Known and unknown about graphene.

Vladimir Falko Lancaster University

I. Graphene 101: pure and disordered monolayer graphene.
II. Electronic properties of bilayer graphene, from high to low energies. Interaction effects in graphenes.

Graphene 101



Graphene for beginners: tight-binding model. Berry phase π electrons in monolayers. Landau levels & the QHE in graphene: epitaxial graphene for quantum metrology. Strained monolayer graphene. Close relative: silicene.



D.I.Y. Graphene Geim & Novoselov (Manchester) 2004



 Prepare a wafer of oxidized silicon, which helps you see graphene layers under a microscope. To smooth out the surface to accept the graphene and to clean it thoroughly, apply a mix of hydrochloric acid and hydrogen peroxide.
 Attach a graphite flake to about six inches of plastic sticky tape with tweezers.

Fold the tape at a 45-degree angle right next to the flake, so that you sandwich it

between the sticky sides. Press it down gingerly and peel the tape apart slowly enough so that you can watch the graphite cleaving smoothly in two.

- 4 Repeat the third step about 10 times. This procedure gets harder to do the more folds you make.
- 5 Carefully lay the cleaved graphite sample that remains stuck to the tape

onto the silicon. Using plastic tongs, gently press out any air between the tape and sample. Pass the tongs lightly but firmly over the sample for 10 minutes. With the tongs, keep the wafer planted on the surface while slowly peeling off the tape. This step should take 30 to 60 seconds to minimize shredding of any graphene you have created.





Graphene

6 Place the wafer under a microscope fitted with a 50× or 100× objective lens. You should see plenty of graphite debris: large, shiny chunks of all kinds of shapes and colors (*upper image*) and, if you're lucky, graphene: highly transparent, crystalline shapes having little color compared with the rest of the wafer (*lower image*). The upper sample is magnified 115×; the lower 200×.

Epitaxial graphene sublimated on the Si face of SiC: SiC/G



Lauffer, Emtsev, Graupner, Seyller (Erlangen), Ley PRB 77, 155426 (2008) Reconstructed dead layer with a large unit cell: can carry defects (donors) in a large variety of positions, therefore, provides a broad band of surface donor states.



Gaskill et al, **(HRL Malibu)** ECS Trans. 19, 117 (2009)



Growth of graphene by chemical vapour deposition on metals



a) Schematic of the process. b) A Cu foil wrapping around a 7.5-inch quartz tube to be inserted into an 8-inch quartz reactor. c) Roll-to-roll transfer of graphene films from a thermal release tape to a PET film.





highly conductive polycrystalline monolayers, with up to 10µm – size single-crystals. 4 electrons in the outer s-p shell of carbon

 sp^2 hybridisation forms strong directed bonds which determine a honeycomb lattice structure.





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 $P^{z}(\pi)$ orbitals determine conduction properties of graphite



Graphene: gapless semiconductor

Wallace, Phys. Rev. 71, 622 (1947) Slonczewski, Weiss, Phys. Rev. 109, 272 (1958)









$$H_{AB,K} = \gamma_0 \left[e^{-i\frac{2\pi}{3}} e^{-i(\frac{a}{2}p_x + \frac{a}{2\sqrt{3}}p_y)} + e^{i\frac{a}{\sqrt{3}}p_y} + e^{i\frac{2\pi}{3}} e^{i(\frac{a}{2}p_x - \frac{a}{2\sqrt{3}}p_y)} \right]$$
$$\approx \frac{\sqrt{3}}{2} \gamma_0 a(p_x - ip_y)$$

$$H_{BA,K} \approx \frac{\sqrt{3}}{2} \gamma_0 a(p_x + ip_y) \equiv v\pi$$

Bloch function amplitudes (e.g., in the valley K) on the AB sites ('isospin') mimic spin components of a massless relativistic particle.





McClure, PR 104, 666 (1956)

 $v = \frac{\sqrt{3}}{2} \gamma_0 a \sim 10^8 \, \frac{cm}{sec}$





Two non-equivalent **K-points**



Also, one may need to take into account an additional real spin degeneracy of all states



$$H = v \begin{pmatrix} 0 & \pi^+ \\ \pi & 0 \end{pmatrix} = v \vec{\sigma} \cdot \vec{p}$$

$$\vec{p} = (p \cos \theta, p \sin \theta)$$
$$\pi = p_x + ip_y = pe^{i\theta}$$
$$\pi^+ = p_x - ip_y = pe^{-i\theta}$$

sublattice 'isospin' $\vec{\sigma}$ is linked to the direction of the electron momentum $\vec{\sigma}$

$$\vec{\sigma} \cdot \vec{n} = 1, \varepsilon = vp$$

 $\vec{n} = -1, \varepsilon = -vp$
valence band \vec{p}

aanduction hand





Electronic states in graphene observed using ARPES



$$H \approx v \begin{pmatrix} 0 & \pi^{+} \\ \pi & 0 \end{pmatrix} - \frac{v^{2} \varsigma}{6 \gamma_{0}} \begin{pmatrix} 0 & \pi^{2} \\ (\pi^{+})^{2} & 0 \end{pmatrix} + \alpha \begin{pmatrix} p^{2} & p^{2} \\ p^{2} & p^{2} \end{pmatrix}$$
trigonal warping term
$$H_{AB,K_{+}} = \gamma_{0} \left[e^{-i\frac{2\pi}{3}} e^{-i(\frac{a}{2}p_{x} + \frac{a}{2\sqrt{3}}p_{y})} + e^{i\frac{a}{\sqrt{3}}p_{y}} + e^{i\frac{2\pi}{3}} e^{i(\frac{a}{2}p_{x} - \frac{a}{2\sqrt{3}}p_{y})} \right]$$

$$\approx \frac{\sqrt{3}}{2} \gamma_{0} a(p_{x} - ip_{y}) - \frac{\gamma_{0}a^{2}}{8} (p_{x} + ip_{y})^{2}$$

$$\pi = p_{x} + ip_{y} = pe^{i\theta}$$

$$\pi = p_{x} - ip_{y} = pe^{-i\theta}$$

$$\vec{p} \rightarrow -\vec{p}; K_{\pm} \rightarrow K_{\mp}$$

A. Bostwick *et al* – Nature Physics 3, 36 (2007)

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2D Landau levels

semiconductor QW / heterostructure (GaAs/AlGaAs)

$$\vec{p} = -i\hbar\nabla - \frac{e}{c}\vec{A}, \quad rot\vec{A} = B\vec{l}_z$$
$$\pi = p_x + ip_y; \quad \pi^+ = p_x - ip_y$$
$$\pi\phi_0 = 0$$
$$\phi_{n+1} = \frac{\lambda_B}{\sqrt{n+1}}\pi^+\phi_n$$

 $H = \frac{\vec{p}^2}{2m} = \frac{\pi \pi^+ + \pi^+ \pi}{4m} \Longrightarrow (n + \frac{1}{2})\hbar\omega_c \quad \text{energies / wave functions}$





$$H_1 \psi = v \begin{pmatrix} 0 & \pi^+ \\ \pi & 0 \end{pmatrix} \begin{pmatrix} \phi_0 \\ 0 \end{pmatrix} = 0 \quad \longrightarrow \quad \mathcal{E} = \mathbf{0}$$

All non-zero eigenvalues can be found by diagonalising H^2

$$\varepsilon^{\pm} = \pm \sqrt{2n} \frac{v}{\lambda_B}$$

with 4-fold degenerate $\varepsilon = 0$ Landau level

McClure - Phys. Rev. 104, 666 (1956) Haldane, PRL 61, 2015 (1988) Zheng & Ando - PRB 65, 245420 (2002)



Graphene for high-end instrumentation: universal resistance standard



Quantum Hall effect metrology: Hall resistance quantisation in monolayer graphene synthesised on Si-terminated SiC.

Precision of one part per 10⁹

Tzalenchuk, Lara-Avila, Kalaboukhov, Paolillo, Syväjärvi, Yakimova, Kazakova, Janssen, VF, Kubatkin Nature Nanotechnology 5, 186 (2010)

Precision of one part per 10¹⁰

Janssen, Fletcher, Goebel, Williams, Tzalenchuk, Yakimova, Kubatkin, Lara-Avila, VF New Journal of Physics 13, 093026 (2011)



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Strained graphene





$$\gamma_0 e^{-i\frac{2\pi}{3}} + \gamma_0 + \gamma_0 e^{i\frac{2\pi}{3}} = 0$$



$$\hat{H} = v\vec{p}\cdot\vec{\sigma} + \zeta\vec{\alpha}_{def}\cdot\vec{\sigma} \equiv v[\vec{p} + \frac{\zeta}{v}\vec{\alpha}_{def}]\cdot\vec{\sigma}$$

shift of the Dirac point in the momentum space, like some vector potential: opposite in K/K' valleys.

Iordanskii, Koshelev, JETP Lett 41, 574 (1985) Ando - J. Phys. Soc. Jpn. 75, 124701 (2006) Morpurgo, Guinea - PRL 97, 196804 (2006)

$$B_{eff} = \frac{\zeta}{v} \left[\nabla \times \vec{\alpha}_{def}(\vec{r}) \right]_{z}$$

Strain-induced pseudo-magnetic fields in graphene nanobubbles



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Silicene: honeycomb 2D layer of silicon

Exper.: Vogt, De Padova, Quaresima, Avila, Frantzeskakis, Asensio, Resta, Ealet, Le Lay - PRL 108, 155501 (2012)



Method	a (Å)	Δz (Å)	$v (10^5 \text{ ms}^{-1})$
PBE (castep)	3.86	0.45	5.27
PBE (vasp)	3.87	0.45	5.31
LDA (CASTEP)	3.82	0.44	5.34
LDA (VASP)	3.83	0.44	5.38
LDA [1]	3.83	0.44	≈ 10
HSE06 (VASP)	3.85	0.36	6.75





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'Long-range' (as compared to graphene lattice period) Coulomb disorder.



Comes from potential of charged impurities in the substrate and deposits on its surface.

Geim and Novoselov - Nature Materials 6, 183 (2007) Jang, Adam, Chen, Williams, Das Sarma, Fuhrer PRL 101, 146805 (2008) Nomura and MacDonald - PRL 96, 256602 (2006) Cheianov and VF - PRL 97, 226801 (2006) Nomura and MacDonald - PRL 98, 076602 (2007) Hwang, Adam, Das Sarma - PRL 98, 186806 (2007)

Monolayer graphene: two-dimensional gapless semiconductor with Berry phase π electrons



$$H = v\vec{\sigma} \cdot \vec{p} + \hat{1} \cdot U(\vec{r})$$

$$\psi_{\vec{p}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{-i\vartheta} \end{pmatrix} e^{i\vec{p}\vec{r}}$$

w(
$$\theta$$
)

Due to the 'isospin' conservation, A-B symmetric perturbation does not backward scatter electrons. Ando, Nakanishi, Saito - J. Phys. Soc. Jpn 67, 2857 (1998)

 $\vec{\sigma} \cdot \vec{n} = 1 \qquad \left\langle \psi_{-\vec{p}} \middle| \hat{1} \cdot U(x) \middle| \psi_{\vec{p}} \right\rangle = 0$

$$w(\theta) \sim \cos^2 \frac{\theta}{2} |U_{\vec{p}-\vec{p}'}|^2$$

Role of scattering from remote charges for graphene conduction in GraFETs





$$H = v\vec{\sigma}\cdot\vec{p} + \hat{1}\cdot U(x)$$

Potential which is smooth at the scale of lattice constant (A-B symmetric) cannot scatter Berry phase π electrons in exactly backward direction: finite conductivity even when E_F=0 (zero density).

$$w_{\vec{p}\to-\vec{p}} = \left|\sum_{i} \psi_{i}\right|^{2} = \left|\sum_{(a,b)} [\psi_{a\to b} + \psi_{b\to a}]\right|^{2} = \left|\sum_{(a,b)} 0\right|^{2} = 0$$

$$\psi_{a \to b} = A e^{i \frac{\pi}{2} \sigma_z} \psi_{\vec{p}}$$
$$\psi_{b \to a} = A e^{i \frac{-\pi}{2} \sigma_z} \psi_{\vec{p}}$$

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$$\sigma > \frac{e^2}{h}$$

$$\psi_{a\to b} = e^{i\pi\sigma_z}\psi_{b\to a} = -\psi_{b\to a}$$

Berry phase π electrons

Suzuura, Ando – PRL 89, 266603 (2002) Aleiner, Efetov – PRL 97, 236801 (2006) Bardarson, Tworzydło, Brouwer, Beenakker - PRL 99, 106801 (2007)

$$H = v \vec{\sigma} \cdot \vec{p} + \hat{1} \cdot U(\vec{r}) + \sum_{\substack{n,l=x,y,z / \\ n,l=x,y,z / \\$$

$$\sigma \sim \frac{e^2 v^2}{\sum_{\#} u_{\#}^2 n_{\#}} + \delta \sigma(B)$$

Different types of disorder: remote charge and strong defects

Inter-valley scattering from strong defects is important for quantum transport characteristics.

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Interference correction to conductivity in MLG: WAL versus WL.

$$w \sim |A_{\Box} + A_{\Box}|^2 = |A_{\Box}|^2 + |A_{\Box}|^2 + [A_{\Box}^*A_{\Box} + A_{\Box}A_{\Box}^*]$$



WL = enhanced backscattering for non-chiral electrons in time-reversal-symmetric systems

$$\sigma = \sigma_{cl} + \frac{e^2}{2\pi h} \ln(\min[\tau_{\varphi}, \tau_B]/\tau)$$

WAL = suppressed backscattering for Berry phase π electrons in MLG

chiral electrons $\psi_{out} = e^{-i\phi(\sigma_z/2)}\psi_{in}$

$$A_{-}A_{-}^{*} = e^{-i2\pi(\sigma_{z}/2)} |A_{-}|^{2} = -|A_{-}|^{2} < 0$$



... but bond disorder has the opposite effect on electrons in K and K' valleys, so that the true time-reversal symmetry is preserved, and the inter-valley

scattering restores the WL behaviour typical for electrons in time-inversion symmetric systems.

$$\sigma = \sigma_{cl} - \frac{e^2}{2\pi h} \ln(\min[\tau_{\varphi}, \tau_B] / \tau_{iv})$$

$$\sigma_{cl}$$

$$\sigma_{cl}$$

$$B$$
McCann, Kech for bilayers:

McCann, Kechedzhi, VF, Suzuura, Ando, Altshuler - PRL 97, 146805 (2006) for bilayers: Kechedzhi, McCann, VF, Altshuler – PRL 98, 176806 (2007)

Weak Localization in Graphene Flakes

F. V. Tikhonenko, D. W. Horsell, R. V. Gorbachev, and A. K. Savchenko

School of Physics, University of Exeter, Stocker Road, Exeter, EX4 4QL, United Kingdom

WL was used to test 'what type' of disorder:

$$L_i = \sqrt{\tau_{iv} D} >> l$$

Spin-orbit, $z \rightarrow -z$ symmetry, and weak localisation

 $z \rightarrow -z$ symmetric SO breaks time inversion for the orbital motion for spin-up/down electrons: no s_z relaxation, two unitary ensembles.

$$V_{so}^{s} = \sum_{n=x,y,z} a_{zn}(\vec{r}) s_{z} \sigma_{n} + \sum_{l=x,y,z} b_{zl}(\vec{r}) s_{z} \tau_{l}$$

 $z \rightarrow -z$ asymmetric SO: symplectic ensemble

$$V_{so}^{a} = \sum_{n=x,y,z}^{s=x,y} a_{sn}(\vec{r}) s_{s} \sigma_{n} + \sum_{l=x,y,z}^{s=x,y} a_{sl}(\vec{r}) s_{s} \tau_{l}$$

McCann, VF - PRL 108, 166606 (2012)

Spin-orbit, $z \rightarrow -z$ symmetry, and weak localisation

McCann, VF - PRL 108, 166606 (2012)

Kozikov, Horsell, McCann, VF - arXiv:1108.2067

SiC/MLG

saturated WL (no WAL), possibly due to flip-flops with local magnetic moments of defects, or, maybe, $z \rightarrow -z$ symmetric SO scattering

Lara-Avila, Tzalenchuk, Kubatkin, Yakimova, Janssen, Cedergren, Bergsten, VF – PRL107, 166602 (2011) Since inter-valley scattering from strong defects is present, graphene should become insulating at zero density $n_e=0$,

$$\sigma(n_e \to 0, \varepsilon_F \tau_{iv} < 1) \to 0$$

Aleiner, Efetov - PRL 97, 236801 (2006)

Theoretical expectation does not work – blame experiment: inhomogeneity of the carrier density!

Cheianov, VF, Altshuler, Aleiner – PRL 99, 176801 (2007) Hwang, Adam, Das Sarma - PRL 98, 186806 (2007); Das Sarma's group (2007 - 2012)

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Chessboard of n- and p-type puddles, separated by pn junctions

Transmission of chiral electrons through the PN junction in graphene

$$w(\theta) = e^{-\pi p_F d \sin^2 \theta} \cos^2 \theta$$

 $1/k_F d$

Due to the isospin conservation, A-B symmetric potential cannot backward scatter chiral electrons.

$$\frac{g_{np}}{L} \sim \frac{e^2}{h} \sqrt{\frac{k_F}{d}}$$

 $\hat{H} = v\vec{\sigma}\cdot\vec{p}$

Cheianov, VF - PR B 74, 041403 (2006)

Random network model of strongly inhomogeneous graphene

$$"n_e = 0"$$

$$\delta N = \delta n \cdot d^2 >> 1$$

$$g_{np} \sim \frac{e^2}{h} \sqrt{\frac{k_F}{d}} \cdot d \sim \frac{e^2}{h} (\delta n \cdot d^2)^{\frac{1}{4}}$$

Conductivity is formed by the interplay between percolation along single-polarity clusters and transport through PN junctions.

scaling of intrinsic conductance of a cluster

$$G(L) \sim \left(\frac{d}{L}\right)^{x} g, \quad x = 0.97$$
$$P(L) \sim \left(\frac{L}{d}\right)^{h} d, \quad h = \frac{7}{4}$$

outer cluster perimeter

$$\xi \sim d \left(\frac{g}{g_{np}}\right)^{1/(x+h)}$$
$$G(\xi) \sim \frac{P(\xi)}{d} g_{np}$$

$$\sigma_{\min} \sim g^{\alpha}_{np} g^{1-\alpha} >> \frac{e^2}{h} \quad \alpha = \frac{x}{h+x} \approx 0.36$$

To observe the insulating behaviour in graphene, one needs to get rid of inhomogeneity in the carrier density.

Insulating state in graphene at $n_e = 0$ Morozov, Nov

Ponomarenko, Geim, Zhukov, Jalil, Morozov, Novoselov, Grigorieva, Hill, Cheianov, VF, Watanabe, Taniguchi, Gorbachev, Nature Physics 7,958 (2011) incl supplementary material

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Lectures 3&4

II. Electronic properties of bilayer graphene, from high to low energies. Interaction effects in graphenes.