

Graphene: massless electrons in a carbon sheet

Jean-Noël Fuchs

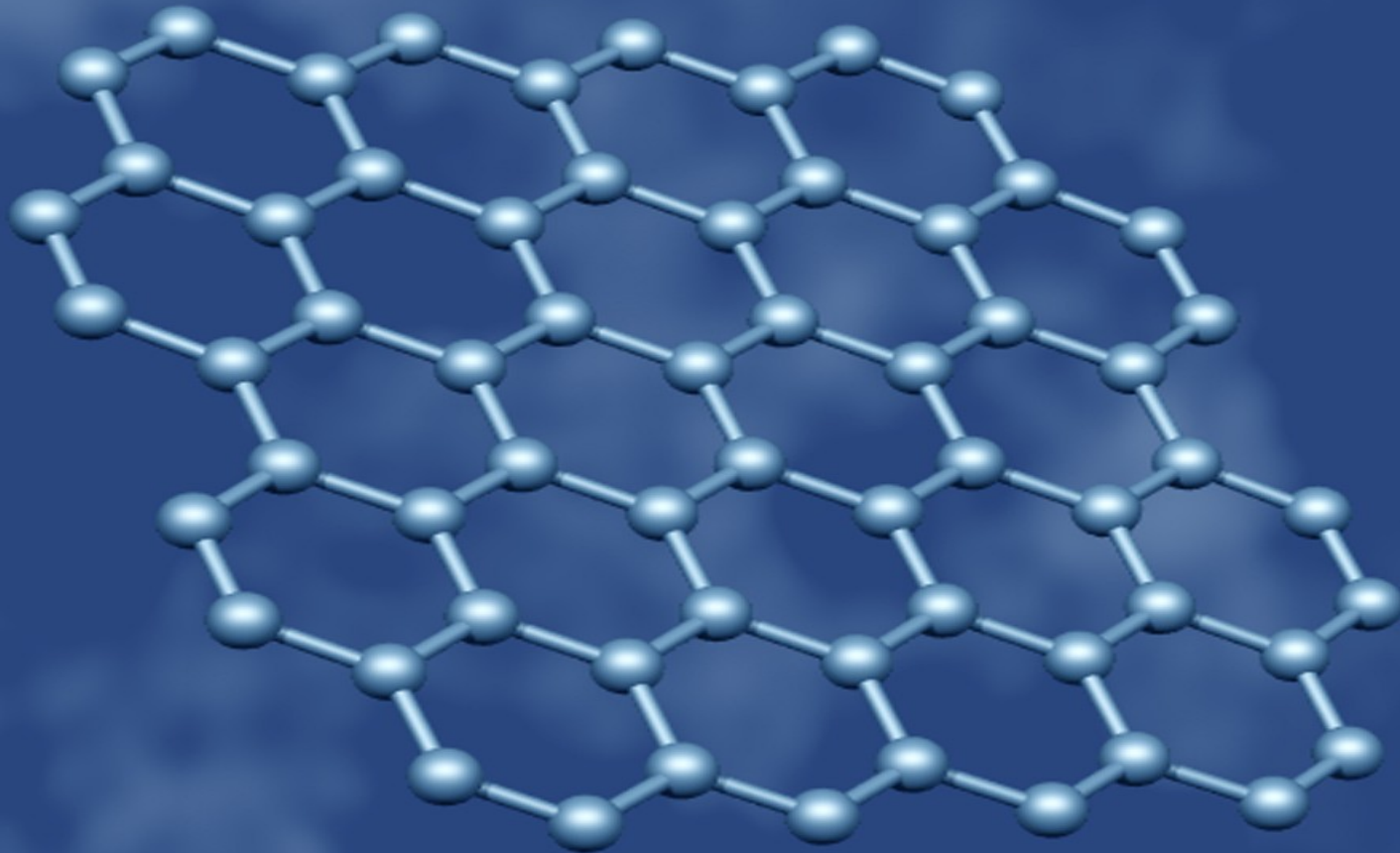
Laboratoire de Physique des Solides (bât. 510 Orsay)
Université Paris-Sud et CNRS

Outline

- I) Introduction: what is graphene?
- II) Short history of hexagonal carbon
- III) Experimental techniques
- IV) Atomic structure
- V) Electronic properties (massless Dirac fermions)
- VI) In a magnetic field (Landau levels)
- VII) Relativistic quantum Hall effect
- VIII) Extras

I) Introduction: what is graphene?

Le graphène = cristal de carbone
2D, de structure en nid d'abeille

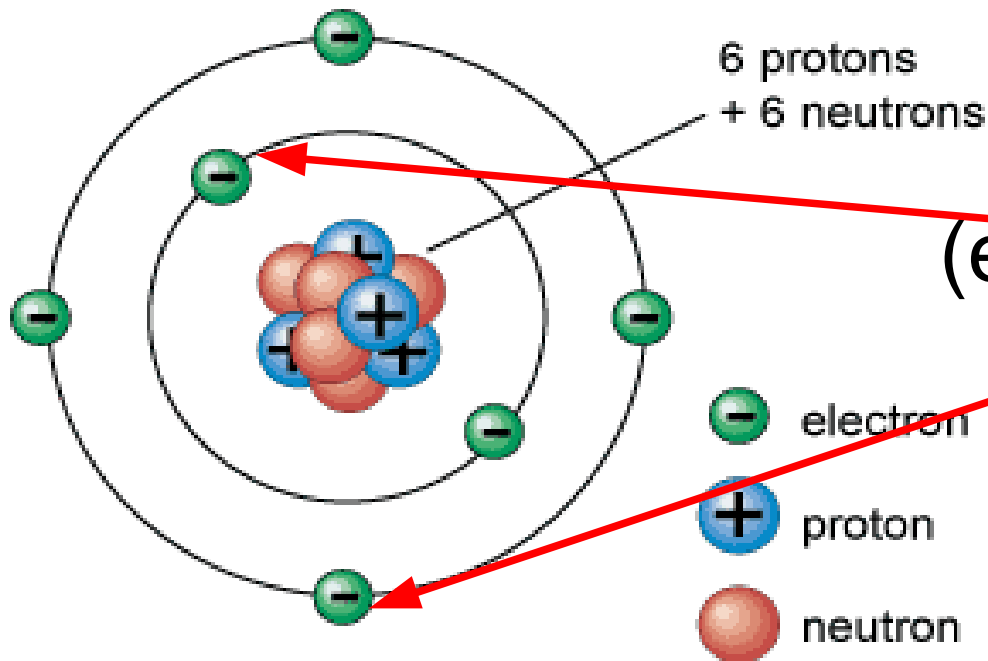


Carbone seul

6 électrons dont:
2 électrons de coeur

(en orbite autour du noyau)

4 électrons de valence
(périphériques)



Carbon atom

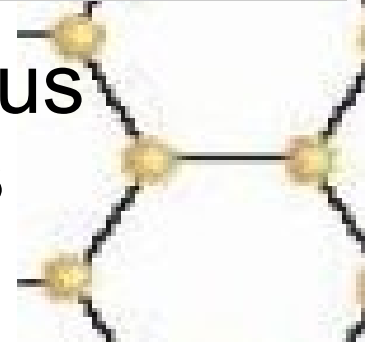
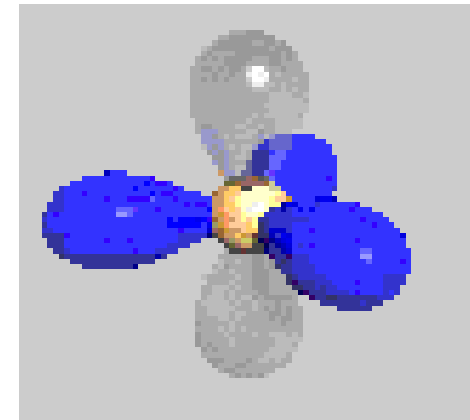
Carbone dans une molécule ou un cristal

par exemple carbone sp^2 :

parmi les 4 électrons de valence

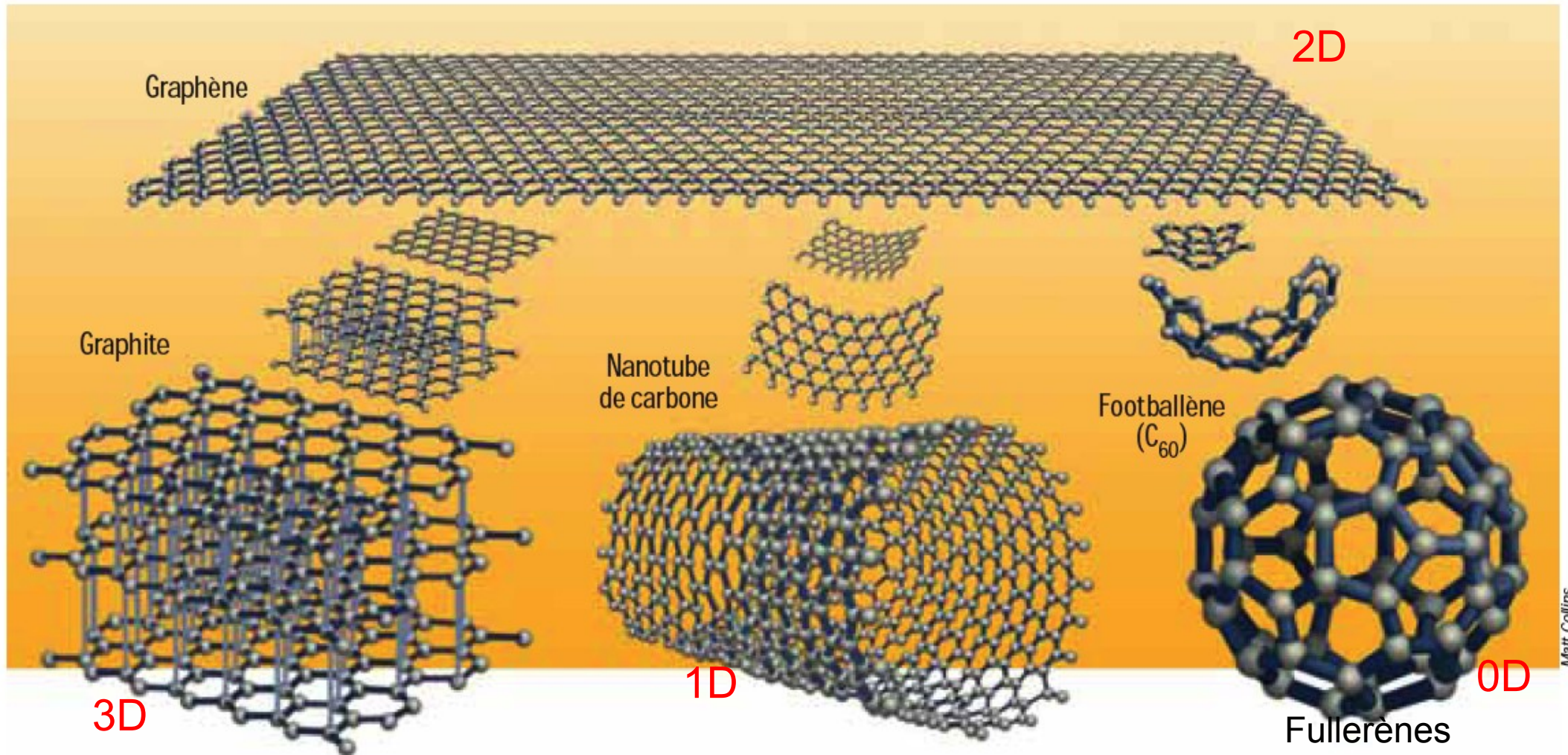
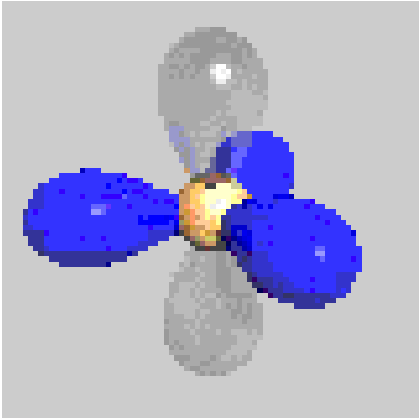
- 3 sont dans des liaisons chimiques avec les plus proches atomes voisins: structure en hexagones

- 1 est libre de se promener dans tout le cristal: électron de conduction



6 él. = 2 coeur(1)+3 liaisons(2)+1 conduction(tous)

Famille du carbone hexagonal (sp^2): la mère et les enfants

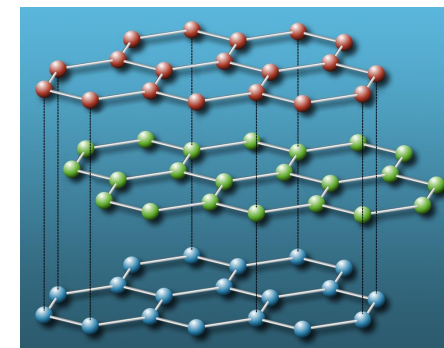


II) Short history of hexagonal carbon

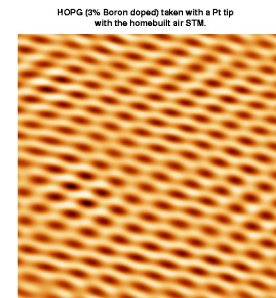
Experiments

II) Pre-history

Graphite: marking of sheep by shepherds (Borrowdale, England, 1565), light bulbs, nuclear moderator,..

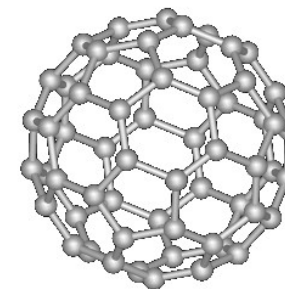


1962 HOPG (graphite monocrystal) [Ubbelohde]



1960-1980 Graphite intercalation compounds

1985 Fullerenes [Kroto, Curl, Smalley]



1991-1993 Carbon nanotubes [Iijima]



1992-1993 Graphene (uncontacted) on metal substrate [Land et al.]

Graphene Milestones

Discovery of graphene

Crystal structure

Graphite band structure calculation

Isolation and observation of freestanding graphene

Official naming of graphene

Debye P, Scherrer P (1916).

Wallace (1947) (includes "Dirac" cone)

Boehm et al (1962)

Boehm et al (1987)

Graphene on transition metals, carbides

Identification of:

"monolayer of graphite"

"single-crystal plane"

"two-dimensional graphite"

SiC Van Bommel, Surf. Sci. (1975)

LaB6 Oshima Appl Phys (1977)

Pt Zi-Du Surface Science (1987)...

Ni Rosei PRB(1983)

Ir Kholin Surf Sci (1984)

Re Gall Sov Phys Sol State (1985)

TaC Aizawa PRL 1990

TiC Nagashima, Surf Sci (1993)

Ru Marchini (2007)

WC TaC, HfC,...

SiC Forbeaux (1998)

Graphene-based electronics conceived

Gateable graphenes

Emphasis on transport

Georgia Tech (2001)

SiO₂ Novoselov Nature (2004)

Transport on transferred exfoliated few layer graphite observation of graphene (GOOD FOR 2D PHYSICS)

SiC Berger J. Chem Phys (2004)

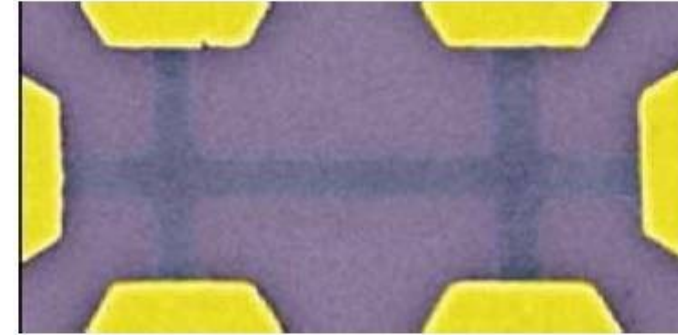
Epitaxial Transport on graphene and few layer graphite (GOOD FOR ELECTRONICS)

II) Modern history

Experiments

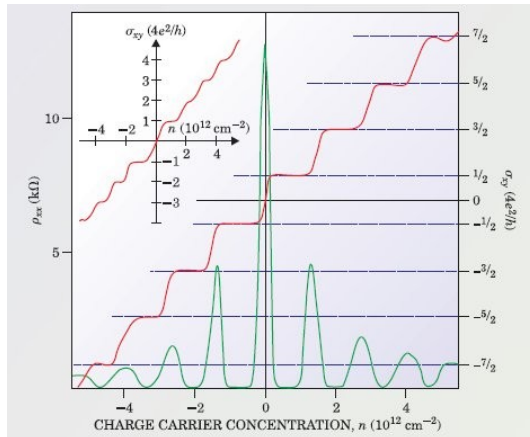
2004 Contacted (and gated) graphene on amorphous SiO_2 substrate

[Novoselov, Geim]



2004 Epitaxial “graphene” on SiC [Berger, de Heer]

2005 Graphene quantum Hall effect [N., G., Zhang, Kim]



2006 Graphene bilayer QHE [N., G., McCann, Falcko]

2009: Macroscopic graphene flake (76 cm) via CVD

2010: Nobel prize in physics for Novoselov and Geim

01/2011: over 2300 papers on the arXiv after the QHE



The Nobel Prize in Physics 2010 Andre Geim, Konstantin Novoselov

• The Nobel Prize in Physics 2010

Andre Geim

Konstantin Novoselov



Photo: Sergeom, Wikimedia Commons

Andre Geim



Photo: University of Manchester, UK

Konstantin Novoselov

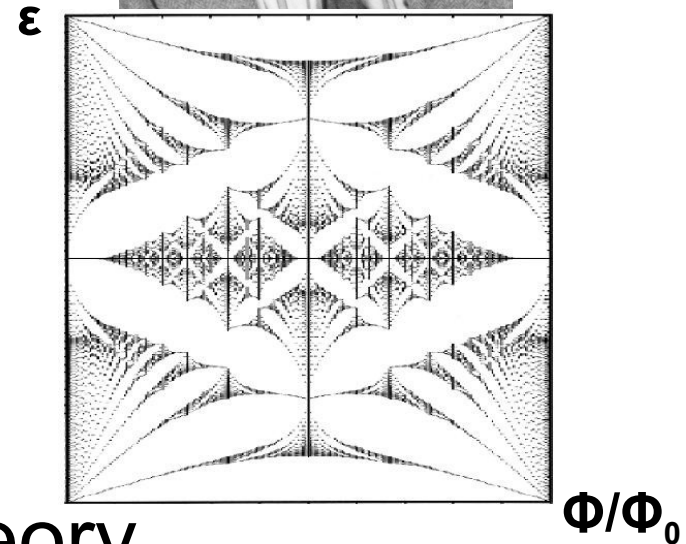
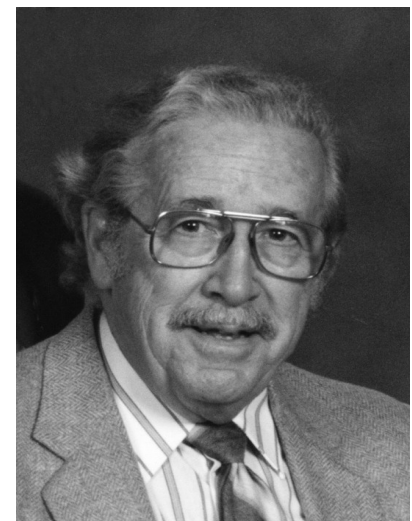
The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

II) History: theories

1947 Graphene band structure [Wallace]

1956 Graphene Landau levels [McClure]

1985 Hofstadter butterfly [Rammal]



1984-1988 Connection to 2+1 field theory

[Semenoff, DiVincenzo & Mele, Fradkin, Haldane, etc.]

~90's Theory of carbon nanotubes

[Dresselhaus², Saito, Ando, etc.]

2005 Z_2 (or QSH) topological insulator: graphene with a (too) strong spin-orbit [Kane and Mele]

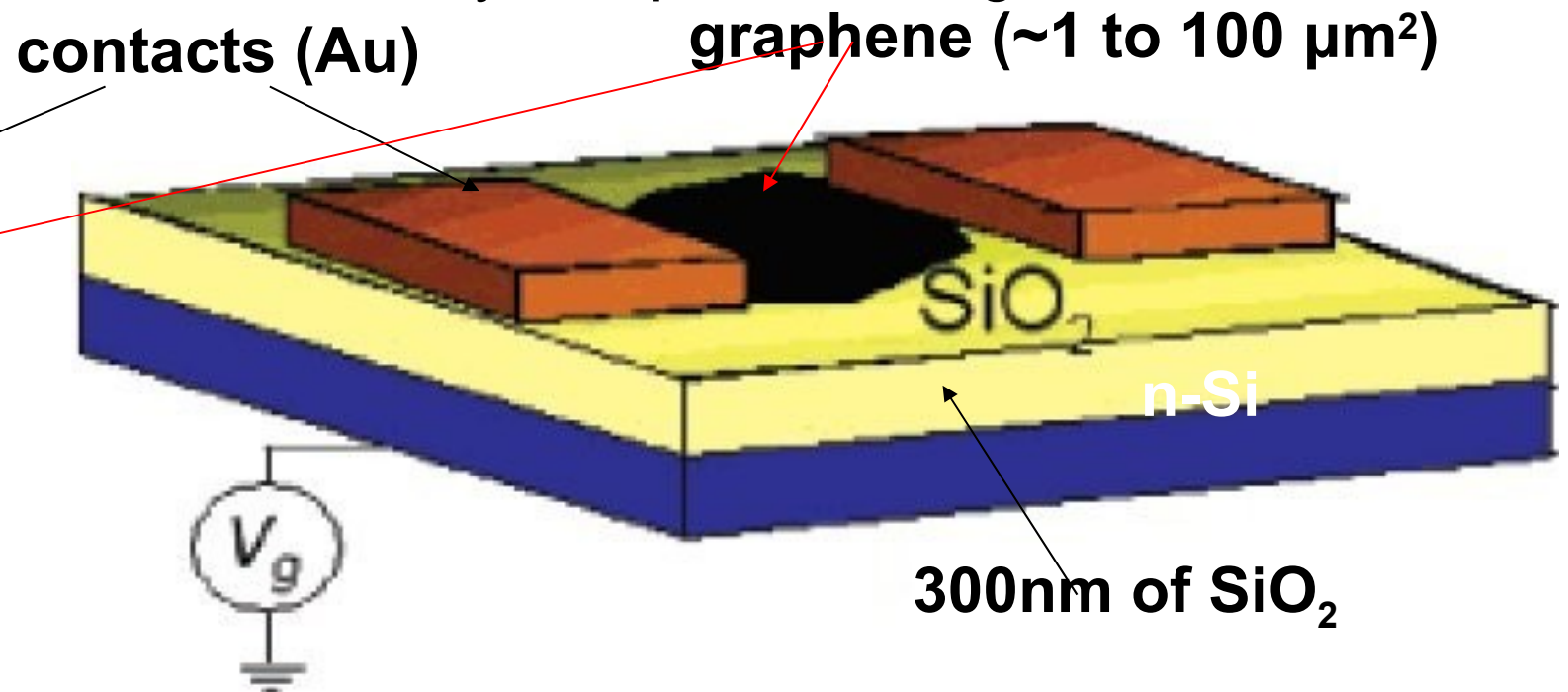
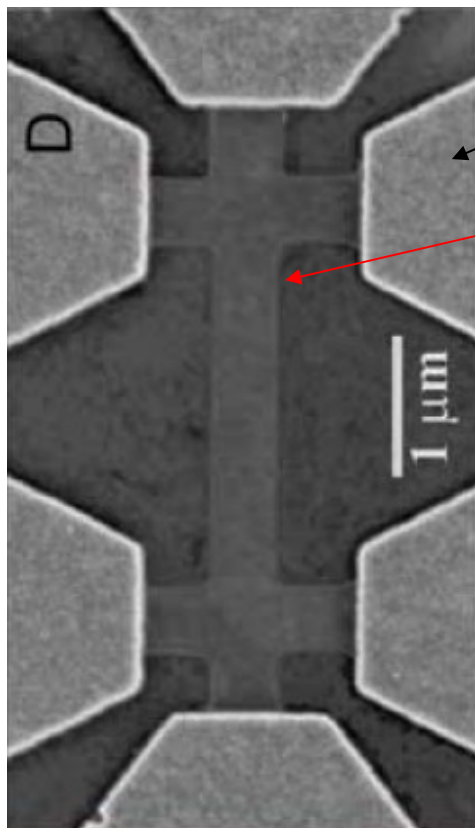
III) Experimental techniques

III) Experimental techniques

Three main techniques:

a) Mechanically exfoliated graphene

Recipe: Take a monocrystal of graphite pencil and cleave it several times using scotch tape. Rub the tape on a silicon substrate to deposit graphite flakes. A small fraction are monolayers. Detect them with an optical microscope (300nm SiO₂ thickness): that's tough. Contact the monolayer with metallic leads (gold e.g.). Apply an electric tension to the heavily n-doped Si backgate.

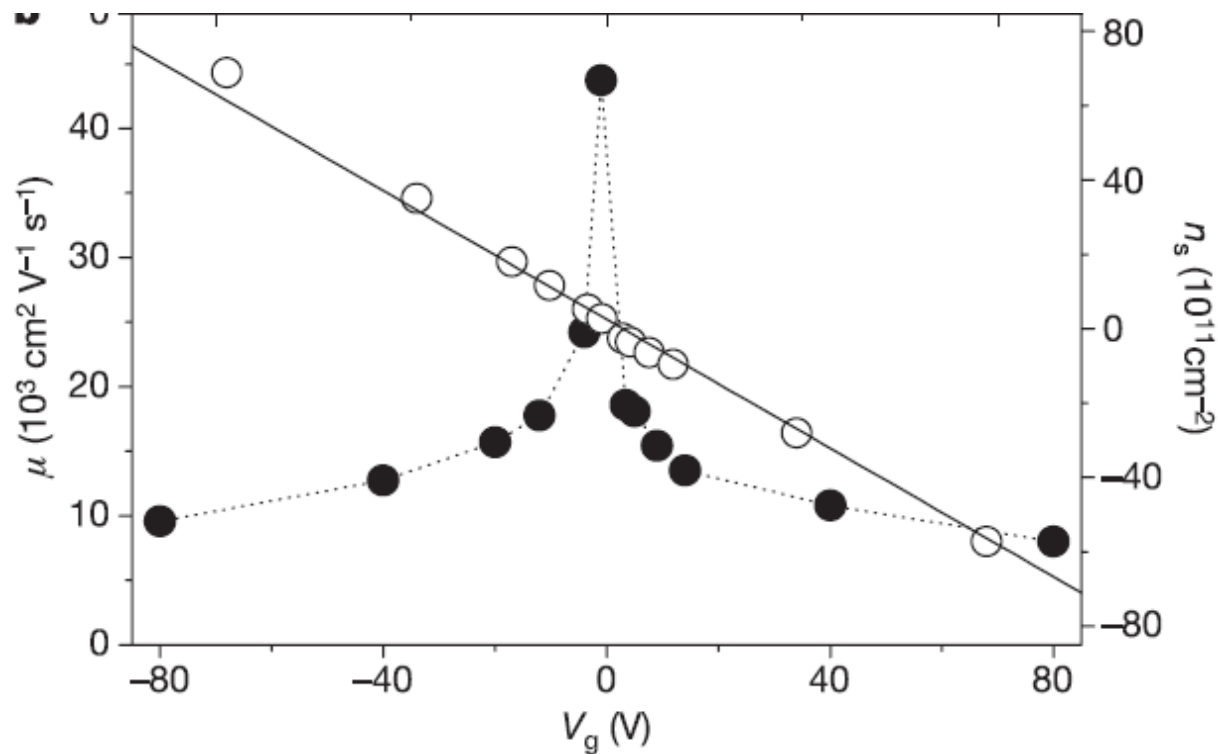


Novoselov et al., Science 2004 and PNAS 2005

III) Experimental techniques

Electric field effect (backgating of graphene): a gate tension V_g allows to control the filling on electrons in the graphene sheet ("doping" of graphene). A capacitor = plate(graphene)/dielectric(SiO_2)/plate(n-doped Si)

Novoselov et al., Science 2004 and PNAS 2005



typical mobility $\mu \sim 1 \text{ m}^2/\text{V.s}$

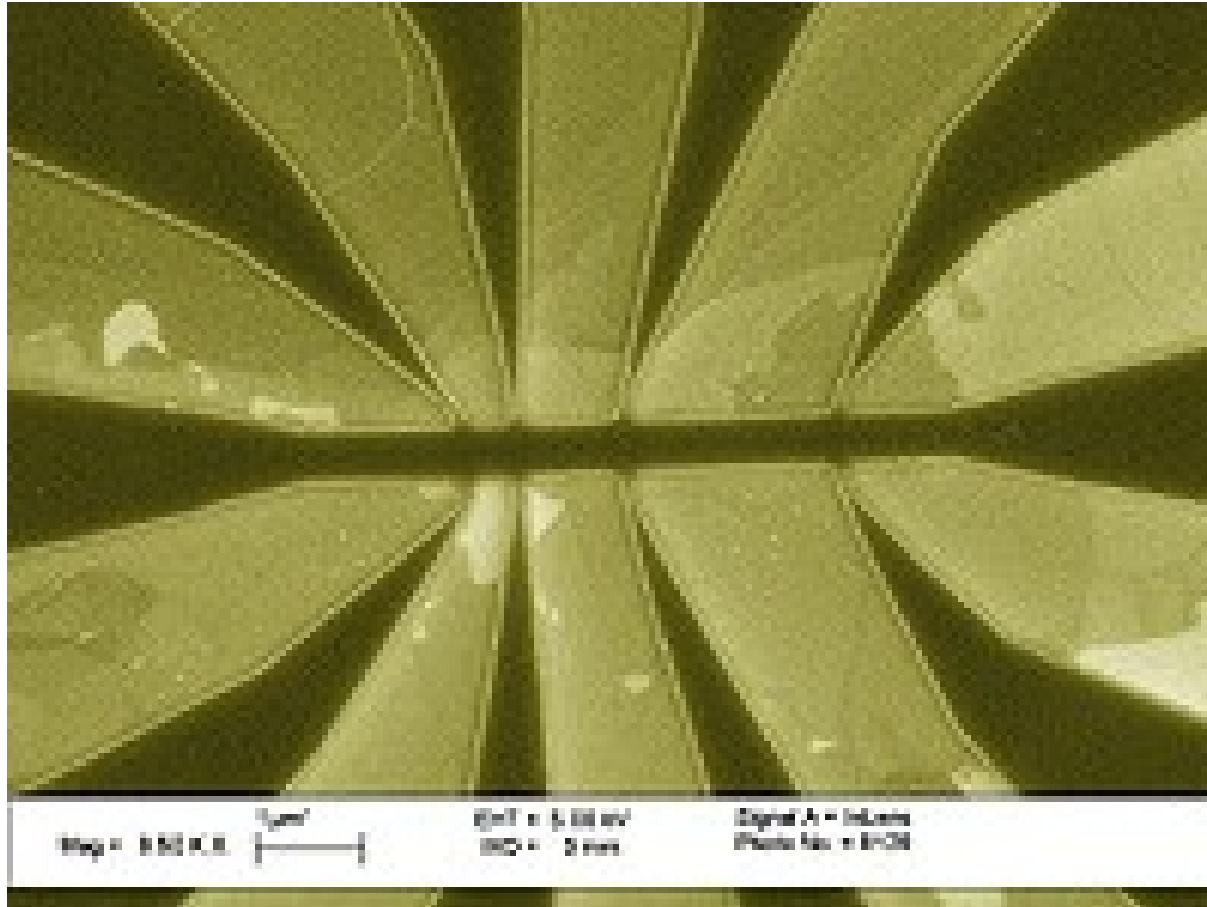
typical density $n \sim 10^{16} \text{ m}^{-2}$

Zhang et al., Nature 2005

Tunable and ambipolar (e⁻ or h⁺) unusual 2D electron gas (2DEG)

III) Experimental techniques

b) Epitaxial graphene on SiC



Berger et al., J. Phys. Chem. 2004 [de Heer's group]

III) Experimental techniques

b) Epitaxial graphene on SiC

Thermal decomposition of hexagonal silicon carbide (SiC) at $>1000^{\circ}\text{C}$ in vacuum leads to surface graphitization.

Two kinds of SiC to start with:

- 1) Si-terminated: slow growth, monolayer (“low” mobility $\sim 1000\text{ cm}^2/\text{V.s}$), multilayers are Bernal stacked (graphite like) and called Few Layer Graphene (FLG).
- 2) C-terminated: fast growth, multilayers (high mobility $\sim 10\,000\text{ cm}^2/\text{V.s}$) but decoupled because of rotational stacking disorder (not graphite like) and are called Multilayer Epitaxial Graphene (MEG). Now also possible to have high mobility monolayer (quantum Hall effect finally observed in 2009).

Berger et al., J. Phys. Chem. B 2004 [de Heer’s group]

III) Experimental techniques

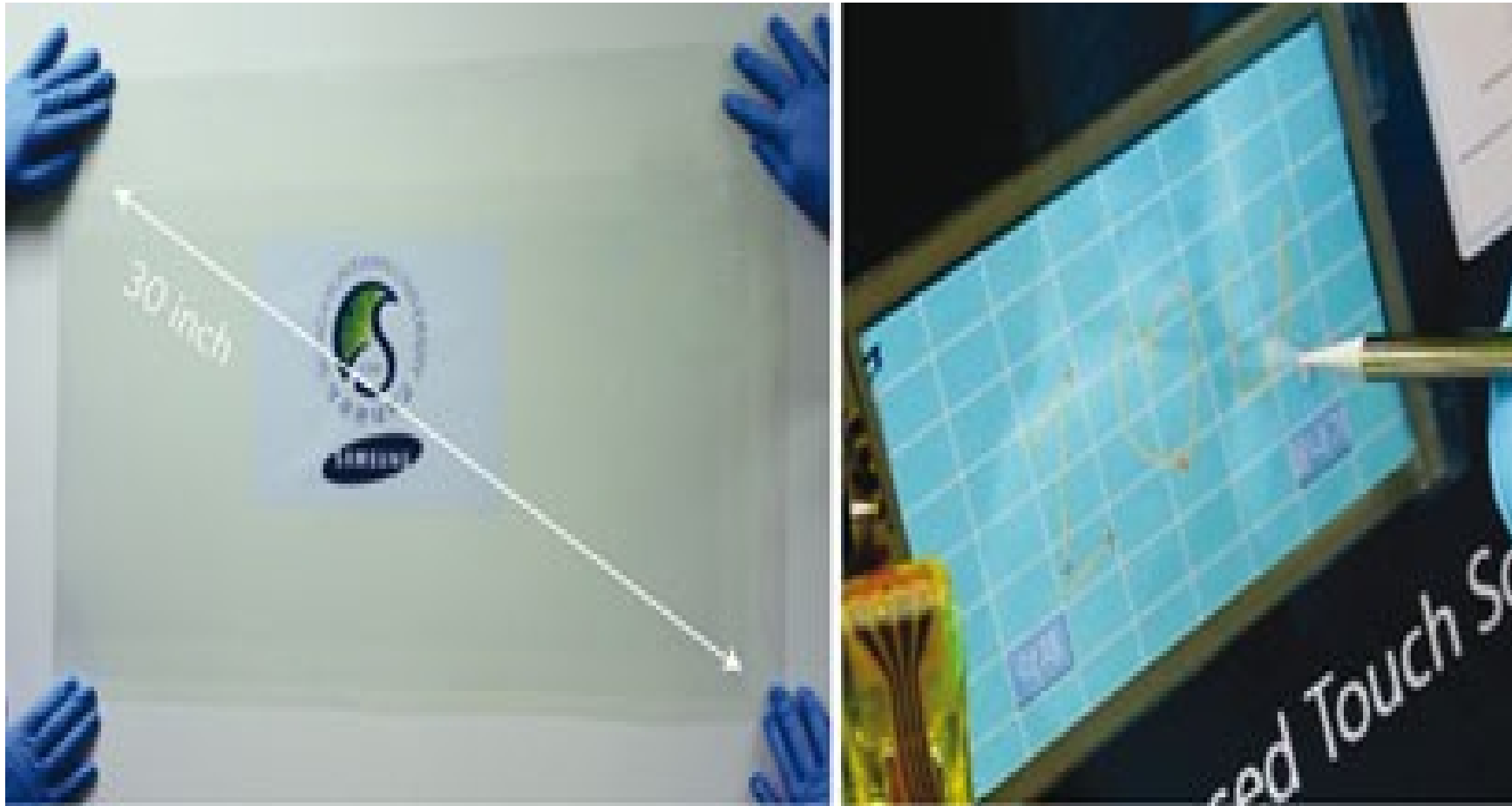
c) Chemical vapour deposition (CVD) graphene

- Chemical vapour decomposition of hydrocarbons (CH_4 e.g.) on metallic surface (such as reactive nickel or copper) allows one to produce macroscopic graphene flakes (cm or almost m).
- Efficient transfer technique to other substrates (such as roll to roll technique)
- Typical mobility of $4000 \text{ cm}^2/\text{V.s}$
QHE was observed

K.S. Kim et al., Nature 2009 [B.H. Hong's group]

III) Experimental techniques

c) Chemical vapor deposition (CVD): macroscopic graphene flake (76cm) and application as touchscreen

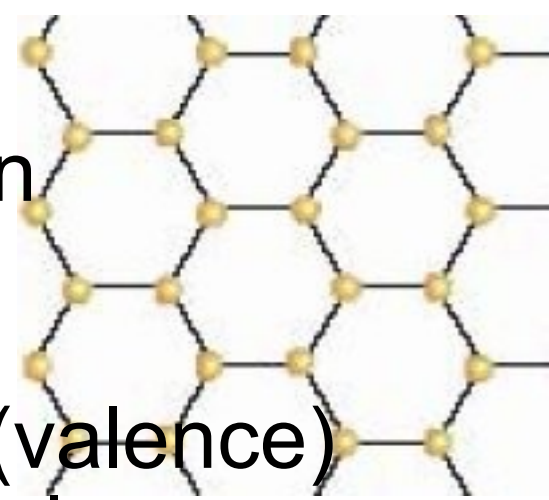


J.-H. Ahn et al, Nature Nanotechnology, 2010 [B.H. Hong's group]

IV) Atomic structure

IV) Atomic structure

Graphene = 2D honeycomb crystal of carbon

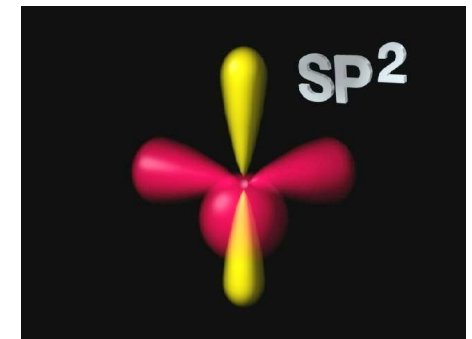


Carbon atom: 6 electrons $1s^2$ (core) $2s^2 2p^2$ (valence)

hybridization: 1 \times 2s orbital and 2 \times 2p orbitals

\rightarrow 3 \times sp^2 orbitals

1 \times $2p_z$ orbital left



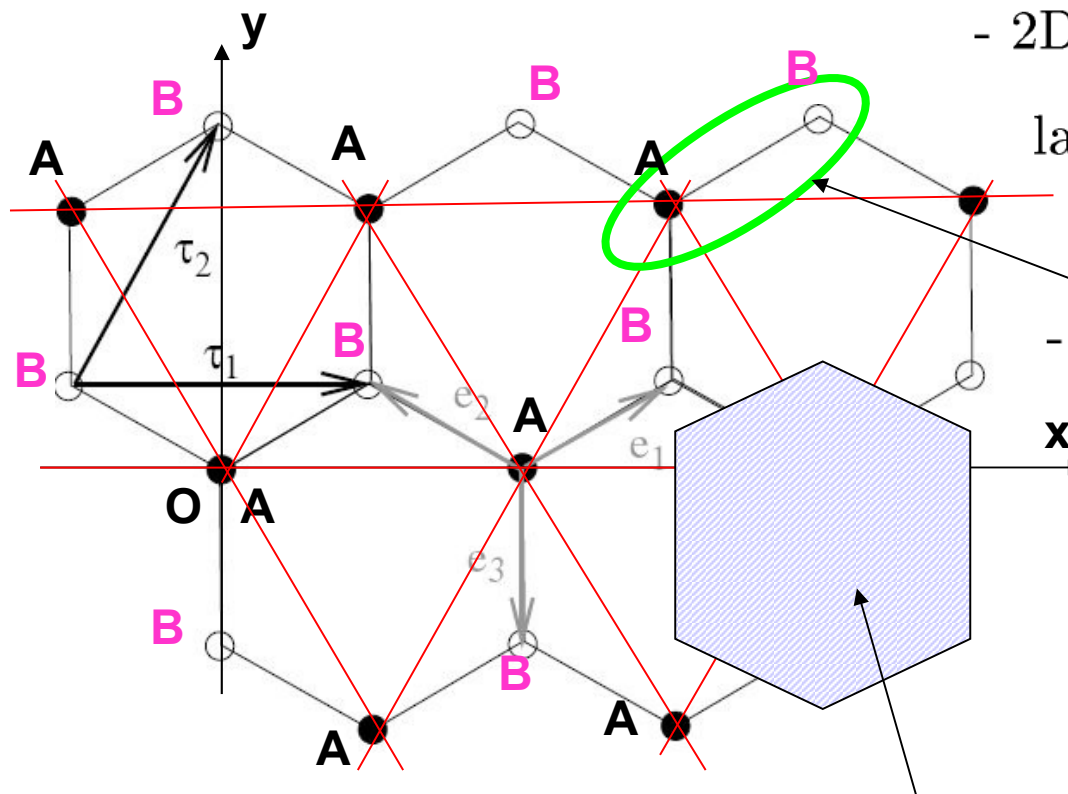
- 3 coplanar σ bonds, with 120° angle: honeycomb structure

- 1 conduction electron per C atom, $2p_z$ orbital, perpendicular to the plane, giving π bands: electronic properties

IV) Atomic structure

Honeycomb crystal = triangular (2D) Bravais lattice + 2 atoms basis (important for Bloch's theorem)

Direct space:



- 2D triangular lattice : lattice vectors (τ_1, τ_2)

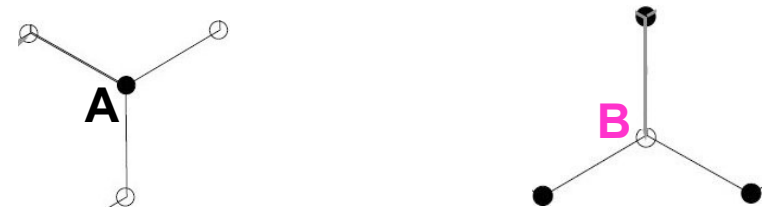
lattice constant = $\tau_1 = \tau_2 = a\sqrt{3} \approx 2.5 \text{ \AA}$

angle = $(\widehat{\tau_1, \tau_2}) = 60^\circ$

- atomic basis : $C_A(0, 0)$ et $C_B(1/3, 1/3)$

$C - C$ distance = $a = 1.42 \text{ \AA}$

nearest neighbors vectors (e_1, e_2, e_3)

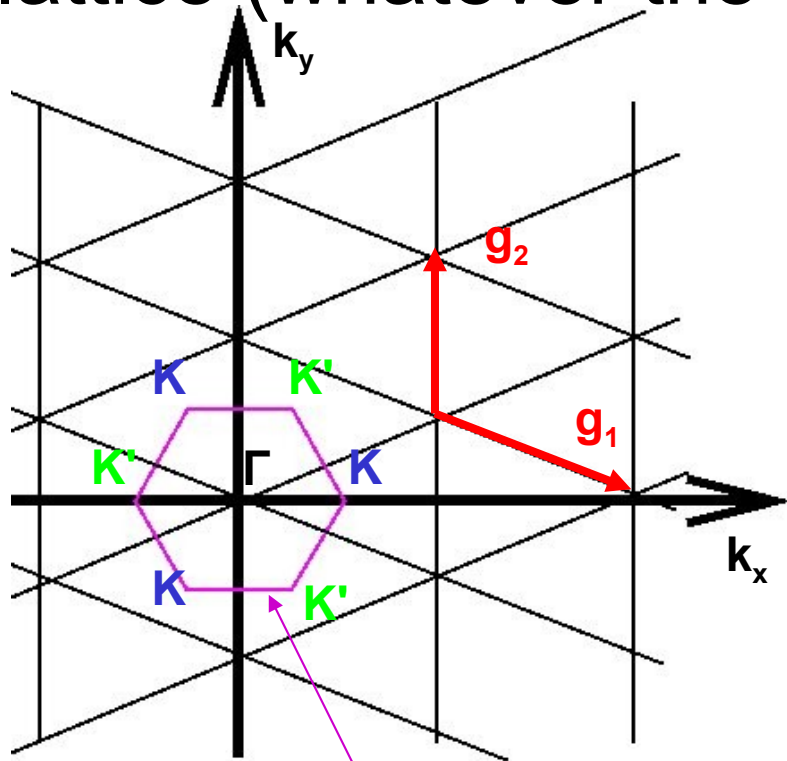


- primitive unit cell contains 2 atoms, 1 C_A and 1 C_B
 \Rightarrow 2 conduction electrons per primitive unit cell
 number of primitive unit cells $N_m = \mathcal{A}/(a^2 3\sqrt{3}/2)$

IV) Atomic structure

Reciprocal space:

Reciprocal lattice of the triangular lattice = triangular lattice (whatever the atomic basis)



1st Brillouin zone (1Bz)

- Reciprocal lattice (RL) =
2D triangular lattice :
lattice vectors ($\mathbf{g}_1, \mathbf{g}_2$)

lattice constant = $g_1 = g_2 = \frac{4\pi}{3a}$

angle = $(\widehat{g_1, g_2}) = 120^\circ$

- primitive unit cell = 1st Brillouin zone
center of 1Bz : Γ

crystal momentum conservation \Rightarrow

only two inequivalent corners of the 1Bz :

we take $\mathbf{K} = \frac{4\pi}{3\sqrt{3}a} \mathbf{e}_x = -\mathbf{K}'$

IV) Atomic structure

Conclusion:

- Direct space: sublattice (basis) index

$$l = A, B$$

- Reciprocal space: valley index
(has no connection to the 2 carbon atoms in the basis, but is related to the Bravais lattice)

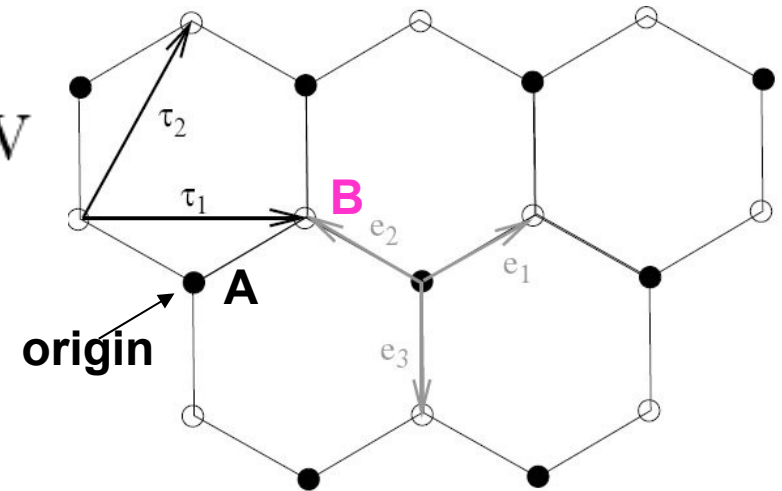
$$\xi = +1(K), -1(K')$$

V) Electronic
properties
(no magnetic field)

V) Electronic properties (B=0)

Nearest neighbor tight binding model for the conduction electrons [Wallace 1947]

- nearest neighbor hopping amplitude : $t \approx 3$ eV
 - no neighboring $2p_z$ orbital overlap
 - $2p_z$ orbital energy : $\varepsilon_{2p_z} = 0$
 - 1 conduction electron per atom
- \Rightarrow Hamiltonian (2nd quantization) :



$$\hat{H} = -t \sum_{\mathbf{R} \in BL} \sum_{m=1}^3 \hat{b}_{\mathbf{R}+\mathbf{e}_m}^\dagger \hat{a}_{\mathbf{R}} + \text{h.c. where } \mathbf{R} = \text{integer} \times \tau_1 + \text{integer} \times \tau_2$$

to be diagonalized.

Bloch's theorem (deals with the Bravais lattice (BL); not a FT) \Rightarrow

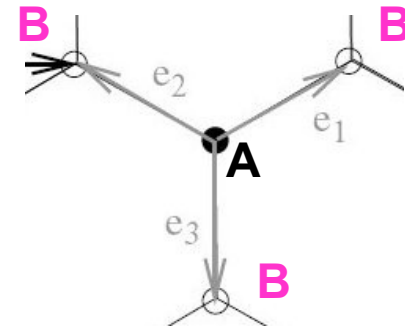
$$\hat{a}_{\mathbf{R}}^\dagger = \frac{1}{\sqrt{N_m}} \sum_{\mathbf{k} \in 1Bz} e^{-i\mathbf{k} \cdot \mathbf{R}} \hat{a}_{\mathbf{k}}^\dagger \text{ et } \hat{b}_{\mathbf{R}+\mathbf{e}_m}^\dagger = \frac{1}{\sqrt{N_m}} \sum_{\mathbf{k} \in 1Bz} e^{-i\mathbf{k} \cdot (\mathbf{R}+\mathbf{e}_m)} \hat{b}_{\mathbf{k}}^\dagger$$

V) Electronic properties (B=0)

$$\hat{H} = \sum_{\mathbf{k} \in 1\text{Bz}} h_{\mathbf{k}} \hat{b}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}} + \text{h.c. with } h_{\mathbf{k}} \equiv -t \sum_{m=1}^3 e^{-i\mathbf{k} \cdot \mathbf{e}_m} = |h_{\mathbf{k}}| e^{i\theta_{\mathbf{k}}}$$

$$= \sum_{\mathbf{k} \in 1\text{Bz}} \begin{pmatrix} \hat{a}_{\mathbf{k}}^\dagger & \hat{b}_{\mathbf{k}}^\dagger \end{pmatrix} \begin{pmatrix} 0 & h_{\mathbf{k}}^* \\ h_{\mathbf{k}} & 0 \end{pmatrix} \begin{pmatrix} \hat{a}_{\mathbf{k}} \\ \hat{b}_{\mathbf{k}} \end{pmatrix}$$

2x2 matrix in sublattice (A,B) space



Then, a rotation in sublattice (A,B) space :

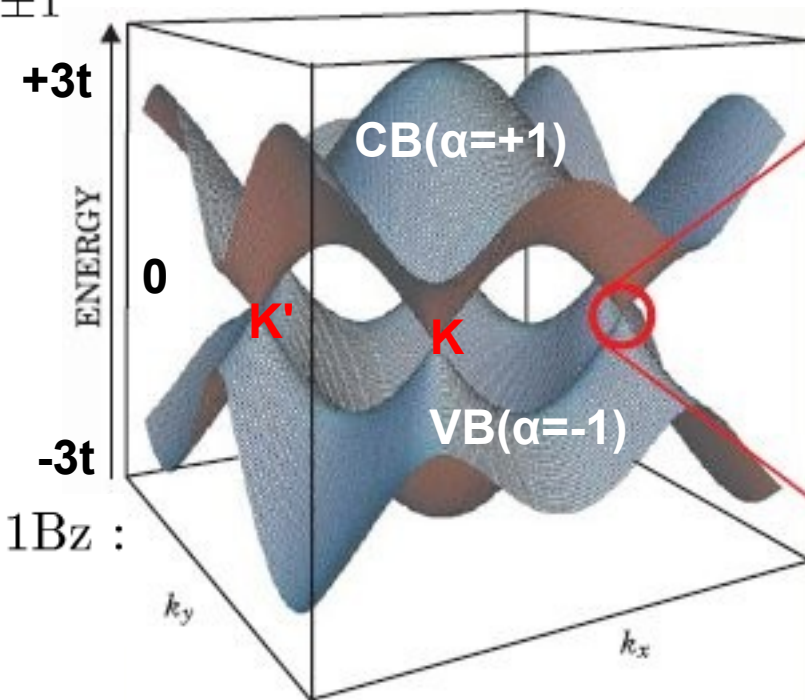
$$\hat{c}_{\mathbf{k},\alpha}^\dagger = \frac{1}{\sqrt{2}} \left(e^{-i\theta_{\mathbf{k}}/2} \hat{a}_{\mathbf{k}}^\dagger + \alpha e^{i\theta_{\mathbf{k}}/2} \hat{b}_{\mathbf{k}}^\dagger \right) \text{ where } \alpha = \pm 1$$

so that the Hamiltonian becomes

$$\hat{H} = \sum_{\mathbf{k} \in 1\text{Bz}} \sum_{\alpha=\pm 1} \varepsilon_{\mathbf{k},\alpha} \hat{c}_{\mathbf{k},\alpha}^\dagger \hat{c}_{\mathbf{k},\alpha} \text{ où } \varepsilon_{\mathbf{k},\alpha} \equiv \alpha |h_{\mathbf{k}}|$$

- the energy vanishes on two points, on the corners of the 1Bz :
 $\varepsilon_{\pm \mathbf{K},\alpha} \equiv \alpha |h_{\pm \mathbf{K}}| = 0$

- band index $\alpha = +1$ (CB, π^* , particle); -1 (VB, π , hole)
 refers to the same space as the sublattice index $l = A, B$



V) Band filling

VB and CB meet on 2 points, corners of the 1Bz (where there usually is a gap!)

Why not here? What is special to graphene?

Undoped graphene ($V_g = 0$) :

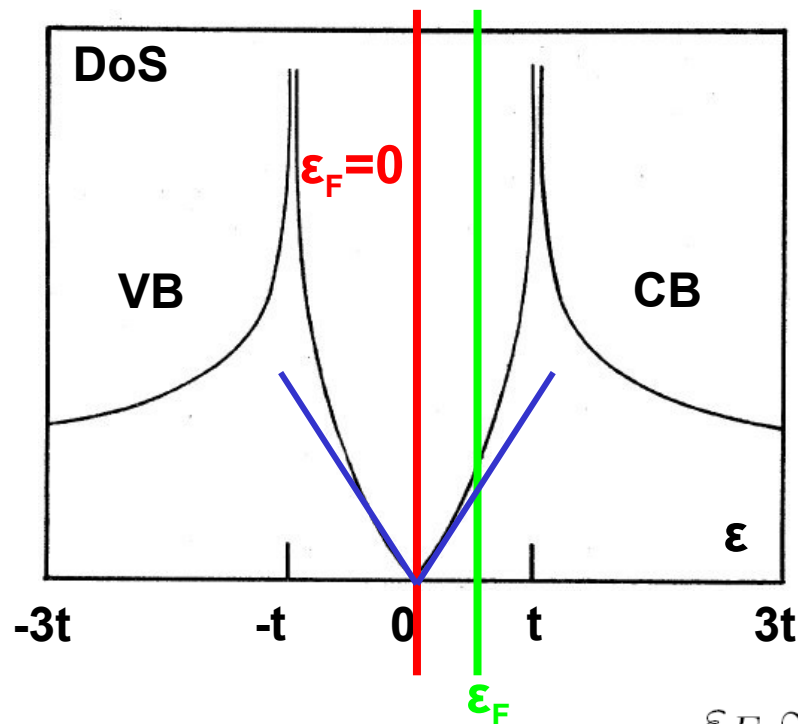
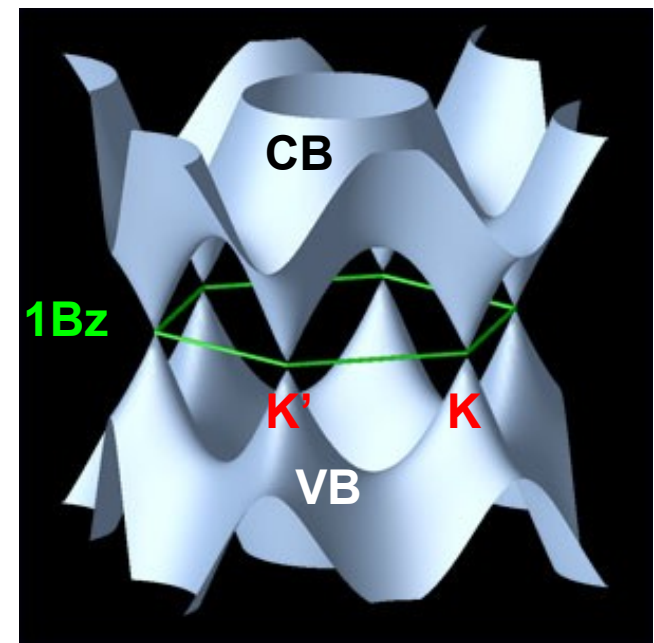
Number of single electron states per band = $2N_m$

Number of conduction electrons = $N_{el} = 2N_m$

$\Rightarrow \frac{N_{el}}{2N_m} = 1$: VB is full and CB is empty.

Graphene is a gapless semiconductor!

Or a metal ($\epsilon_F = 0$) with a vanishing density of states at the Fermi level!



The big band (CB+VB) is half-filled.

Doped graphene ($V_g \neq 0$) :

$N_{el} = 2N_m + N_c$ where $N_c = C_g V_g / e$

\Rightarrow filling = $\frac{N_c}{2N_m} \propto V_g$

Metal with a small (tunable) density of states.

$\epsilon_F \propto \sqrt{V_g}$ typically : $\epsilon_F \sim 0.1t$ when $V_g = 100V$

V) Low energy effective theory

Close to the K point where $\varepsilon = 0 = \varepsilon_F$ (similarly close to the K' point, except for a few signs), we expand the dispersion relation :

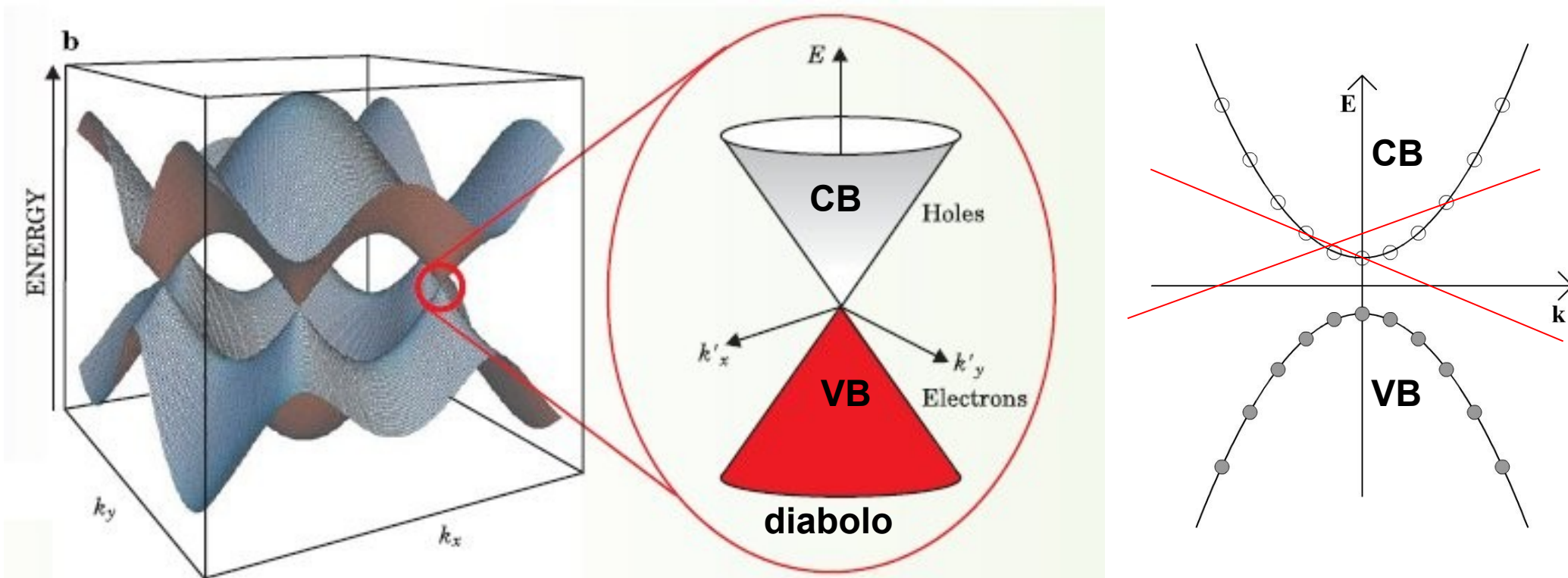
$\mathbf{k} = \mathbf{K} + \mathbf{p}/\hbar$ with $p/\hbar \ll 1/a$ i.e. $|\varepsilon| \ll t$. Hence

$$\varepsilon_{\mathbf{k},\alpha} \approx \alpha \frac{3}{2} ta |\mathbf{k} - \mathbf{K}| = \alpha v_F p$$

where $v_F \equiv 3ta/(2\hbar) \approx 10^6$ m/s $\approx c/300$ is an “effective speed of light”.

The dispersion relation is linear (rather than parabolic) : therefore the effective

electron mass m^* vanishes ! ($\varepsilon = \alpha \sqrt{m^{*2} v_F^4 + p^2 v_F^2} = \alpha v_F p$)



V) 2D massless Dirac Hamiltonian

The (2nd quantized) Hamiltonian becomes (with $\mathbf{k} = \mathbf{K} + \mathbf{p}/\hbar$) :

$$\hat{H}_K \approx \sum_{\mathbf{p}} (\hat{a}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}}^\dagger) \begin{pmatrix} 0 & v_F(p_x + ip_y) \\ v_F(p_x - ip_y) & 0 \end{pmatrix} \begin{pmatrix} \hat{a}_{\mathbf{k}} \\ \hat{b}_{\mathbf{k}} \end{pmatrix}$$

$\mathbf{h}_{\mathbf{k}}^* \approx v_F \mathbf{p} \exp(i \text{Arctg}(p_y/p_x))$

$$= \sum_{\mathbf{p}} (\hat{a}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}}^\dagger) v_F \mathbf{p} \cdot \boldsymbol{\sigma}^* \begin{pmatrix} \hat{a}_{\mathbf{k}} \\ \hat{b}_{\mathbf{k}} \end{pmatrix} \text{ where } \sigma_x \text{ and } \sigma_y \text{ are the Pauli matrices}$$

$\boldsymbol{\sigma} = (\sigma_x, \sigma_y)$ is the sublattice spin.

Therefore the single electron Hamiltonian is a 2D massless Dirac Hamiltonian (with a 2×2 matrix structure in sublattice space) :

$$H_K = v_F \mathbf{p} \cdot \boldsymbol{\sigma}^* = v_F \boldsymbol{\sigma}^* \cdot (-i\hbar \nabla)$$

Close to the K' point, one finds :

$$H_{K'} = -v_F \mathbf{p} \cdot \boldsymbol{\sigma}$$

Changing the representation : $A \rightleftharpoons B$ and $\psi = {}^t [KA, KB, K'B, K'A]$

$$\boxed{H_\xi = \xi v_F \mathbf{p} \cdot \boldsymbol{\sigma}} \quad [H = v_F \mathbf{p} \cdot \boldsymbol{\sigma} \otimes \tau_z^{\text{valley}}]$$

**Fermion doubling
(Nielsen & Ninomiya th.)**

V) Dirac equation

The Dirac equation is

$$i\hbar\partial_t\psi = H_D\psi, \text{ with } H_D = cp \cdot \alpha + mc^2\beta$$

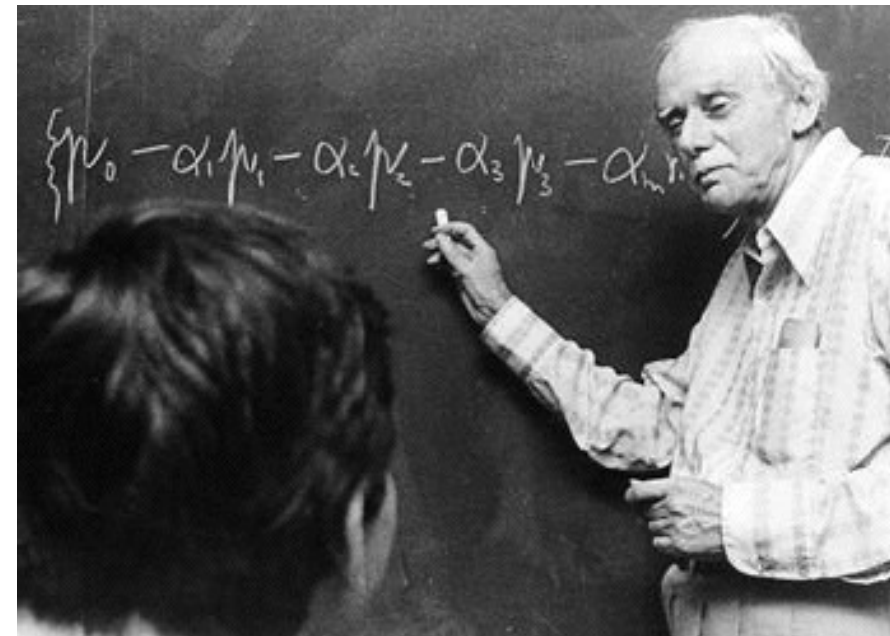
where α has d components (d =space dimension) : $\alpha_1, \dots, \alpha_d$. Let $\alpha_{d+1} = \beta$.
In order to have the correct relativistic dispersion relation, Dirac requires that

$$H_D^2 = c^2p^2 + m^2c^4$$

which implies

$$\{\alpha_\mu, \alpha_\nu\} = 2\delta_{\mu,\nu} \text{ with } \mu = 1, \dots, d+1$$

(Clifford algebra)



Dirac 1928

I) Dirac 3+1 versus Weyl 2+1

Usual Dirac equation 3+1 : QED

relativistic electron

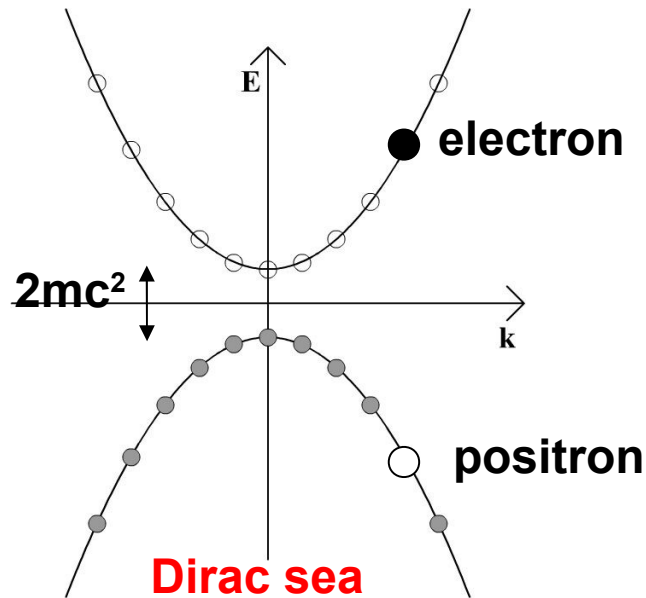
$$\varepsilon = \pm \sqrt{p^2 c^2 + m^2 c^4}$$

$$H_D = cp \cdot \alpha + mc^2 \beta$$

c =light velocity

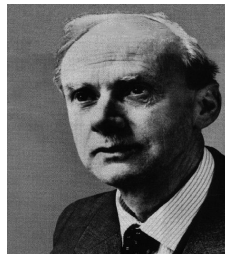
$\alpha_x, \alpha_y, \alpha_z, \beta$: four 4×4 matrices

spin \uparrow / \downarrow and electron/positron



Dirac equation 1928

Positron (Dirac 1930)



Massless Dirac (Weyl) 2+1 : graphene

massless electron (\sim charged neutrino)

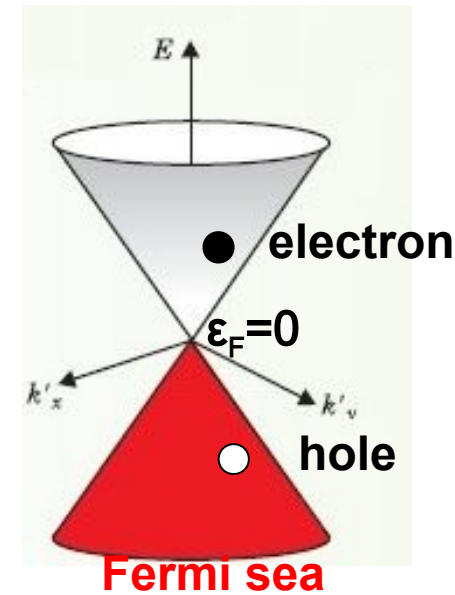
$$\varepsilon = \pm v_F p$$

$$H_W = v_F p \cdot \alpha$$

v_F =Fermi velocity $\approx c/300$

$\alpha_x, \alpha_y, \beta$: three 2×2 (Pauli) matrices

electron/hole (no spin)



Weyl equation for neutrino 1929

Hole in semiconductors (Peierls 1929

Heisenberg 1930)



II) Chirality (helicity) and sublattice spin

Chirality = helicity = projection of sublattice spin σ on the direction of motion

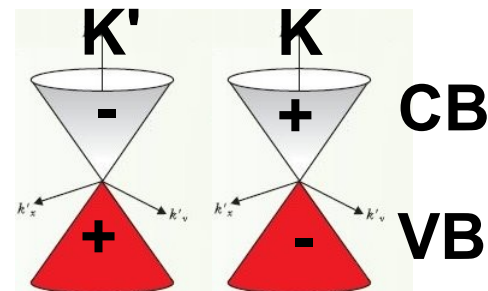
$$C \equiv \sigma \cdot \frac{\mathbf{p}}{p}$$

is the chirality operator. Its eigenvalues are $\gamma = \pm 1$. Chirality is conserved $[H_\xi, C] = 0$. The Hamiltonian $H_\xi = \xi v_F \mathbf{p} \cdot \boldsymbol{\sigma} = v_F p \xi C$. Eigenvectors of H_ξ can be indexed as $|\mathbf{p}, \gamma, \xi\rangle$:

$$\langle \mathbf{r}, l, \xi' | \mathbf{p}, \gamma, \xi \rangle = e^{i\mathbf{p} \cdot \mathbf{r} / \hbar} \delta_{\xi, \xi'} \frac{1}{\sqrt{2}} \begin{cases} 1 & \text{if } l = A \\ \gamma e^{i\xi\theta_{\mathbf{p}}} & \text{if } l = B \end{cases} \quad \text{and } \varepsilon_{\mathbf{p}, \gamma, \xi} = \xi \gamma v_F p = \alpha v_F p$$

where $\tan \theta_{\mathbf{p}} = p_y / p_x$.

Therefore: band index (α) = valley (ξ) \times chirality (γ)



Electrons in graphene are massless and chiral.

V) Velocity and Zitterbewegung

Velocity operator $v \sim$ sublattice spin σ

$$\underline{v} \equiv \frac{d\mathbf{r}}{dt} = \frac{1}{i\hbar} [\mathbf{r}, H_\xi] = \underline{\xi v_F \sigma} \quad (\text{Breit 1928})$$

Therefore $H_\xi = \mathbf{v} \cdot \mathbf{p}$.

Velocity is not conserved $[H_\xi, \mathbf{v}] \neq 0 \Rightarrow$ Zitterbewegung (jittering motion).

On average :

$$\langle \mathbf{v} \rangle = \alpha v_F \frac{\mathbf{p}}{p}$$

Velocity is not proportional to \mathbf{p}



Schrödinger 1930

V) Absence of backscattering

A smooth impurity potential at the lattice scale :

$$H = v_F \mathbf{p} \cdot \boldsymbol{\sigma} \otimes \tau_z + V(\mathbf{r}) \mathbb{I}_{4 \times 4}$$

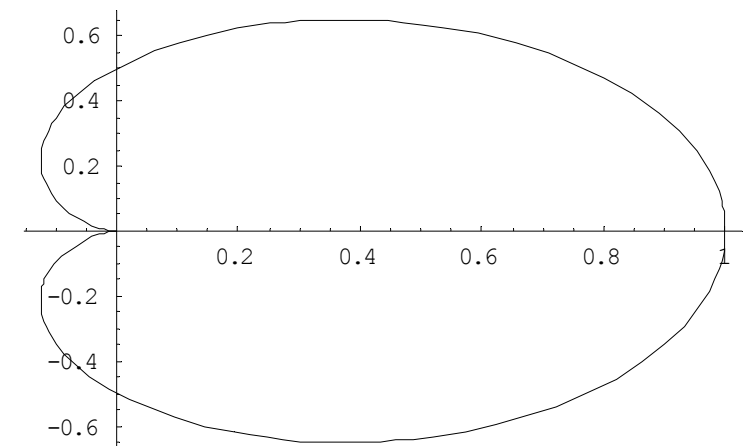
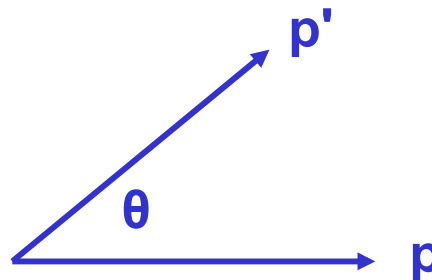
It can not scatter between valleys. It does not act on the sublattice spin $\boldsymbol{\sigma}$. It does act on \mathbf{p} .

Initial state $|\mathbf{p}, \gamma, \xi\rangle$. Final state $|\mathbf{p}', \gamma', \xi'\rangle$. Elastic scattering and intravalley $\Rightarrow \xi' = \xi, \gamma' = \gamma, p' = p$.

Scattering probability at the Born approximation :

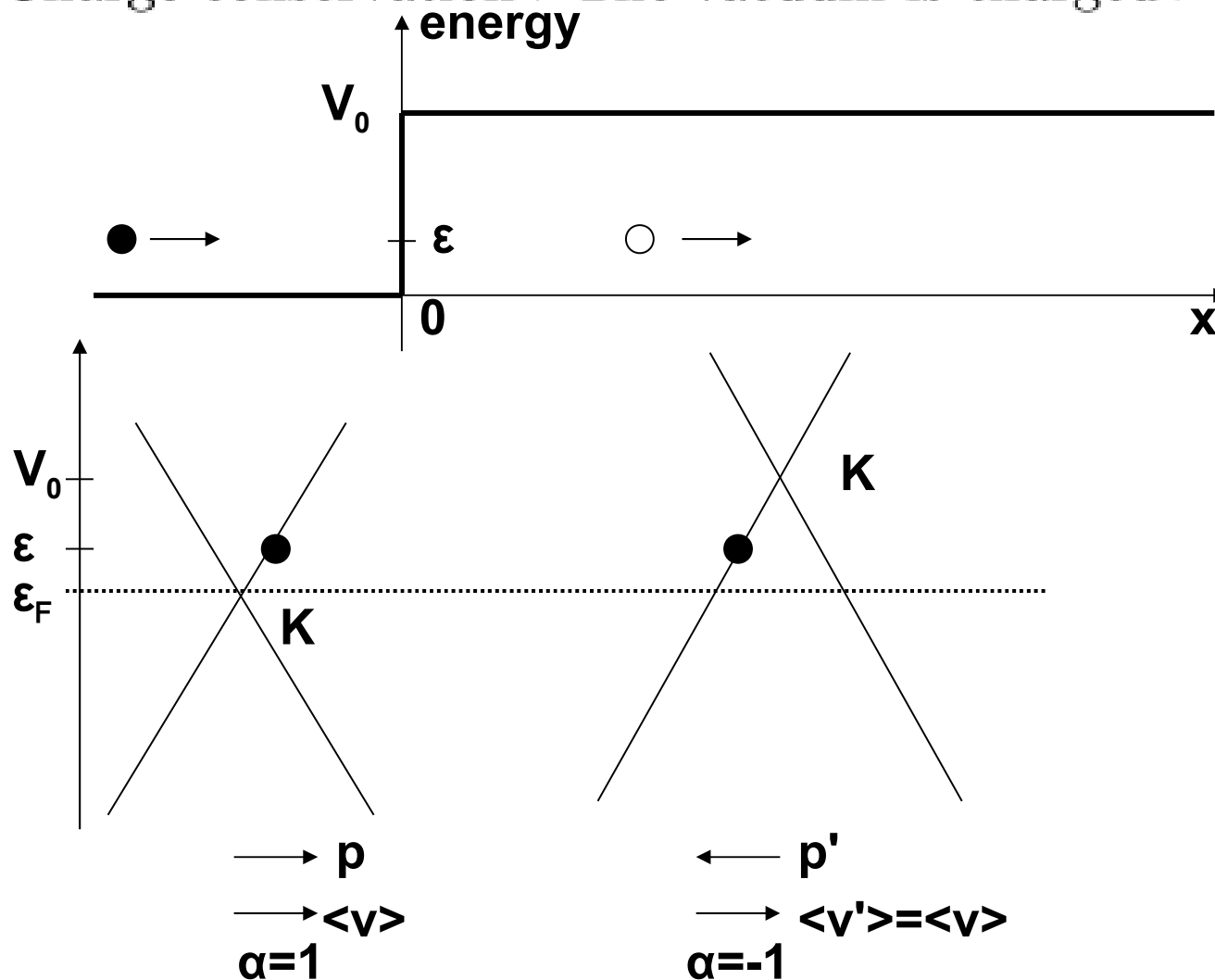
$$P(\theta) \propto |\langle \mathbf{p}', \gamma, \xi | V_{\text{imp}} | \mathbf{p}, \gamma, \xi \rangle|^2 = |\tilde{V}_{\text{imp}}(\mathbf{p}' - \mathbf{p})|^2 \cos^2(\theta/2)$$

Absence of backscattering : $P(\pi) = 0$.



V) Klein tunneling

An electron normally incident on a high potential step ($V_0 \gg 2mc^2$) is perfectly transmitted. Indeed it can not be backscattered. It propagates in the potential step as a hole. Charge conservation? The vacuum is charged!



O. Klein 1929

Proposal for an experimental observation with graphene:
Katsnelson, Novoselov, Geim, Nature Physics 2006.

V) Effective theory: summary

The 2×2 structure of the Dirac Hamiltonian is in sublattice space (sublattice index $l = A, B$), i.e. band space. Physically : one has to consider the two bands simultaneously.

There are 4 copies of the Dirac equation (4 types of electrons) :

$$4 = 2(\text{spin}) \times 2(\text{valley})$$

$$\Rightarrow 8 \times 8 \text{ Hamiltonian } H = v_F \mathbf{p} \cdot \boldsymbol{\sigma} \otimes \tau_z^{\text{valley}} \otimes \mathbb{I}^{\text{spin}}.$$

Spin index $s_z = \uparrow, \downarrow$ and valley index $\xi = +1(K), -1(K')$.

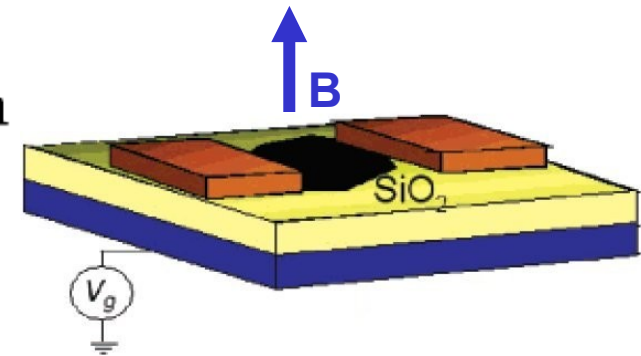
In the absence of interactions, disorder, special boundary conditions, etc., the four types of electrons are (almost) independent.

Beware of “spin”, “pseudospin”, “isospin” that may refer to the (real) spin, or to the sublattice index, or to the valley index!

VI) In a magnetic field

VI) Electronic properties ($B \neq 0$)

Strong perpendicular magnetic field B : $\omega_c \tau = \mu B \gg 1$
 where $\mu \sim 1 \text{ m}^2/\text{V.s}$ is the mobility, τ the time between collisions and $B \sim 10 \text{ T}$.

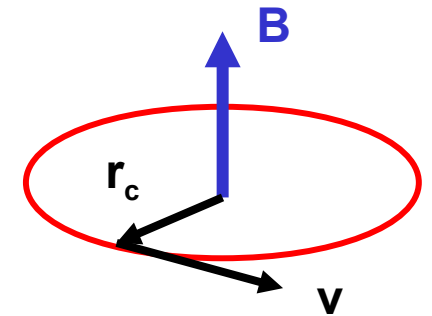


- Classical 2D cyclotron motion for an isotropic dispersion relation $\varepsilon(p)$:

$$\frac{d\mathbf{p}}{dt} = -e \frac{d\mathbf{r}}{dt} \times \mathbf{B} \text{ où } \mathbf{p} = \text{momentum}$$

hence

$$r_c = \frac{p}{eB} \text{ and } \omega_c = \frac{v}{r_c} = \frac{eB}{p} \frac{\partial \varepsilon}{\partial p}$$



examples :

$$\varepsilon = \frac{p^2}{2m^*} \Rightarrow \omega_c = \frac{eB}{m^*} \text{ independent of } \varepsilon \text{ and } r_c = \frac{\sqrt{2m^* \varepsilon}}{eB}$$

$$\varepsilon = v_F p \Rightarrow \omega_c = \frac{eB}{\varepsilon/v_F^2} \propto \varepsilon^{-1} \text{ and } r_c = \frac{\varepsilon}{eB v_F}$$

effective cyclotron mass $m_c = \varepsilon/v_F^2 = \hbar k_F/v_F \propto \sqrt{n_c}$

VI) Electronic properties ($B \neq 0$)

- Semiclassical quantization of the cyclotron orbits :

Bohr's correspondence principle \Rightarrow

$$\varepsilon_{n+1} - \varepsilon_n \approx \hbar \omega_c^{\text{cl.}}(\varepsilon_n) \text{ when } n \text{ integer } \gg 1$$

hence

$$\int \frac{d\varepsilon}{\hbar \omega_c^{\text{cl.}}(\varepsilon)} = n + \gamma \text{ où } 0 \leq \gamma < 1$$

examples :

$$\varepsilon = \frac{p^2}{2m^*} \Rightarrow \varepsilon_n = \hbar \frac{eB}{m^*} (n + \gamma) \propto Bn$$

$$\varepsilon = \alpha v_F p \Rightarrow \varepsilon_n = \alpha \sqrt{2\hbar v_F^2 eB} (n + \gamma) \propto \alpha \sqrt{Bn}$$



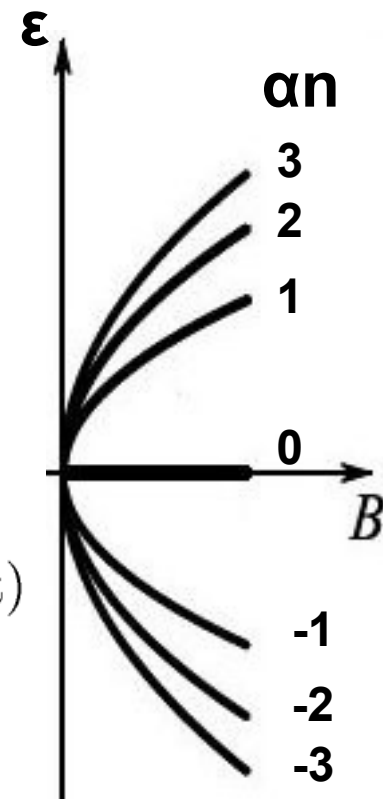
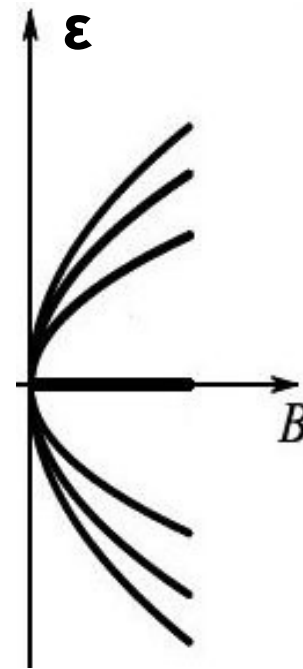
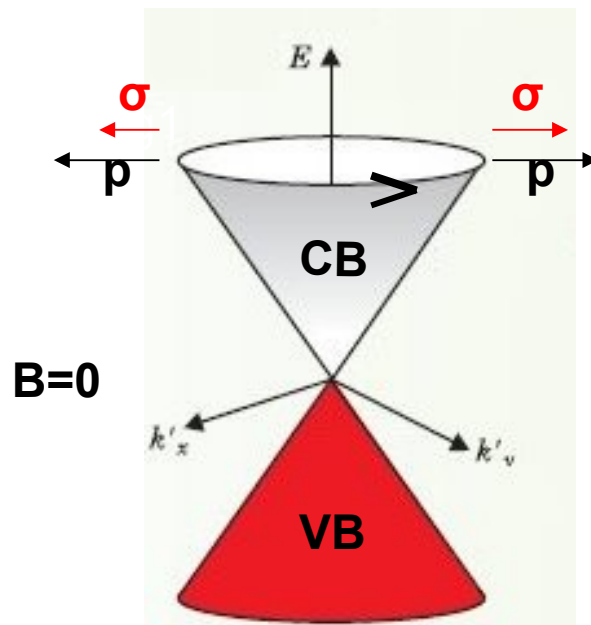
$n = 0, 1, 2, \dots =$ Landau level index

$\gamma =$ phase mismatch (integration constant)

VI) Electronic properties ($B \neq 0$)

• Phase mismatch γ , Berry phase and zero energy states :

- usually : $\gamma = 1/2$ (cf. Bohr-Sommerfeld) and $\varepsilon_n = \hbar\omega_c(n + 1/2)$
- if the cyclotron trajectory in reciprocal space surrounds a contact point between two linear bands, there is an extra (Berry) phase of π in the semiclassical quantization condition and therefore $\gamma = 0$ (Mikitik and Sharlai, PRL 1999) :



Hence

$$\varepsilon_{n,\alpha} = \alpha \sqrt{2\hbar v_F^2 e B n} \text{ où } n = 0, 1, 2, \dots \text{ [McClure 1956]} \text{ (exact result)}$$

- there are zero energy states : $n = 0, \varepsilon_0 = 0, r_c = 0!$

VI) Electronic properties (B≠0)

- Cyclotron radius and Landau level degeneracy :

$$r_n = \frac{|\varepsilon_n|}{eBv_F} = \sqrt{2n} \sqrt{\frac{\hbar}{eB}} = \sqrt{2nl_B} \text{ where } l_B = \text{magnetic length}$$

Area occupied by a quantized cyclotron orbit : $\pi r_{n+1}^2 - \pi r_n^2 = 2\pi l_B^2$

Number of orbits with energy ε_n in the sample :

$$N_\phi \equiv \frac{\mathcal{A}}{2\pi l_B^2} = \frac{BA}{h/e} = \frac{\text{flux in the sample}}{\text{flux quantum}}$$

Landau level degeneracy : $2(\text{spin}) \times 2(\text{valley}) \times N_\phi = 4N_\phi$

- Landau level filling :

- Undoped graphene : the big band (VB + CB) is half-filled.

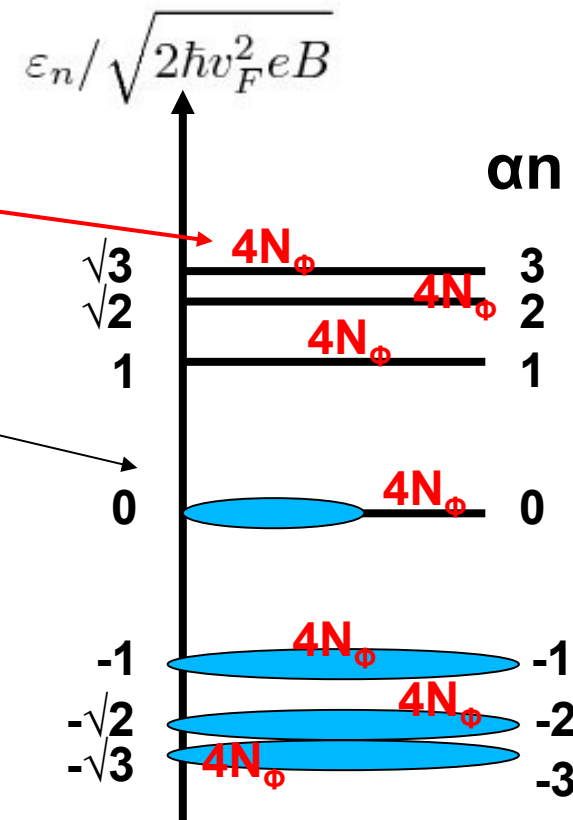
Filling factor defined so that $\nu(V_g = 0) = 0$

- Doped graphene ($V_g \neq 0$) :

$$\nu \equiv \frac{N_c}{N_\phi} \propto \frac{V_g}{B}$$

- No partially filled Landau level when :

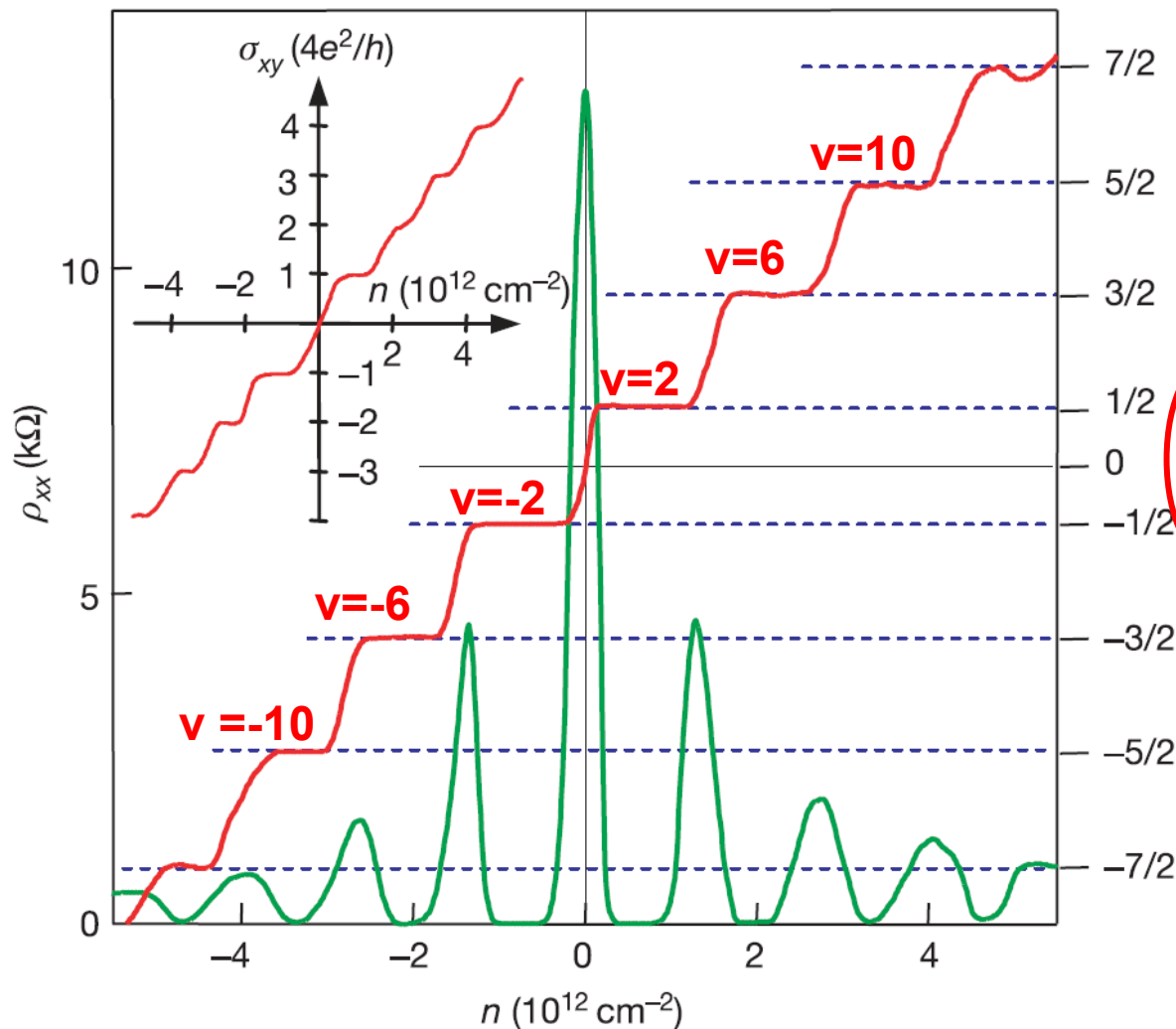
$$\nu = \pm 2; \pm 6; \pm 10; \dots = \pm 4(n + 1/2)$$



VII) “Relativistic” quantum Hall effect

VII) « Relativistic » quantum Hall effect

Plateaux in the Hall conductivity $\sigma_{xy} = \nu e^2/h$ expected when all LLs either full or empty $\nu = \pm f(n + 1/2 + \gamma) = \pm 4(n + 1/2)$ where $f = \text{extra LL degeneracy} = 2(\text{spin}) \times 2(\text{valley}) = 4$
 $\gamma = \text{phase mismatch} = 0$ in graphene



Usual IQHE : $\gamma = 1/2$ and $f = 2$

Experiment : $\gamma = 0$ and $f = 4$

Novoselov et al., Nature 2005
Zhang et al., Nature 2005

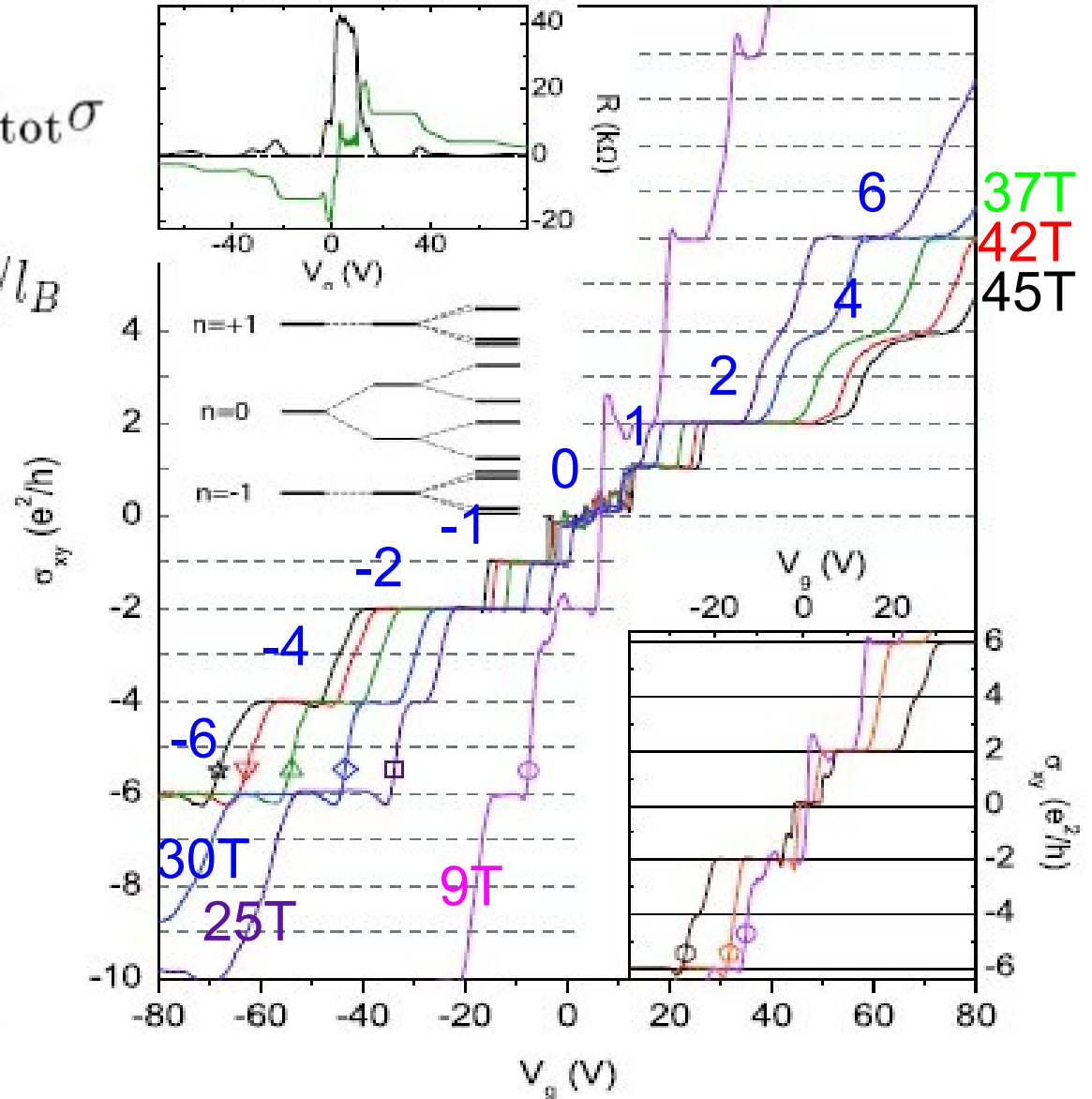
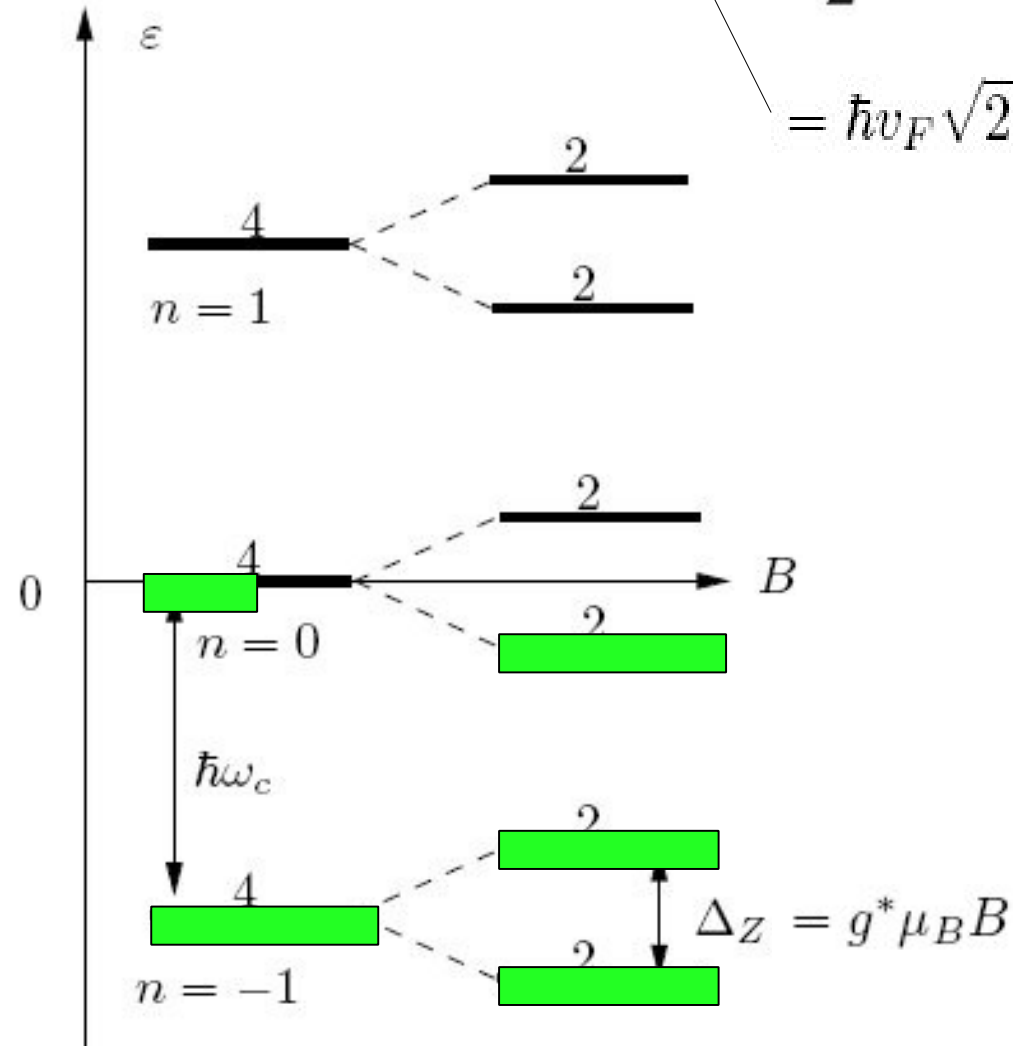
VII) Graphene at large B: extra QH states

Th.: Landau levels + Zeeman:
filling factor = $0; \pm 2; \pm 4; \pm 6; \pm 8; \text{etc.}$

Exp.: filling factor = $0; \pm 1; \pm 2; \pm 4; \pm 6$
but not filling factor = $\pm 3; \pm 5$

$$\varepsilon_{n,\sigma} = \text{sgn}(n) \sqrt{|n|} \hbar \omega_c + \frac{g^*}{2} \mu_B B_{\text{tot}} \sigma$$

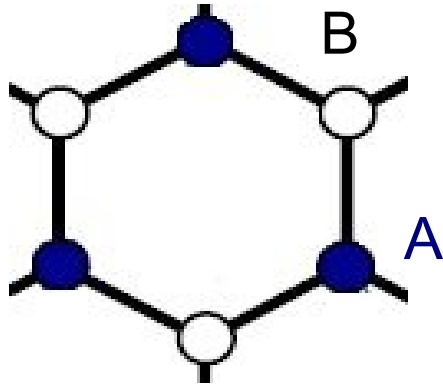
$$= \hbar v_F \sqrt{2} / l_B$$



Zhang et al., Phys. Rev. Lett. 2006.

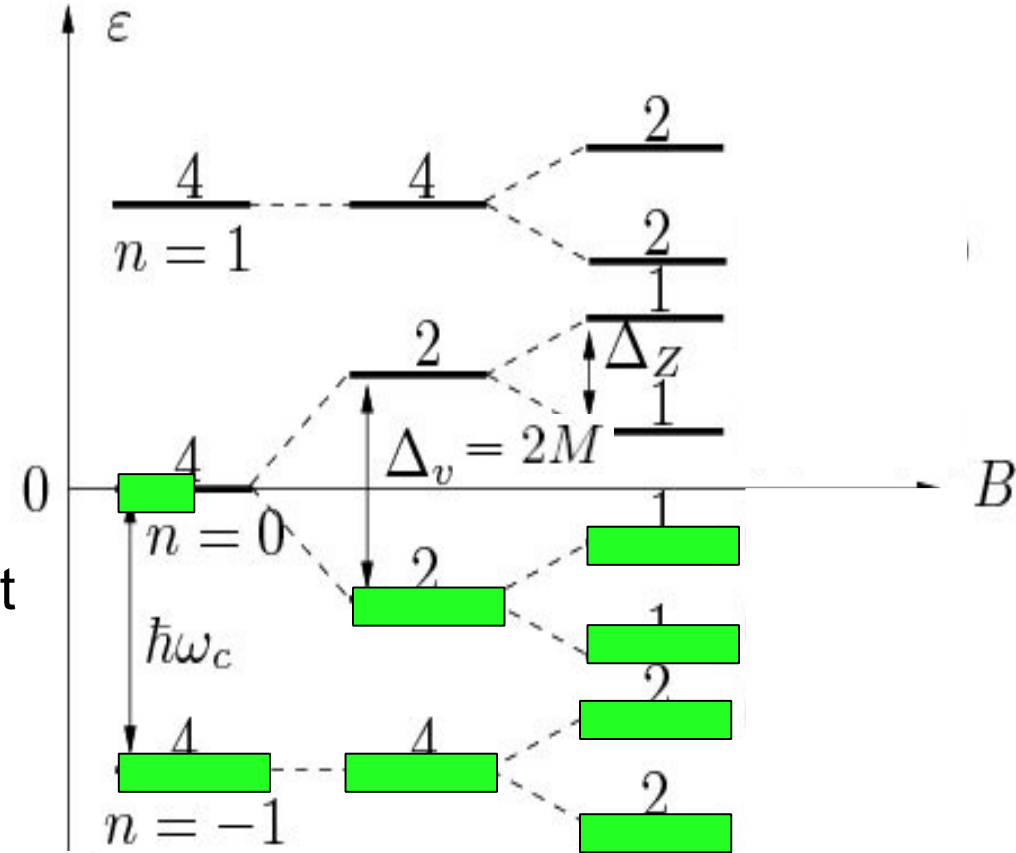
Parity breaking of the honeycomb lattice

If A and B atoms are different (e.g. boron nitride) then the honeycomb lattice's inversion symmetry is broken and the valley degeneracy is lifted (in $n=0$).



A and B carbon atoms are now assumed to be different. Tight-binding model with different on-site energies $\pm M$ (Haldane, PRL 1988):

$$\begin{aligned} \varepsilon_{n,\sigma,\alpha} &= \text{sgn}(n) \sqrt{M^2 + (\hbar\omega_c)^2 |n|} + \frac{\Delta_Z}{2} \sigma \text{ if } n \neq 0 \\ &= \alpha M + \frac{\Delta_Z}{2} \sigma \text{ if } n = 0 \end{aligned}$$



Central Landau level ($n=0$): $\alpha = +1 = A$ and $\alpha = -1 = B$
 Not true for the other Landau levels ($n \neq 0$)

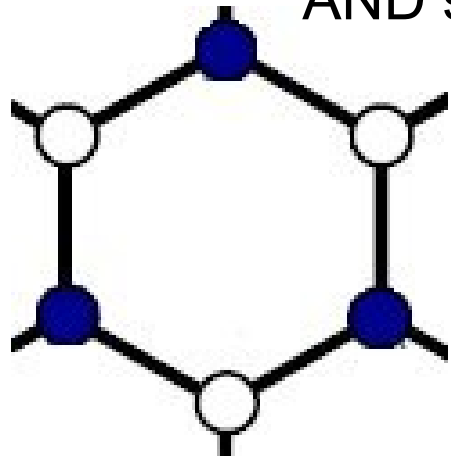
Magnetic field driven Peierls distortion

Fuchs and Lederer, Phys. Rev. Lett. 2007

How can one have $A \neq B$?

Out-of-plane lattice distortion

AND substrate (SiO_2) \neq superstrate (air)



B moves towards the silicon dioxide substrate ($-\eta$)

A moves away from the substrate ($+\eta$)

Electronic energy (gain): $E_{n=0} = -N_\phi(2 - |\nu|)M$; $E_{n<0} = -0.7 \frac{N_p a}{\hbar v_F} M^2$; $M = D\eta$

Elastic energy (cost): $E_{\text{elastic}} = N_p G \eta^2$ where $N_p =$ number of unit cells.

Effective elastic energy: $E'_{\text{elastic}} \equiv E_{\text{elastic}} + E_{n<0} = N_p G' \eta^2$ with $G' \equiv G - 0.7 D^2 a / \hbar v_F$

Total energy: $E_{\text{tot}} = E_{n=0} + E'_{\text{elastic}}$

Minimizing the total energy: $\Delta_v = \frac{N_\phi}{N_p} (2 - |\nu|) \frac{D^2}{G'} \propto B_\perp$

Estimate of the constants D and G

G = elastic constant corresponding to the out-of-plane optical phonon mode (ZO)

$$\omega_0/2\pi c \sim 800\text{cm}^{-1} \text{ (for graphite)} \quad Ga^2 \approx m_c \omega_0^2 a^2 / 4 \sim 14\text{eV}$$

D = “deformation potential”, coupling to the substrate

Rough estimate of the coupling to the substrate via the Lennard-Jones interaction of a carbon atom with the substrate: $Da \approx 1$ to 14 eV

No deformation when $B=0$: $G' > 0$ therefore $Da < 9,8\text{eV}$

Valley splitting is larger than Zeeman splitting if $Da > 6.3\text{eV}$

To explain the experiments, we choose $Da \approx 7.8$ eV, therefore $G'a^2 \approx 4,2\text{eV}$

$$\Delta_v = 2M \approx 4.2\text{K} \times (1 - |\nu|/2) B_{\perp} [\text{T}]$$

$$\hbar\omega_c \approx 420\text{K} \times \sqrt{B_{\perp} [\text{T}]}$$

$$\Delta_Z = g^* \mu_B B_{\text{tot}} \approx 1.5\text{K} \times B_{\text{tot}} [\text{T}]$$

$$\Delta_{\text{imp}} \approx 30\text{K}$$

Experimental tests

Experiments should decide which mechanism is responsible for lifting the valley degeneracy in graphene. Out-of-plane lattice distortion implies:

- Valley gap as a function of the magnetic field: $\Delta_v \propto B_{\perp}$
- Valley gap as a function of the gate voltage: $\Delta_v \propto (2 - |\nu|)$ with $\nu \propto V_g$
- Lattice distortion: X-ray diffraction at grazing incidence; STM; Helium surface diffraction; etc.
- IR absorption spectroscopy of the ZO phonons
- In a symmetric dielectric environment, the lattice distortion should vanish (e.g. for a suspended graphene sheet).

Recent experiments: Checkelsky, Li and Ong, Phys. Rev. Lett. And Phys. Rev. B (2009).

VIII) Extras

2010 Nobel prize awarded for what?



Andre Geim



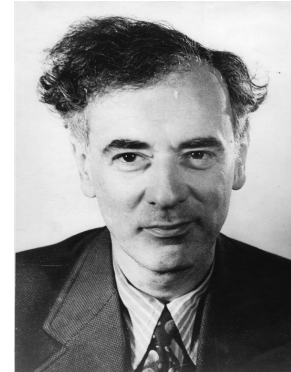
Kostya Novoselov

1) Scotch tape trick: brought graphene to every lab (but certainly not as an industrial material). Brought graphene to the masses (researchers but not laymen).

2) Graphene isolated on a dielectric substrate, contacted and gated: it provides a new tunable and ambipolar 2D electron gas (2DEG) with unique properties unlike standard 2DEGs such as those based on semiconductors (silicon-MOSFET, AsGa/AsGaAl heterostructures, etc.). The most spectacular consequence being the « relativistic » quantum Hall effect that confirms the presence of massless Dirac fermions.

There is no such thing as a 2D crystal!

A theorem stating that 2D crystals can not exist at finite temperature (Mermin et Wagner 1968; physical arguments by Peierls et Landau 1930)

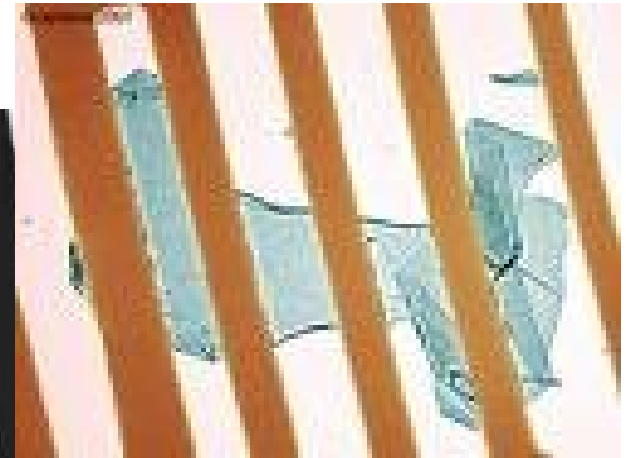


Actually, this theorem assumes a 2D crystal embedded in a 2D space and proves by contradiction that the crystalline order is destroyed by thermal fluctuations.

However, graphene is a 2D crystalline membrane embedded in a 3D space: the out-of-plane (bending) fluctuations couple to the in-plane ones (stretching) and stabilise the membrane. It neither melts nor crumples, but it ripples.

Suspended graphene

J. Meyer et coll., Nature 2007

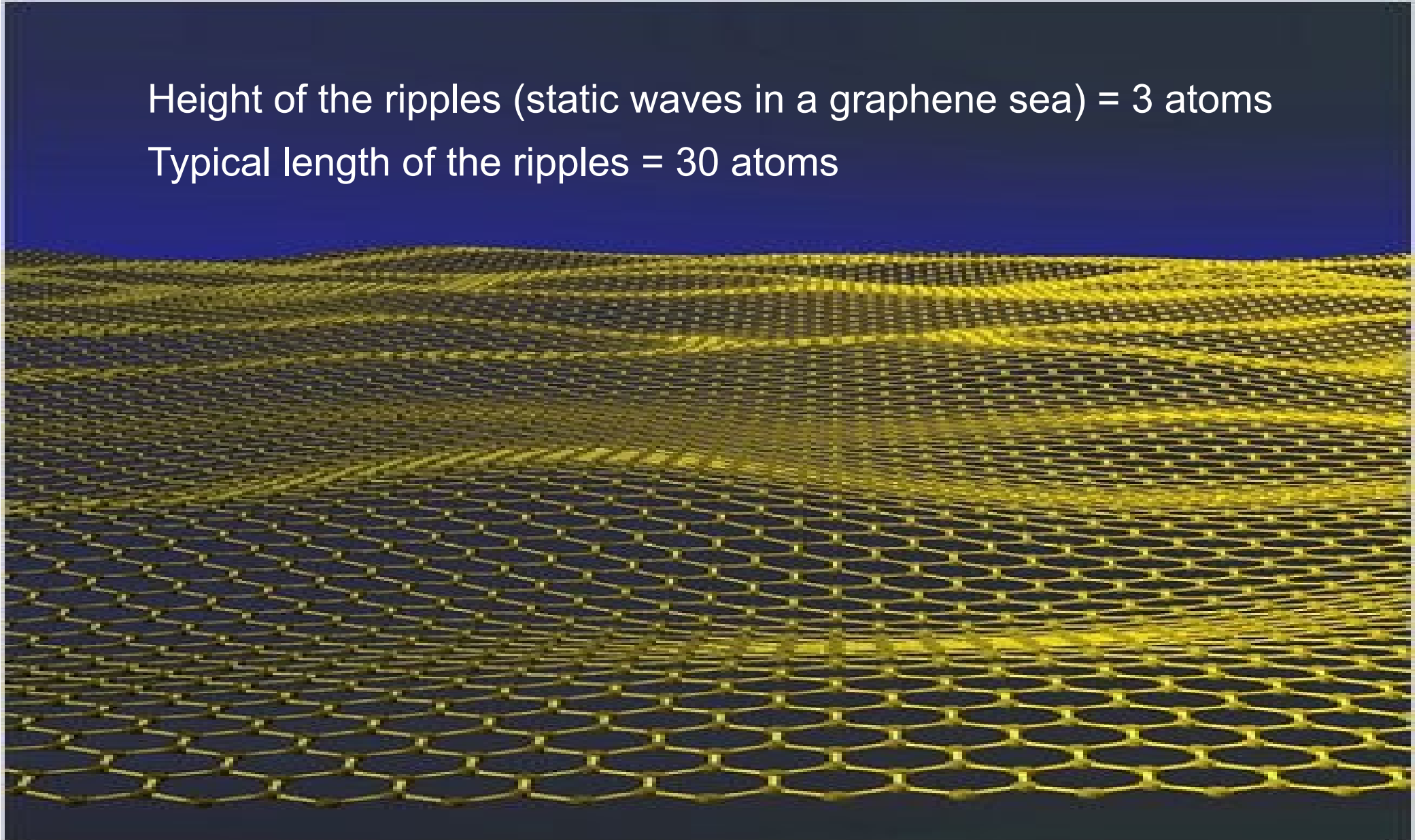


Recently B.E. Kane's proposal of floating and spinning graphene (PRB 2010)

Graphene crinkles in order to exist

J. Meyer et coll., Nature 2007

Height of the ripples (static waves in a graphene sea) = 3 atoms
Typical length of the ripples = 30 atoms

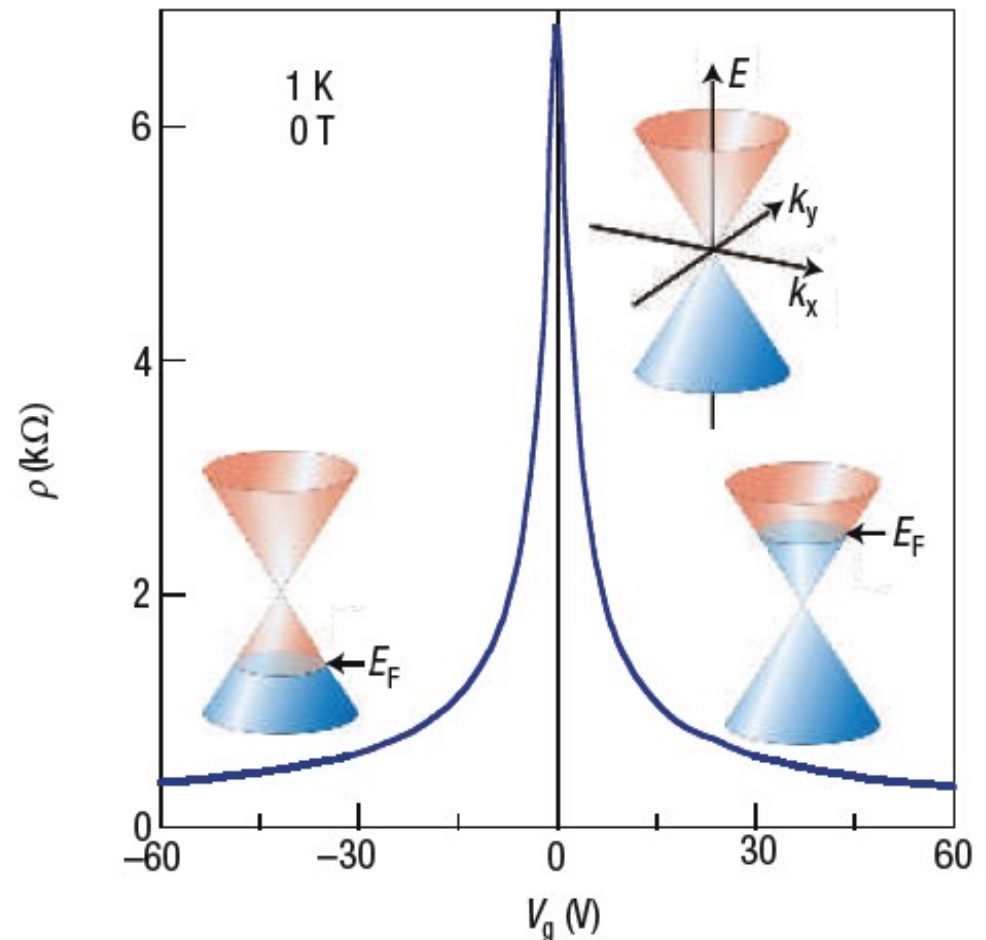


There is no such thing as a 2D metal!

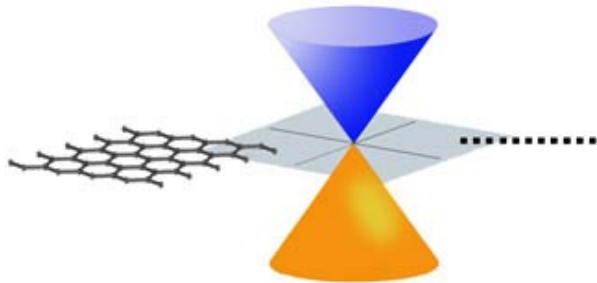
Still conducting even in the absence of doping (minimal conductivity of the order of the conductance quantum e^2/h)

Ando calls it a 2D semi-metal with zero band overlap rather than a 2D gapless semiconductor

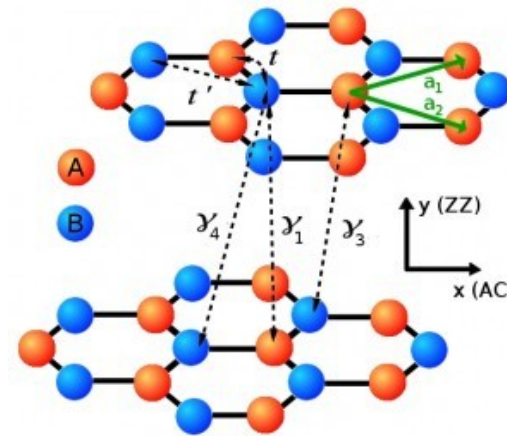
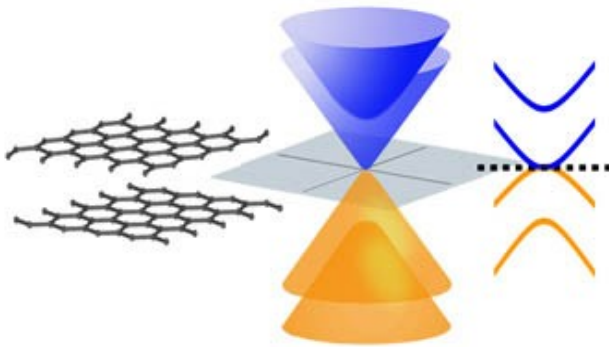
And at the lowest temperature despite the presence of disorder: no localization by disorder? Seems to contradict the scaling theory of localization.



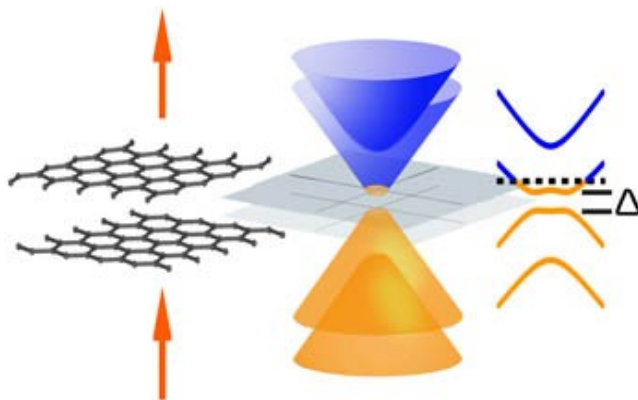
Bilayer: different and also unique



Monolayer: massless Dirac electrons
(chiral: π Berry phase, gapless, 2 bands)

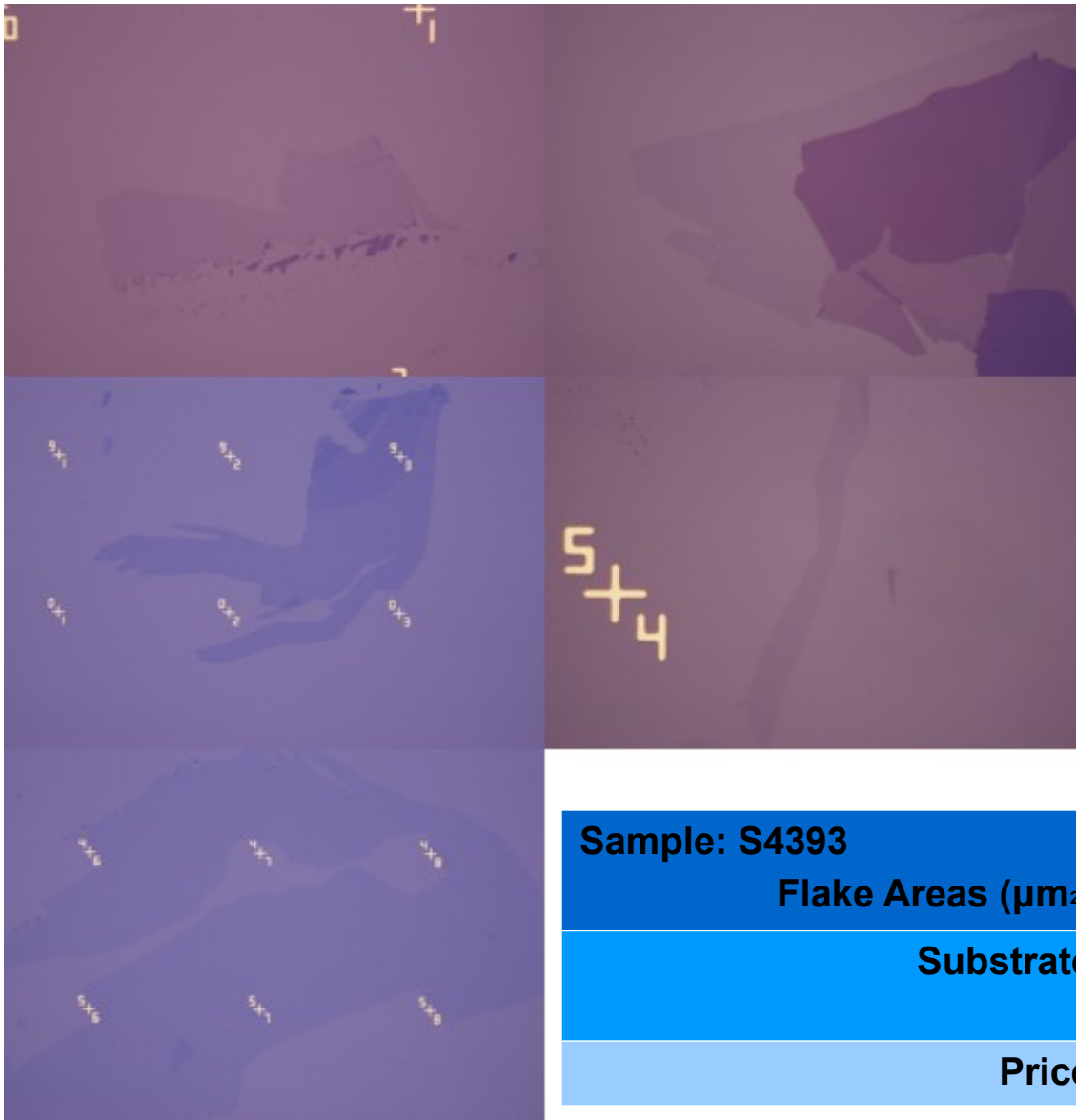


Bilayer: massive chiral (2π Berry phase)
electrons (but still gapless, 4 bands)



Gated bilayer: gapped and massive chiral
Electrons (4 bands, inversion symmetry lost)

Is graphene expensive?



www.grapheneindustries.com

Roughly: « scotch tape trick » graphene cost about 1000 euros for 10000 squared microns (but remember the 76cm flake by CVD)

Sample: S4393	3500, 1500, 25000 (bilayer), 400, 150000
Flake Areas (μm^2)	
Substrate	300nm SiO ₂ on n-doped 380 μm Si
Price	£2300

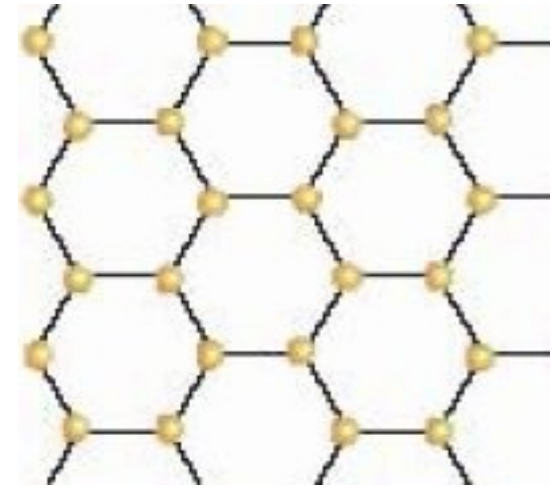
Conclusion: main ideas

Graphene = 2D honeycomb carbon crystal (thickness of a single atom), a carbon membrane that is rippled.

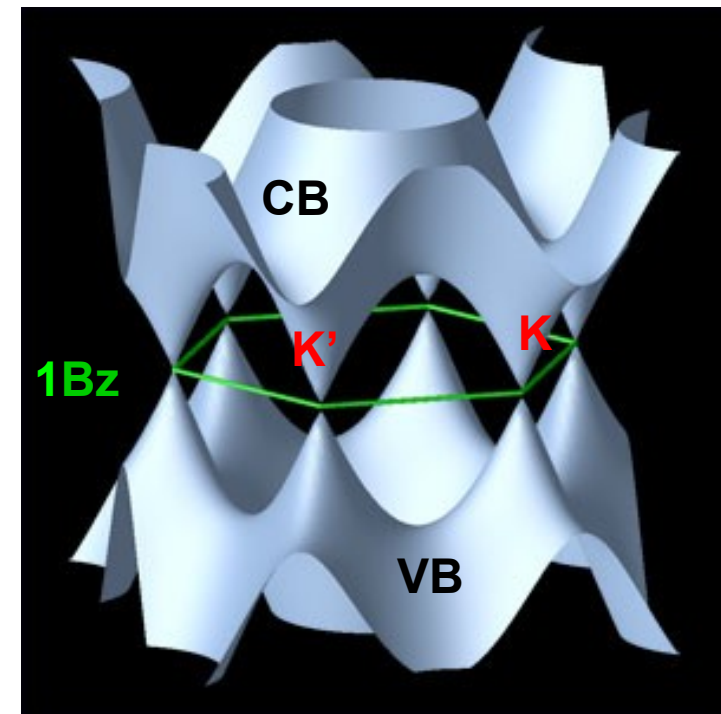
Graphene's magic comes from its peculiar band structure:

- The valence (VB) and conduction bands (CB) meet in 2 (not 6) points (K, K') in reciprocal space [Dirac points].
 - The dispersion relation close to the Dirac points is linear [diabolo].
 - The VB is full, the CB is empty: the Fermi level is right at the Dirac points.
- Graphene is a 2 valleys (K, K') 2D semi-metal (with zero band overlap).

Direct space



Reciprocal space



Références générales

Articles de vulgarisation scientifique:

- J.N Fuchs et M.O. Goerbig, Pour la Science, mai 2008, page 36
- D. Larousserie, Sciences et Avenir, juillet 2007, page 73

Sur la toile:

- J.N. Fuchs, M.O. Goerbig et M. Potemski, Images de la physique 2007 (CNRS), page 50
<http://www.cnrs.fr/publications/imagesdelaphysique/2007.htm>
- Site d'Andre Geim et de son équipe à Manchester
<http://onnes.ph.man.ac.uk/nano/>
- Faire du graphène soi-même (site de Scientific American):
<http://www.sciam.com/article.cfm?id=diy-graphene-how-to-make-carbon-layers-with-sticky-tape>
- Transparents de cours sur le graphène (école de Cargèse octobre 2010):
<http://www.graphene-nanotubes.org/fr/nanotubes-summer-school/lectures.html>
- Site du prix Nobel de physique 2010:
http://nobelprize.org/nobel_prizes/physics/laureates/2010/

