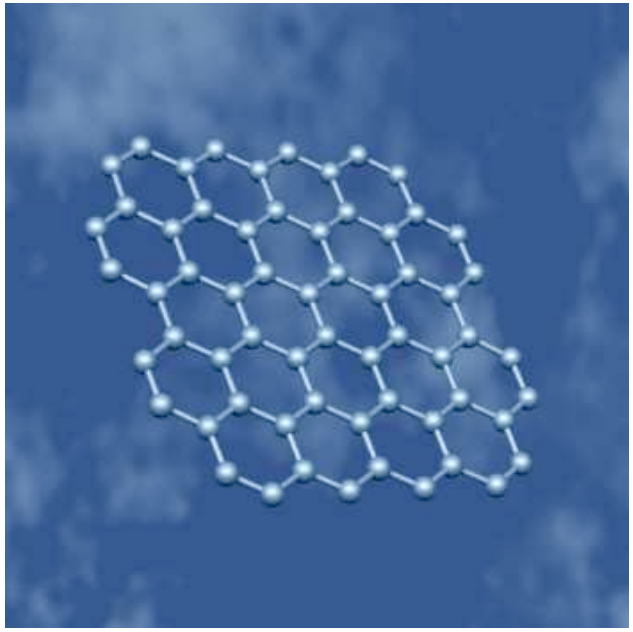
Science 306, 666-669 (2004)
PNAS 102, 10451-10453 (2005)

Two-dimensional atomic crystals

K. S. Novoselov*, D. Jiang*, F. Schedin*, T. J. Booth*, V. V. Khotkevich*, S. V. Morozov†, and A. K. Geim*‡

Previous theoretical work by: P. Wallace (1947!), J. Gonzalez, F. Guinea, M. Vozmediano, T. Ando, K. Wakabayashi, M. and G. Dresselhaus, M. Fujita, and others (NMRP).

Graphene's lattice



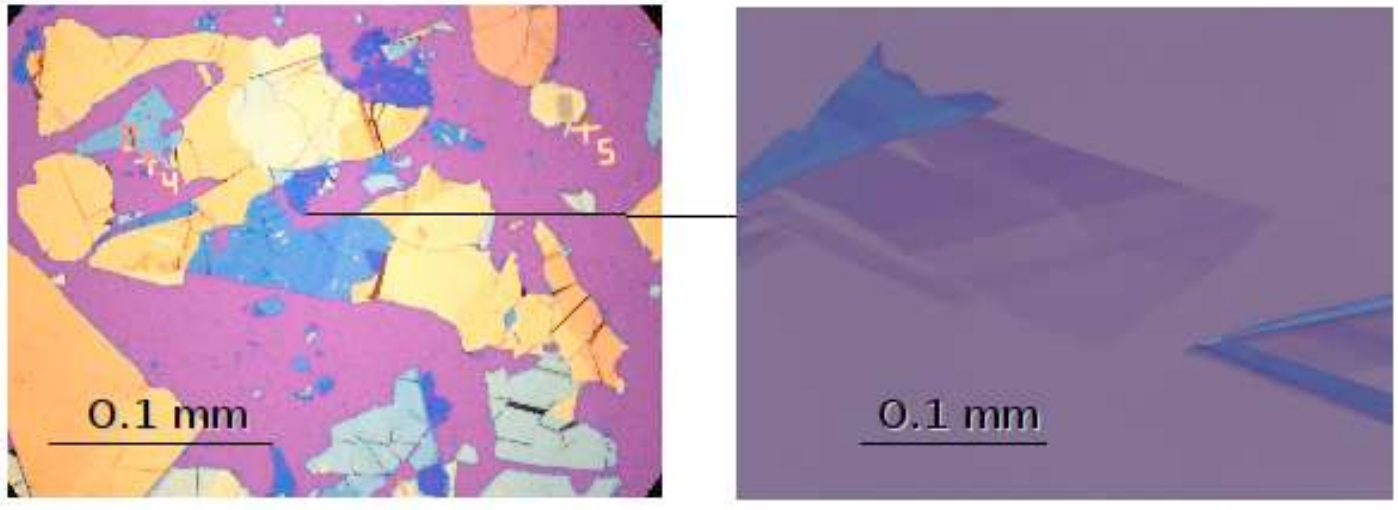
Zig-zag and arm-chair edges.

C-C distance 1.42 Å.

Effective thickness $\sim$ 0.23 Å.

GRAPHENE – THE ULTIMATE THIN FILM. (D6h)

Visible light images

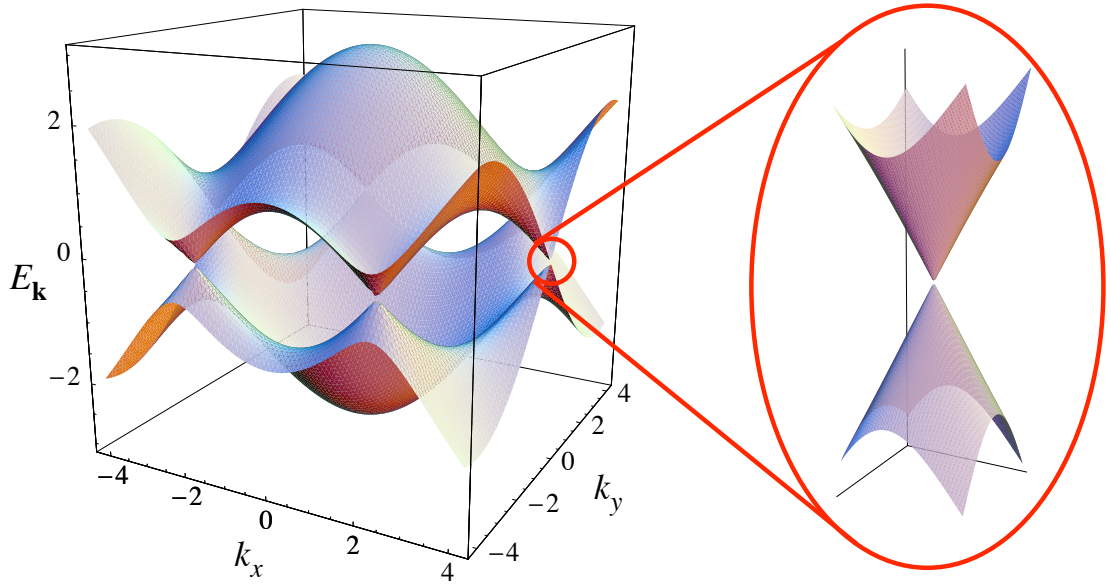


(courtesy of A. K. Geim)

General physical properties

1. Stiffness : Young modulus E^{2D} =340 N/m $\rightarrow$ $E \simeq 1$ TPa. (Iron: E$\simeq$ 211 GPa);
2. High thermal conductivity: K =5000 W/(m·K). (Diamond: K$\simeq$ 1500 W/(m·K));
3. Chemically stable and almost impermeable to gases, but lipophilic;
4. Very high mobilities in its suspendend form: $\mu \simeq$ 200.000 cm^2/Vs;
5. Ambipolar behavior;
6. Ballistic transport over sub-micron distances ($\sim$ 1 deffect per μm^2);

Band structure



Dirac cones in the scale of 1 eV. The effective theory is that of massless Dirac fermions in two dimensions. ($E = \sqrt{m^2c^4 + p^2c^2}$, $m \to 0$.)

Emergent complex behavior!

$k \cdot p$ approach

We assume the original problem has been solved for $\boldsymbol{k} = \boldsymbol{K}$:
$\psi_{\boldsymbol{K},j=c,v}(\boldsymbol{r}) = e^{i\boldsymbol{K}\cdot\boldsymbol{r}} u_{\boldsymbol{K},j=c,v}(\boldsymbol{r})$ is known.

Further, we know that $c-$ and $v-$band are degenerate at $\boldsymbol{K}$.

We propose: $\psi_{\boldsymbol{q},\alpha}(\boldsymbol{r}) = \sum_{j=c,v} f_j^{\alpha}(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \psi_{\boldsymbol{K},j}(\boldsymbol{r})$

We now solve for $H\psi_{\boldsymbol{q},\alpha}(\boldsymbol{r}) = E\psi_{\boldsymbol{q},\alpha}(\boldsymbol{r})$:

$$\sum_{j=v,c} \left(\frac{q^2\hbar^2}{2m} - i\frac{\hbar^2}{m}\boldsymbol{q}\cdot\boldsymbol{\nabla} \right) f_j^{\alpha}(\boldsymbol{q})\psi_{\boldsymbol{K},j}(\boldsymbol{r}) = E \sum_{j=v,c} f_j^{\alpha}(\boldsymbol{q})\psi_{\boldsymbol{K},j}(\boldsymbol{r})$$

Remembering that:

$$\int d\boldsymbol{r}\psi^*_{\boldsymbol{K},j}\psi_{\boldsymbol{K},j'} = \delta_{j,j'} \longrightarrow \frac{\hbar}{m}\boldsymbol{q}\cdot \begin{pmatrix} \boldsymbol{p}_{11} & \boldsymbol{p}_{12} \\ \boldsymbol{p}_{21} & \boldsymbol{p}_{22} \end{pmatrix} \begin{pmatrix} f_1^{\alpha}(\boldsymbol{q}) \\ f_2^{\alpha}(\boldsymbol{q}) \end{pmatrix} = E \begin{pmatrix} f_1^{\alpha}(\boldsymbol{q}) \\ f_2^{\alpha}(\boldsymbol{q}) \end{pmatrix}$$

The spectrum

Diagonalizing the previous problem one obtains:

$$
\begin{aligned}
E &= \epsilon_{\alpha=\pm 1}(\boldsymbol{q}) = \alpha \hbar v_F |\boldsymbol{q}| \,, \\
\chi_{\alpha=\pm}(\boldsymbol{q}) &= \begin{pmatrix} f_1^\alpha(\boldsymbol{q}) \\ f_2^\alpha(\boldsymbol{q}) \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \alpha e^{i\theta(\boldsymbol{q})} \end{pmatrix} \\
\theta(\boldsymbol{q}) &= \arctan \frac{k_y}{k_x} \,.
\end{aligned}
$$

The spinorial nature of the wave function led people to talk about PSEUDO-SPIN.
Fourier transforming the eigenproblem to real space:

$$
\frac{\hbar}{i} v_F \boldsymbol{\sigma} \cdot \boldsymbol{\nabla} \psi(\boldsymbol{r}) = E \psi(\boldsymbol{r})
$$

(after DiVincenzo and Mele)

Ambipolar field effect

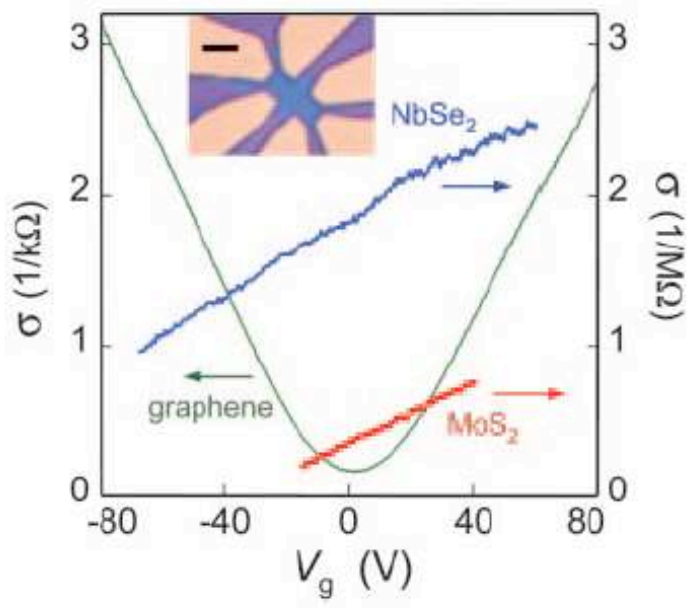
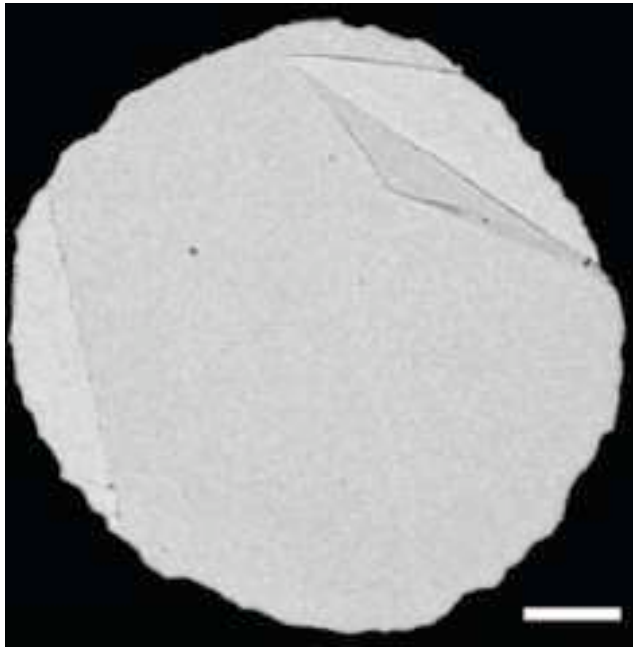


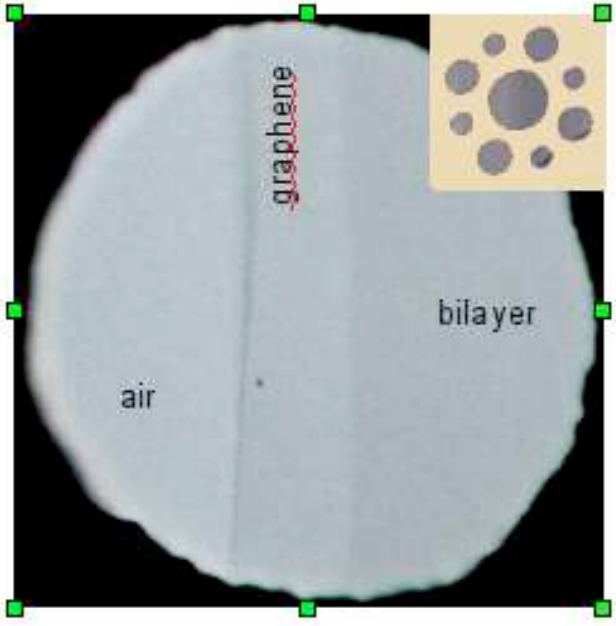
Fig. 3. Electric field effect in single-atomic-sheet crystals. Changes in electrical conductivity σ of 2D $NbSe_2$, 2D MoS_2, and graphene as a function of gate voltage are shown (300 K). (*Inset*) Our typical devices used for such measurements: It is an optical image (in white light) of 2D $NbSe_2$ on top of an oxidized Si wafer (used as a gate electrode) with a set of Au contacts. The crystal is seen as a bluer region in the center. (Scale bar: 5 μm.)

Dynamical conductivity of graphene

Seeing graphene with bare eyes

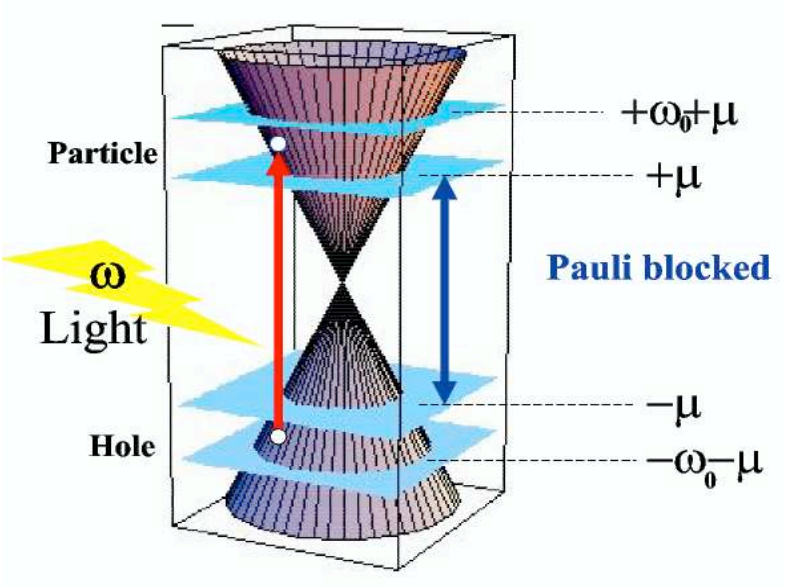


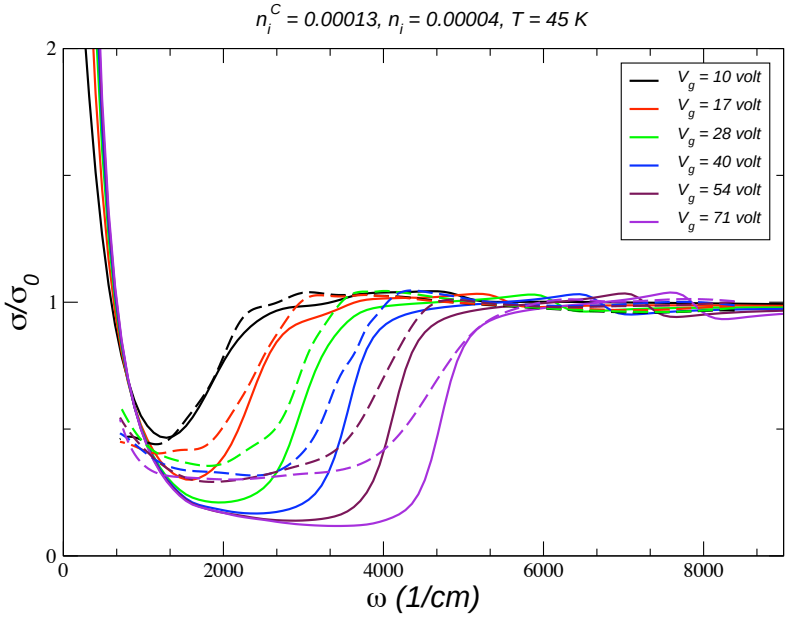
TEM micrograph of 30 μm aperture covered with graphene.



Optical photograph of a 50 μm aperture partially covered by graphene and its bilayer. The aperture is illuminated with white light from a xenon lamp ($\lambda \in$[250,1200] nm).

Graphene's optical conductivity





NMRP *et al.*, EuroPhys. Lett. (2008).

There is a lot to work on!

Kubo formula

The transmissivity T across an interface where light can be absorbed reads (Born and Wolf):

$$T = \frac{1}{|1 + \sigma(\omega)/(2\epsilon_0 c)|^2} \, .$$

The question is: what is the value of the dynamical (optical) conductivity of graphene?

$$\sigma_{xx}(\omega) = \frac{< j_x^D >}{iA_s(\omega + i0^+)} + \frac{\Lambda_{xx}(\omega + i0^+)}{i\hbar A_s(\omega + i0^+)} \, ,$$

with $A_s = N_c A_c$ the area of the sample, and $A_c = 3\sqrt{3}a^2/2$ (a is the carbon-carbon distance) the area of the unit cell, from which it follows that

$$\Re\sigma_{xx}(\omega) = D\delta(\omega) + \frac{\Im\Lambda_{xx}(\omega + i0^+)}{\hbar\omega A_s} \, , \qquad \Lambda_{xx}(i\omega_n) = \int_0^{\beta\hbar} d\tau e^{i\omega_n \tau} < T_\tau j_x^P(\tau) j_x^P(0) > \, .$$

The current operator

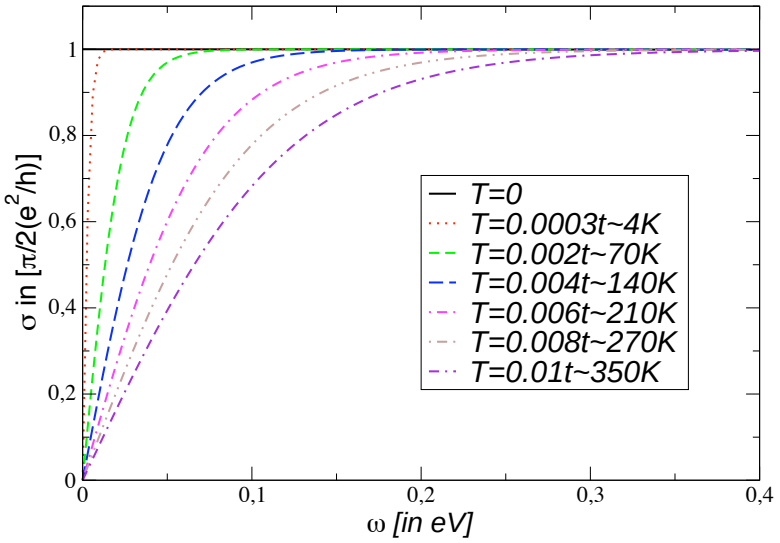
The operator j_x^P reads:

$$
\begin{aligned}
j_x^P &= \frac{tie}{\hbar} \sum_{\boldsymbol{R},\sigma} \sum_{\boldsymbol{\delta}=\boldsymbol{\delta}_1-\boldsymbol{\delta}_3} [\delta_x a_\sigma^\dagger(\boldsymbol{R}) b_\sigma(\boldsymbol{R}+\boldsymbol{\delta}) - H.c.] \\
&+ \frac{t'ie}{2\hbar} \sum_{\boldsymbol{R},\sigma} \sum_{\boldsymbol{\delta}=\boldsymbol{\delta}_4-\boldsymbol{\delta}_9} [\delta_x a_\sigma^\dagger(\boldsymbol{R}) a_\sigma(\boldsymbol{R}+\boldsymbol{\delta}) - H.c.] \\
&+ \frac{t'ie}{2\hbar} \sum_{\boldsymbol{R},\sigma} \sum_{\boldsymbol{\delta}=\boldsymbol{\delta}_4-\boldsymbol{\delta}_9} [\delta_x b_\sigma^\dagger(\boldsymbol{R}) b_\sigma(\boldsymbol{R}+\boldsymbol{\delta}) - H.c.] \,.
\end{aligned}
$$

t is the first nearest neighbor hoping integral; t' is the second nearest neighbor hoping integral.

What are the results in the Dirac cone approximation with $t' = 0$?

$\sigma(\omega)$ *in the Dirac cone approximation*



$\sigma(\omega)$ is in units of $\sigma_0 = \frac{\pi}{2}\frac{e^2}{h}$. So at low T, $\sigma(\omega)$ is determined by universal constants only, as long as T is small.

V.P. Gusynin *et al.*, Phys. Rev. Lett. **96**, 256802 (2006). NMRP and Tobias Stauber, International Journal of Modern Physics B (2008).

Transmissivity in the IR

The transmissivity in the IR and at low temperature can now be computed and reads:

$$T = \frac{1}{(1+\pi\alpha/2)^2} \simeq 1 - \pi\alpha, \qquad \alpha = \frac{e^2}{4\pi\epsilon_0 c\hbar} .$$

Same result by : A. B. Kuzmenko *et al.*, Phys. Rev. Lett. **100**, 117401 (2008).

The problem of the Manchester group: the experimental measurement were being done in the visible region of the spectrum. **Does the above result still holds good?**

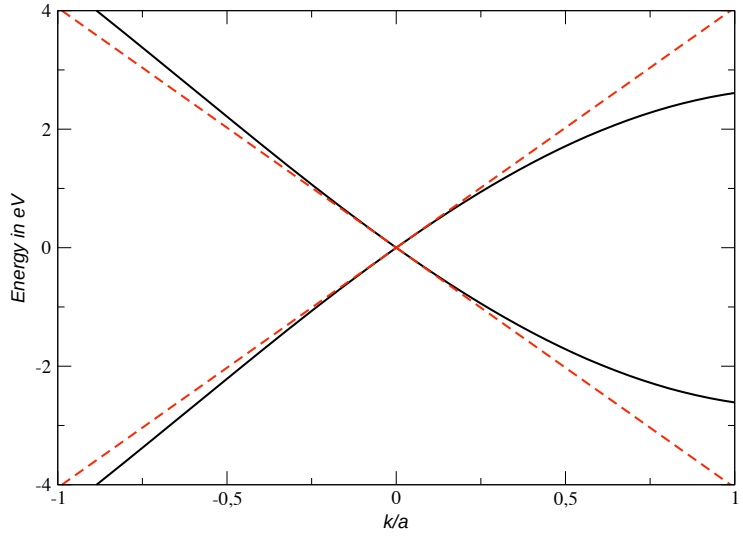
There were two associated problems to be solved:

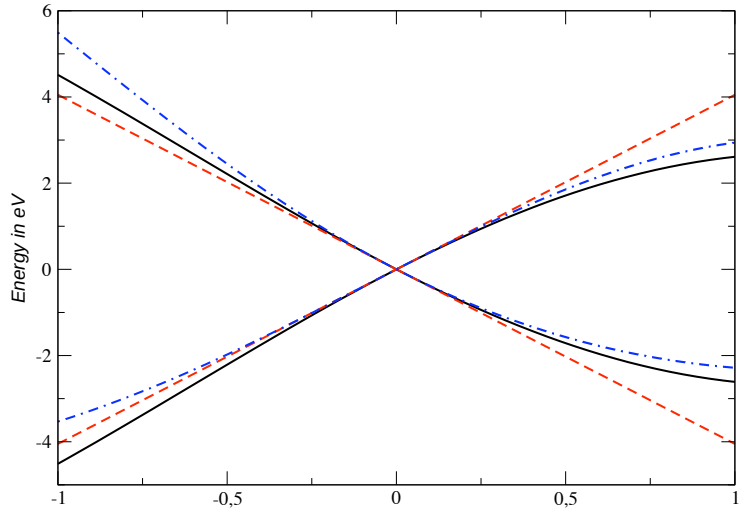
1.) In the visible range the spectrum is not Dirac-like any more;

2.) The value of $t' \simeq 0.13t$, with $t = 3$ eV.

The energy spectrum

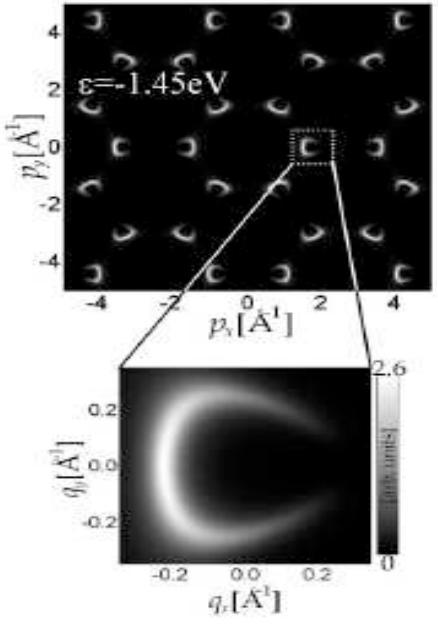
To better appreciate the problem:

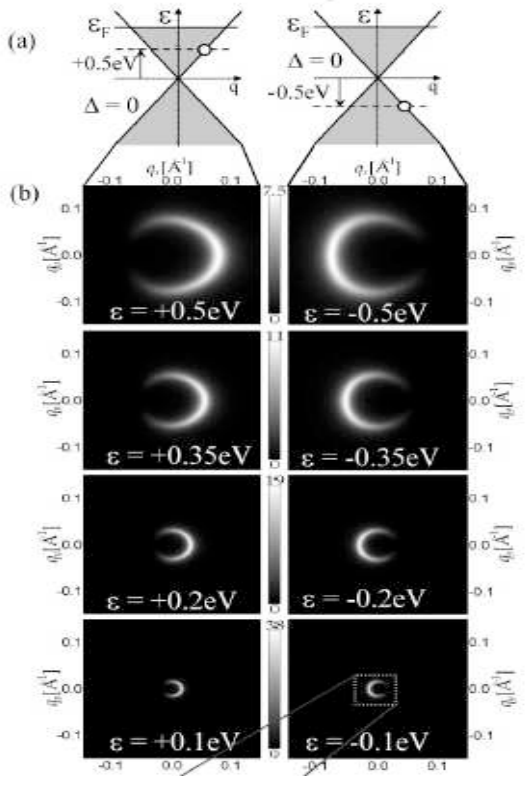




Dirac cone approximation and full band. t and t' compared.

ARPES

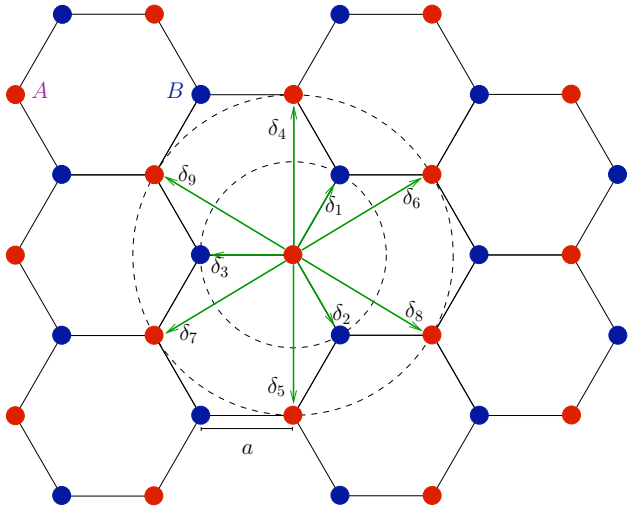




M. Mucha-Kruczynski *et al.*, Phys. Rev. B **77**, 195403 (2008).

The calculation of the conductivity

$$< T_\tau j_x^P(\tau) j_x^P(0) > \rightarrow A t^2 + B t' t + C t'^2.$$



One can show that $B = C = 0$.

The result for the C term is easy to understand: it corresponds to the contribution to the optical conductivity of electrons in a triangular lattice.

The fact that $B = 0$ can be understood in terms of gauge invariance.

As a final result we have: $\boxed{< T_\tau j_x^P(\tau) j_x^P(0) > \rightarrow A t^2.}$ So t' only enters in the band structure.

The conductivity again

The full form is:

$$\Re\sigma_{xx}(\omega) = \sigma_0 \frac{\pi t^2 a^2}{8 A_c \hbar\omega} \rho(\hbar\omega/2)[18 - (\hbar\omega)^2/t^2] \left[\tanh \frac{\hbar\omega+2\mu}{4k_B T} + \tanh \frac{\hbar\omega-2\mu}{4k_B T}\right] .$$

There are two contributions in the general result that opose each other:

1. $[18 - (\hbar\omega)^2/t^2]$ decreases with frequency;

2. $\rho(\hbar\omega/2)$ increases with frequency.

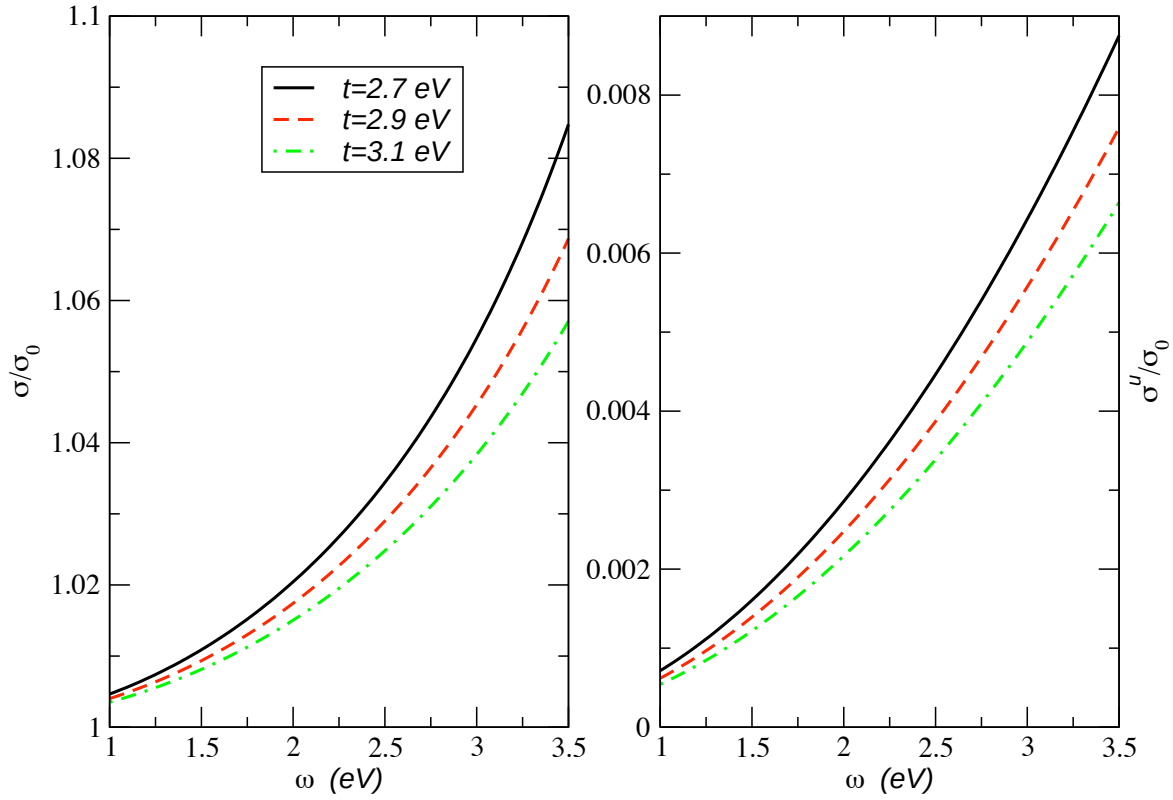
The asymptotic form is:

$$\Re\sigma_{xx}(\omega) = \sigma_0 \left(\frac{1}{2} + \frac{1}{72}\frac{(\hbar\omega)^2}{t^2}\right) \left(\tanh \frac{\hbar\omega+2\mu}{4k_B T} + \tanh \frac{\hbar\omega-2\mu}{4k_B T}\right) .$$

Which has a frequency dependence, contrary to the case of the Dirac cone approximation.

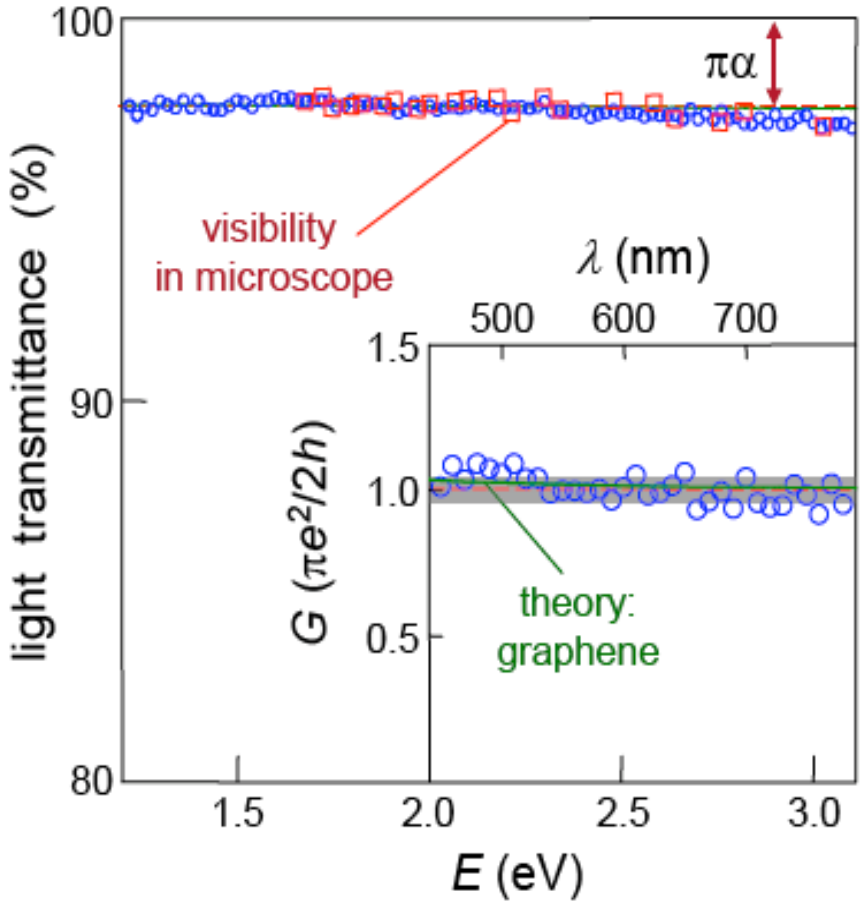
(...)

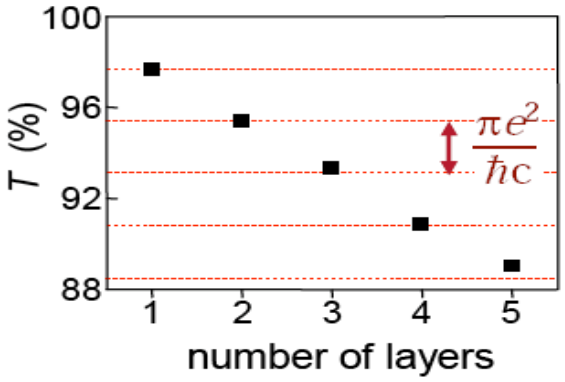
How important is the correction introduced by the full calculation?



At the most one has a 10% correction!

The experimental results



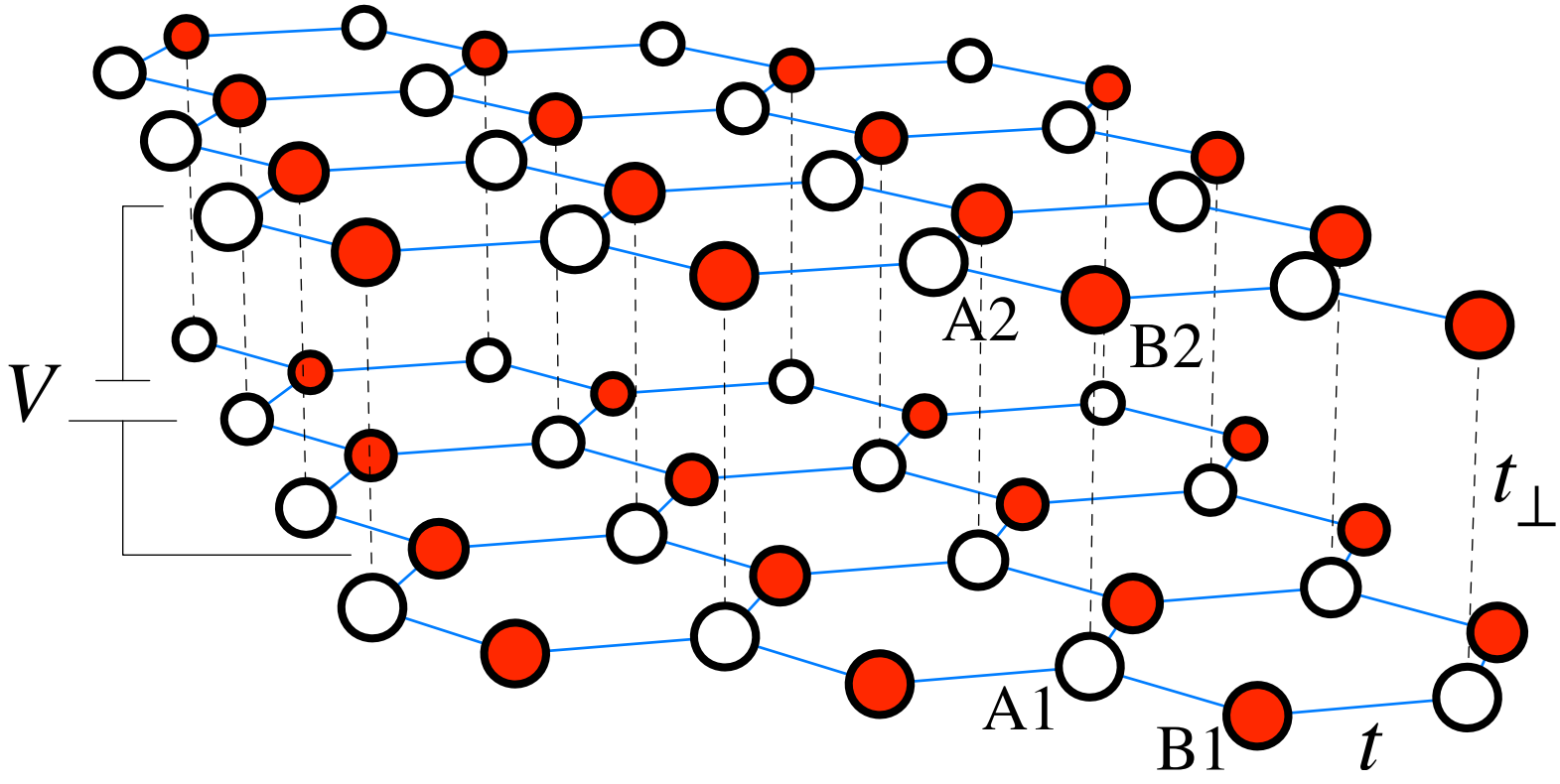


R. R. Nair *et al.* Science (2008).

Band structure and density states of a BGB:

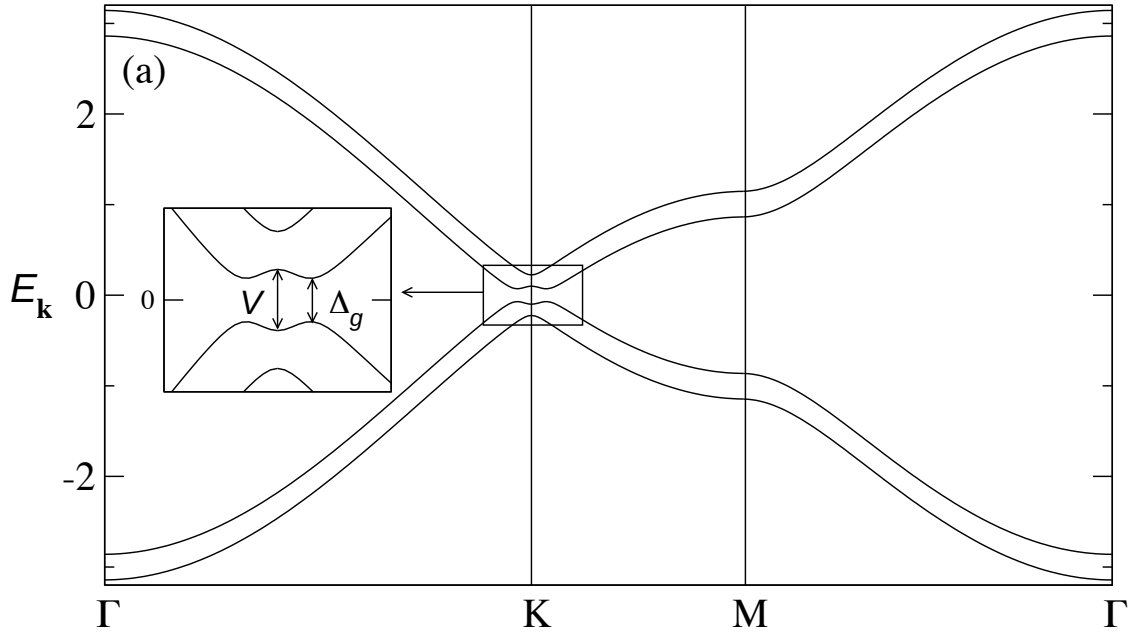
a never seen before type of semiconductor

The lattice structure of a GB



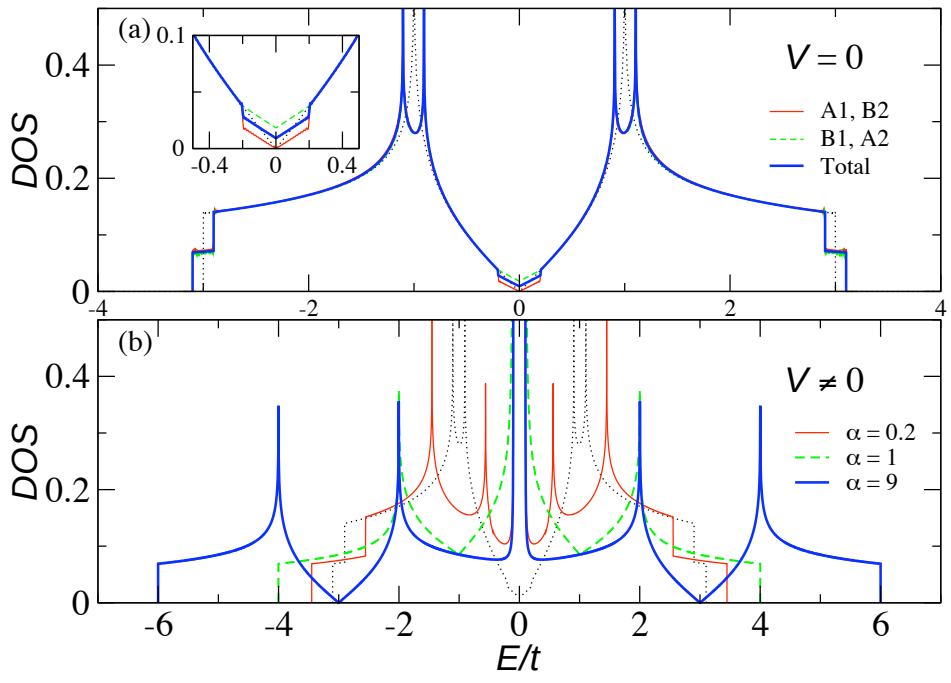
Four atoms per unit cell $\rightarrow$ 4 bands

Band structure of a BGB



$$E_{\mathbf{k}}^{\pm\pm} = \pm t\sqrt{\epsilon_{\mathbf{k}}^2 + \frac{t_\perp^2}{2t^2} + \frac{V^2}{4t^2} \pm \sqrt{\frac{t_\perp^4}{4t^4} + \frac{t_\perp^2 + V^2}{t^2}\epsilon_{\mathbf{k}}^2}}, \qquad \Delta_g = V\sqrt{\frac{t_\perp^2}{t_\perp^2 + V^2}}.$$

Density of states



$$E(k) \approx \Delta - \alpha k^2 + \lambda k^4$$

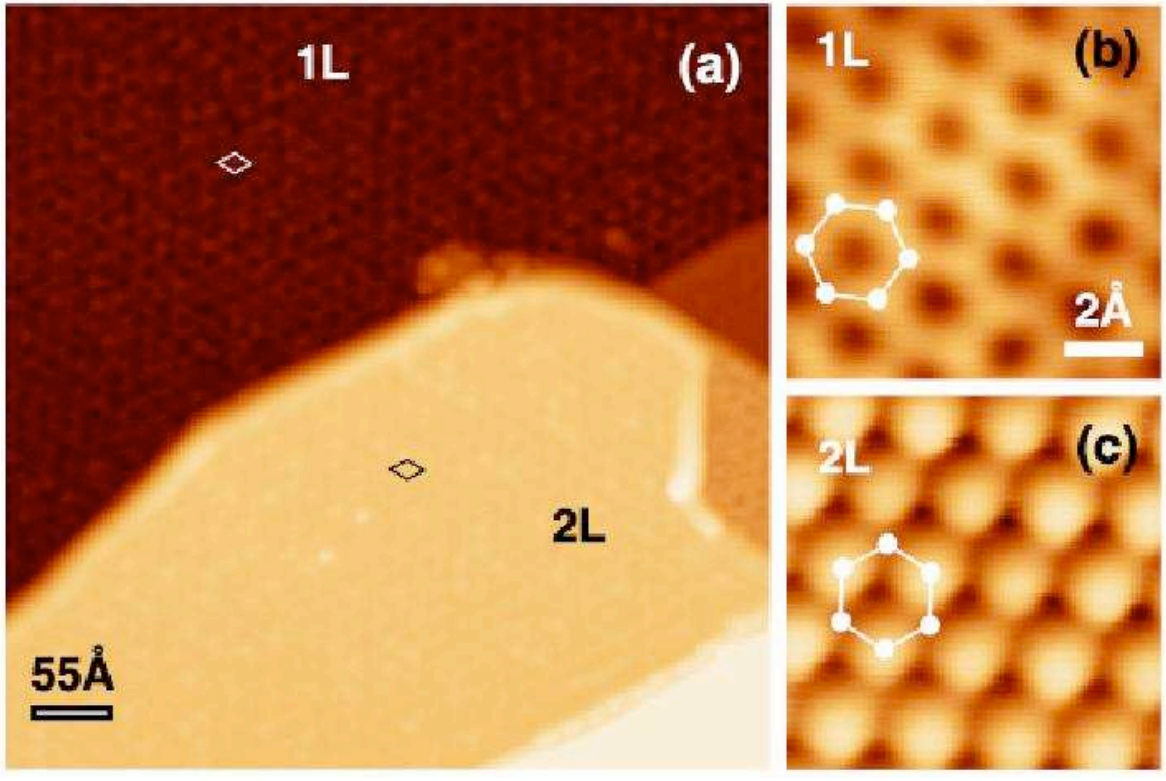
$$\rho(\epsilon) = \frac{1}{4\pi\sqrt{\lambda}} \frac{1}{\sqrt{\epsilon - \epsilon_{\min}}}$$

Stoner instability? $[U\rho(\epsilon_F) = 1]$. **Phys. Rev. Lett. 100, 186803 (2008).**

Note that a single graphene layer has $U = \infty$; including long range interactions it is ferromagnetic only for unphysical values of the coupling parameter.

Only the disconnected sites, for $V = 0$, have a finite density of states at zero energy.

STM: epitaxial graphene from SiC



Brar *et al.*, APL **91**, 122102 (2007)

STM image of graphene/SiC (-0.1V, 0.3 nA)

Gap versus electronic density; screening:

How to control de gap and the electronic density?

Doping by atomic/molecular absorption

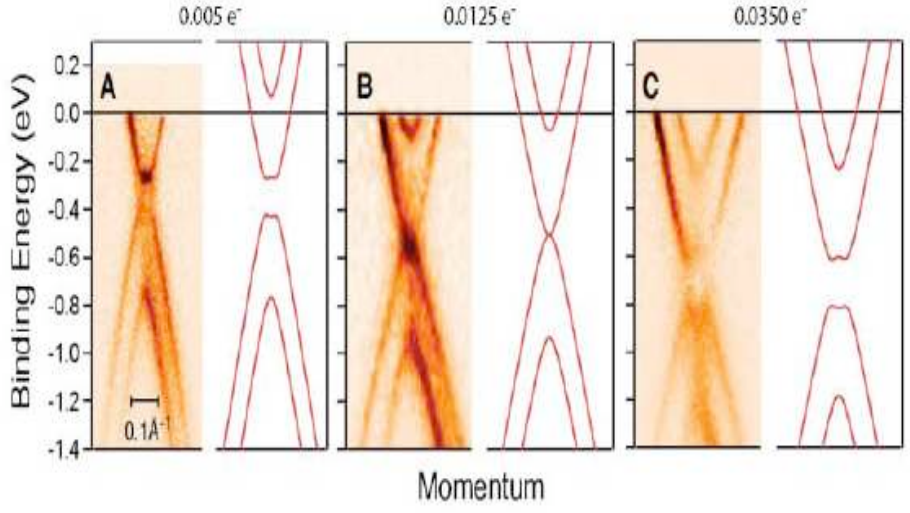
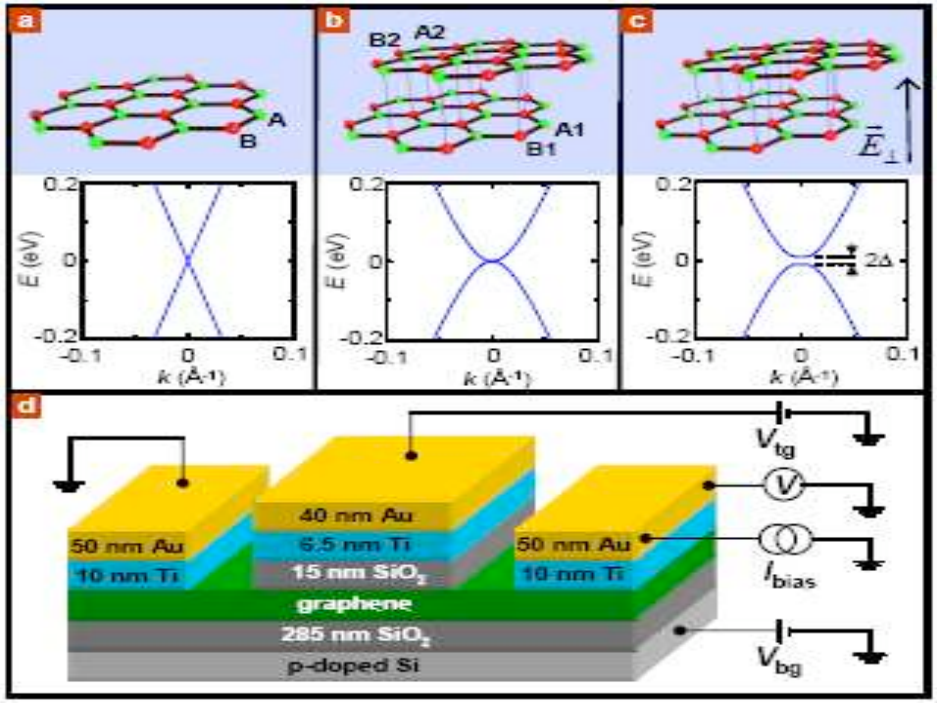


Fig. 3. Evolution of gap closing and reopening by changing the doping level by potassium adsorption. Experimental and theoretical bands (solid lines) (**A**) for an as-prepared graphene bilayer and (**B** and **C**) with progressive adsorption of potassium are shown. The number of doping electrons per unit cell, estimated from the relative size of the Fermi surface, is indicated at the top of each panel.

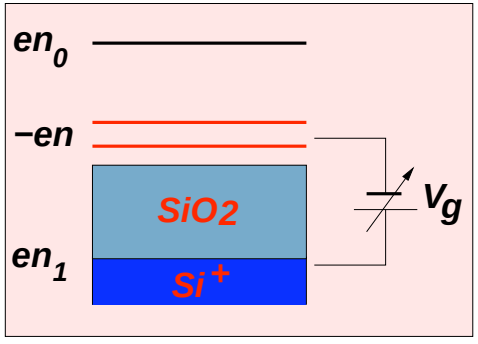
On top of a Silicon Carbide substrate. Depletion of the substrate dopant carriers gives a $n-$type doping. Covered with Potassium atoms. Science **313**, 951 (2006).

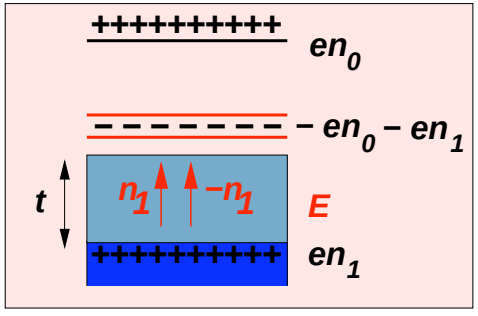
Top and bottom gates



Top and bottom gates setup. Nature Materials **7**, 151 (2008).

Doping by molecular absorption; gap controlled by bottom gate gap





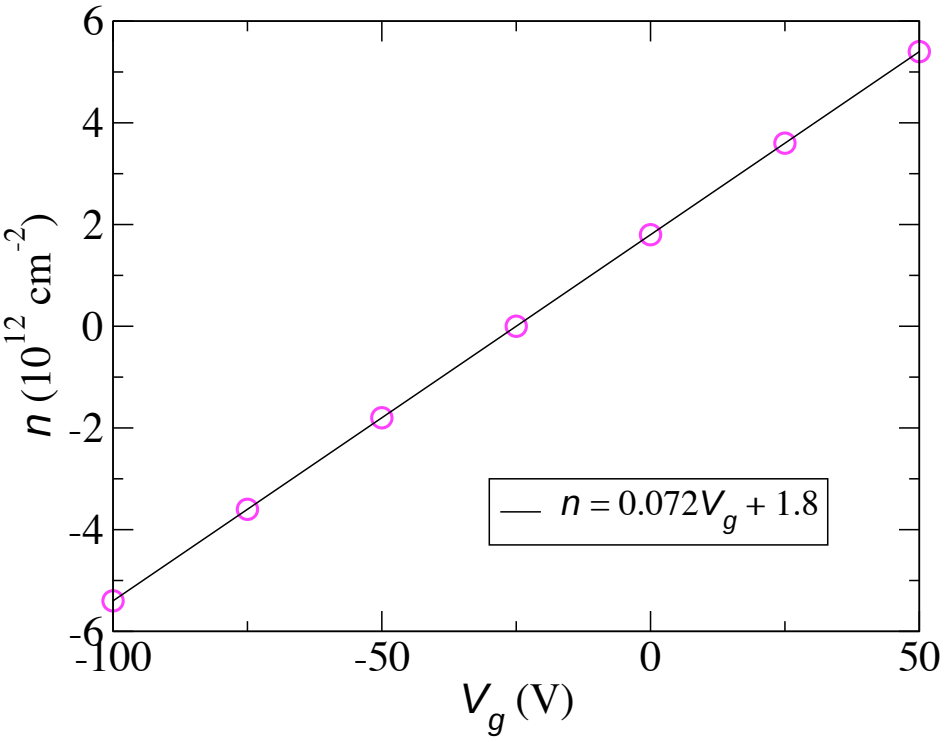
The top layer can be either potassium or NH_3.

$$E = \frac{n_1 e}{2\epsilon\epsilon_0} + \frac{n_1 e}{2\epsilon\epsilon_0} = \frac{n_1 e}{\epsilon\epsilon_0}$$

$$V_g = Et = \frac{n_1 et}{\epsilon\epsilon_0}$$

$$V_g = \frac{(n - n_0)et}{\epsilon\epsilon_0} \Leftrightarrow n = \frac{\epsilon\epsilon_0}{te} V_g + n_0 \, .$$

(...)



n from the Hall effect

n_0 from the fit to:

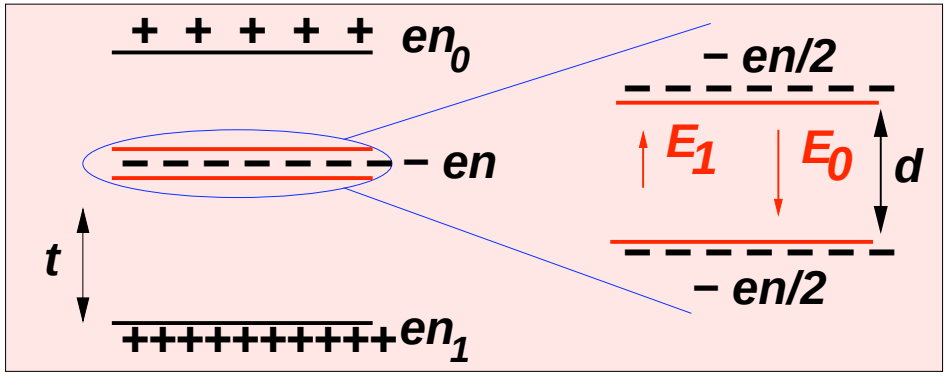
$$n = \frac{\epsilon\epsilon_0}{te} V_g + n_0$$

$$\begin{aligned} n_0 &= 1.79 \times 10^{12}\mathrm{cm}^{-2}\,, \\ \frac{\epsilon\epsilon_0}{te} &= 7.22 \times 10^{10}\mathrm{cm}^{-2}\cdot\mathrm{V}^{-1}\,. \end{aligned}$$

If we compute $(\epsilon\epsilon_0)/(te)$ using $\epsilon = 3.9$, as for the SiO_2, we obtain an agreement with above value.

This allow us to determine the density of charge carriers n_0 induced by the potassium or the NH_3 layer.

Potential difference between the graphene layers



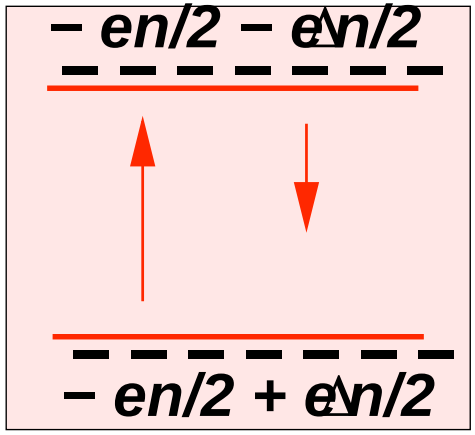
$$E = E_1 + E_0 = \frac{n_1 e}{2\epsilon_0 \epsilon_r} - \frac{n_0 e}{2\epsilon_0 \epsilon_r} \Rightarrow V = \frac{n_1 e d}{2\epsilon_0 \epsilon_r} - \frac{n_0 e d}{2\epsilon_0 \epsilon_r} .$$

Since $n = n_1 + n_0$

$$V = \left(\frac{n}{n_0} - 2 \right) \frac{n_0 e d}{2\epsilon_0 \epsilon_r} .$$

Which implies that electrons and holes see a different V! Also $V = 0$ for $n = 2n_0$.

Screening



Because the two planes of the bilayer are now at different electric potentials there is an imbalance of charge between the two planes.

$$E = -\frac{n/2 - \Delta n/2}{2\epsilon_0\epsilon_r}e + \frac{n/2 + \Delta n/2}{2\epsilon_0\epsilon_r} = \frac{e\Delta n}{2\epsilon_0\epsilon_r} \Rightarrow$$

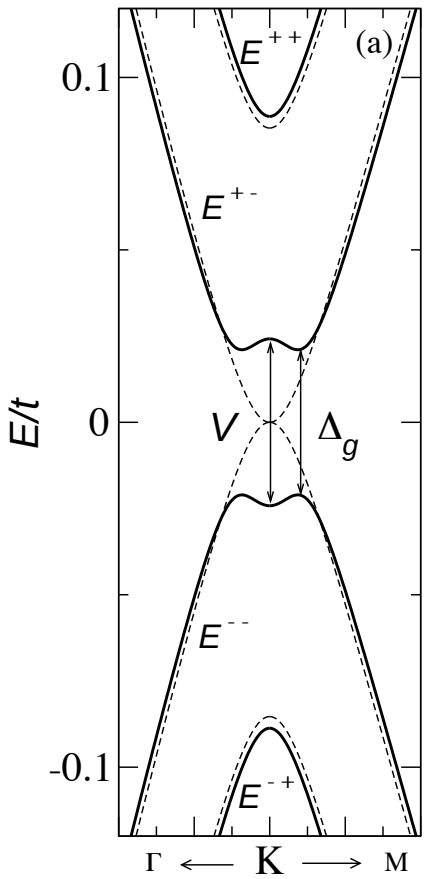
$$V_s = \frac{de\Delta n}{2\epsilon_0\epsilon_r}$$

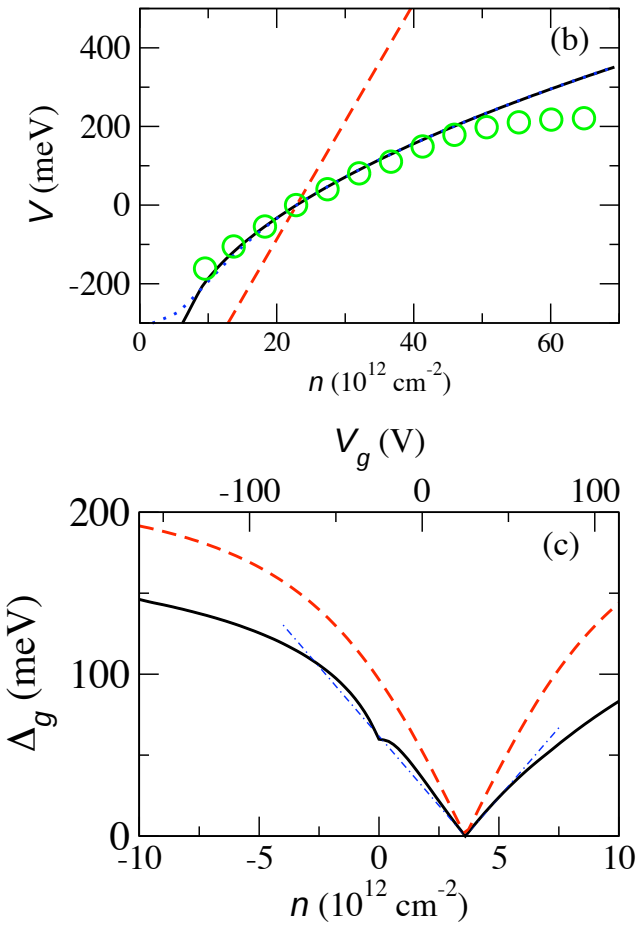
Therefore the total V_T is :

$$V_T = V + V_s = \left(\frac{n}{n_0} - 2 + \frac{\Delta n}{n_0}\right)\frac{n_0 ed}{2\epsilon_0\epsilon_r}\,.$$

For similar results see also: Edward McCann, Phys. Rev. B 74, 161403(R) (2006).

Fit of the V versus n in the bilayer





t =3.1 eV

$t_\perp = 0.2$ eV (full)

$t_\perp = 0.4$ eV (dotted)

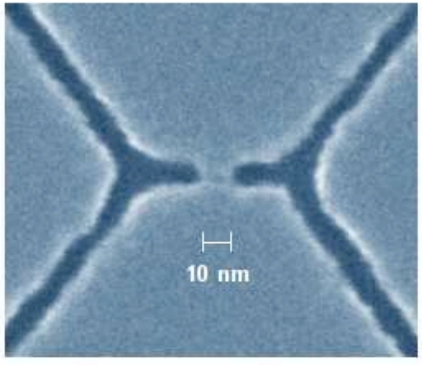
Zero gap for $n = 23 \times 10^{12}$ cm^{-2}, which implies $n_1 = 11.5 \times 10^{12}$ cm^{-2} (n-doped bilayer.)

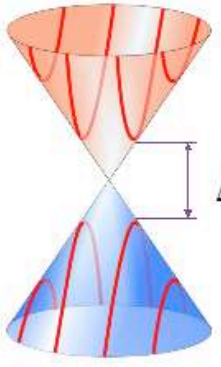
Recent applications

Application I : nano-circuits

GRAPHENE NANO-CIRCUITS

$\Delta E = v_F h/2D$





$\Delta E \approx \frac{1\ eV}{D(nm)}$

not $1/D^2$
as for electrons
but much larger $1/D$
as for slow photons

(courtesy of A. K. Geim)

See also *Single Electron Transistor* in Nano Letters **8**, 2378 (2008).

Application II : Graphene on industrial scale

(courtesy of A. K. Geim)

Geim's opinion

"–MANY POTENTIAL APPLICATIONS–“

”maybe not as much exaggerated as in some other research areas “

Summary

Details on the work presented here can be found in :

- R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, NMRP, A.K. Geim, Science **320**, 1308 (2008).
- Eduardo V. Castro, NMRP, T. Stauber, N. A. P. Silva, Phys. Rev. Lett. **100**, 186803 (2008).
- Eduardo V. Castro, NMRP, J. M. B. Lopes dos Santos, A. H. Castro Neto, F. Guinea, Phys. Rev. Lett. **100**, 026802 (2008).
- Eduardo V. Castro, N. M. R. Peres, J. M. B. Lopes dos Santos, Europhys. Lett. **84**, 17001 (2008).
- NMRP, T. Stauber, A. H. Castro Neto Europhys. Lett. **84**, (2008). (in press)
- Eduardo V. Castro, K. S. Novoselov, S. V. Morozov, NMRP, J.M.B. Lopes dos Santos, Johan Nilsson, F. Guinea, A. K. Geim, A. H. Castro Neto, Phys. Rev. Lett. **99**, 216802 (2007)

Last but not least

In collaboration with :

- Eduardo V. Castro (University of Porto)
- Tobias Stauber (University of Minho)
- J. M. B. Lopes dos Santos (University of Porto)
- A. H. Castro Neto (Boston University)
- F. Guinea (**ICM-Madrid**)
- Johan Nilsson (Instituut Lorentz for Theoretical Physics)
- K. S. Novoselov (University of Manchester)
- S. V. Morozov (University of Manchester)
- A. K. Geim (University of Manchester)