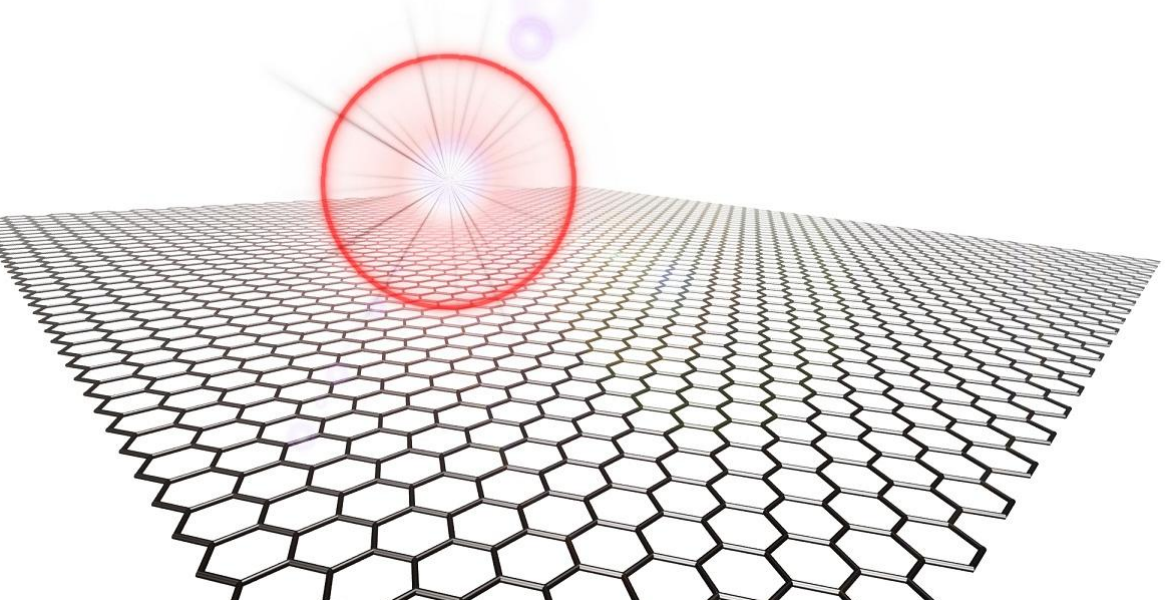
Shining Light on Transport in Disordered Graphene

Towards amorphous graphene and Magnetic ordering fingerprints

Stephan Roche



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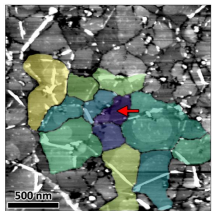
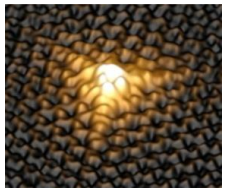
Kavli Inst. Theoret. Phys. March 2012

OUTLINE

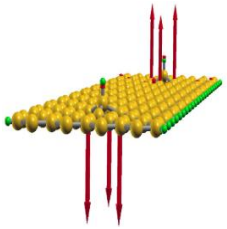
1. *"Clean versus dirty graphene ?"*



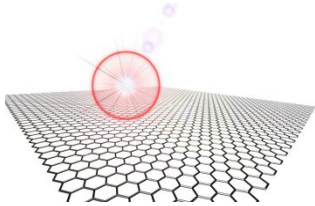
2. *From long range to short range disorder*
   Towards amorphous sp2 carbon membrane



3. *Local magnetic ordering (hydrogenation) and metal-insulator transition*

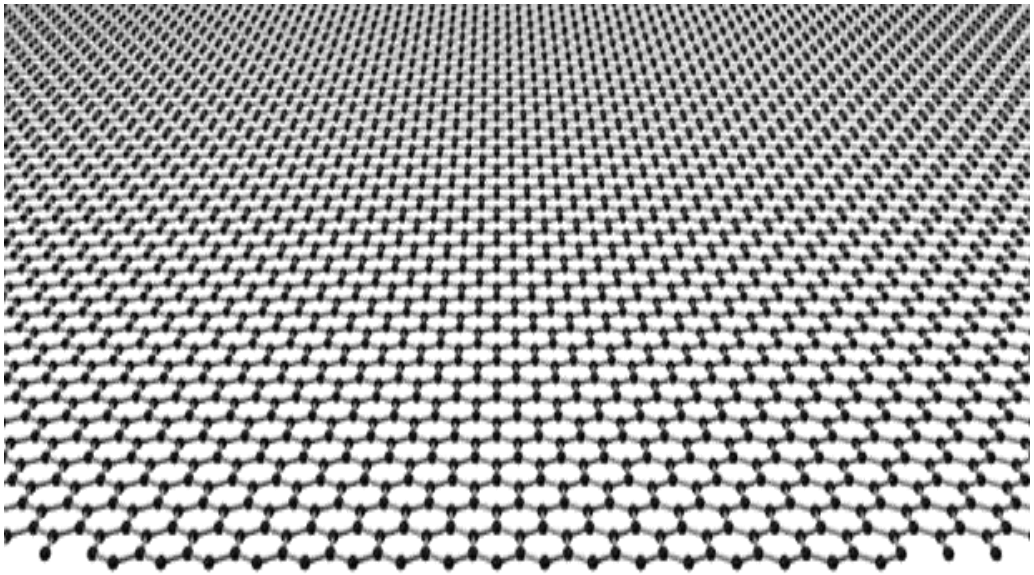


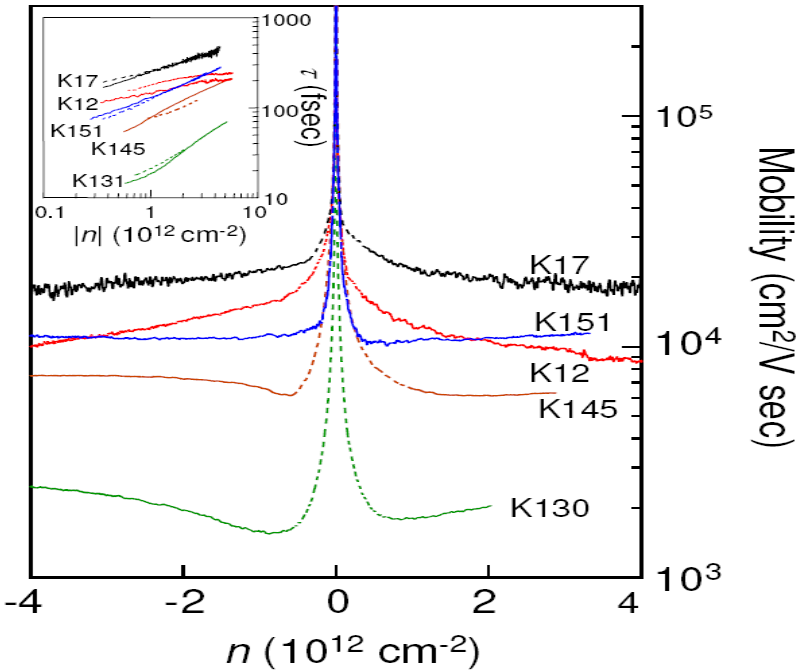
4. *Band gap tunability using a mid-infrared laser field*



The “clean 2D world”

Ph. Kim s group **[PRL 99, 246803 (2007)]**





A.K. Geim, **Bull. Am. Phys. Soc. 55 (2010)**

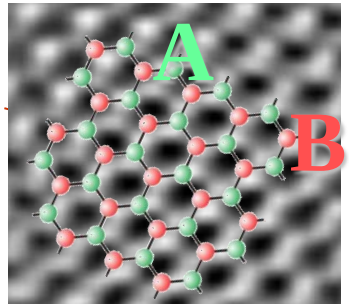
Suspended graphene	$\mu \sim 10^6 \mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$
Top gated graphene MOS channels	$\mu \sim 23.000 \mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$
Large area (catalytic growth) graphene	$\mu \sim 3.700 \mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$

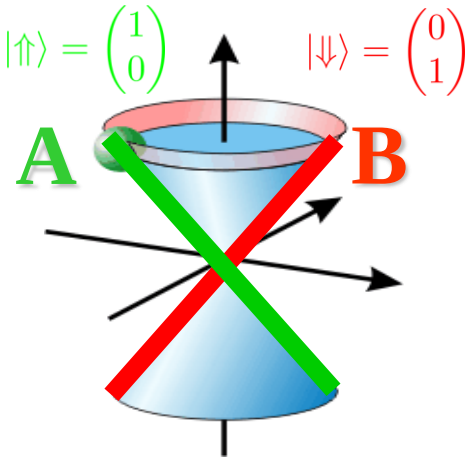
Pseudospin / e-h symmetry and Berry s phase
Single scatter level

$$\mathcal{H}_{K_+} = v_F \vec{\sigma}.\vec{p}$$

4 Dirac point (2 valley * 2 spin)

$$\Psi^{\pm}_{\vec{p}} = \frac{1}{\sqrt{2}} \begin{pmatrix} \Psi^{\pm}_{p}(A) \\ \Psi^{\pm}_{p}(B) \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} s e^{i\theta/2} \\ e^{-i\theta/2} \end{pmatrix}$$





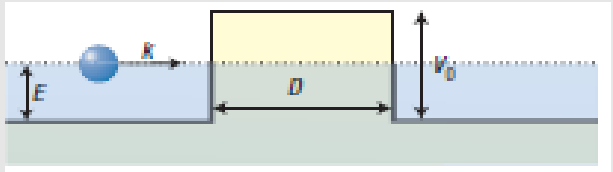
$$\hat{h} = \frac{1}{2}\vec{\sigma}.\frac{\vec{p}}{|\vec{p}|} \qquad \hat{h}|\Psi_{\vec{p}}(s=\pm 1)\rangle = \pm\frac{1}{2}|\Psi_{\vec{p}}(s)\rangle$$

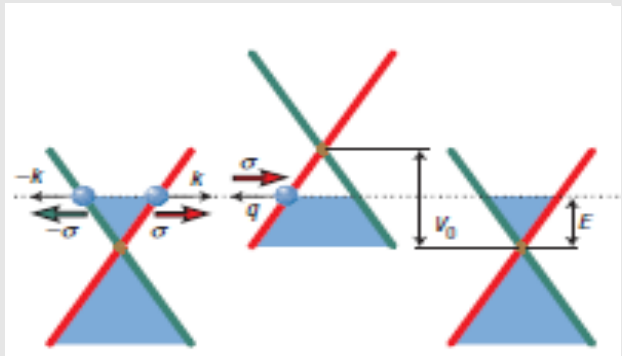
eigenstates have a well defined helicity (good q.n.)

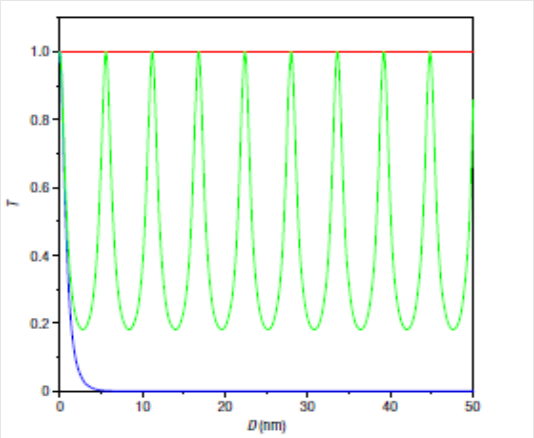
Klein Tunneling

"perfect transmission through a potential barrier of increasing width/depth"

Katsnelson, Novoselov, Geim Nature Physics 2006



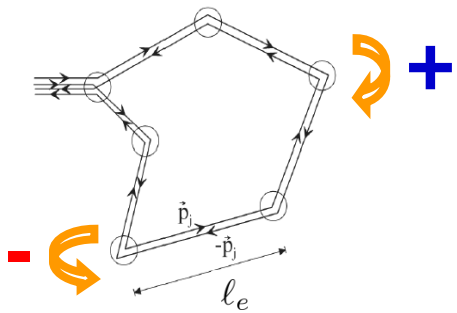




Berry s phase effects and quantum interferences (multiple scattering)

Disorder (static/dynamic) induces multiple scattering events

↓



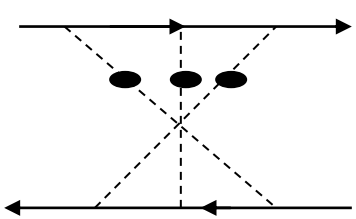
Weak localization

Strong localization **(Insulating state)**

$$\sigma(L) = \sigma_{\rm sc} + \delta\sigma(L)$$

$$\delta\sigma(L) = -\frac{2e^2 D}{\pi\hbar\Omega}\int_0^\infty dt\,\mathcal{Z}(t)(e^{-t/\tau_\varphi} - e^{-t/\tau_e})$$

$$\mathcal{Z}(t) = \int d^d r P(\mathbf{r},\mathbf{r},t)$$



B.L. Altshuler and A.G. Aronov (80)

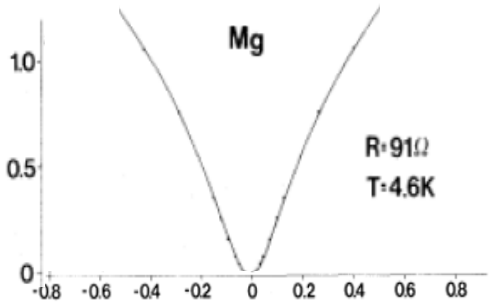
Additional QIE due to Berry s phase

Weak antilocalization

(Robust metallic state)

Negative magnetoresistance

$\Delta G(B)/G(B=0)$



$B(T)$

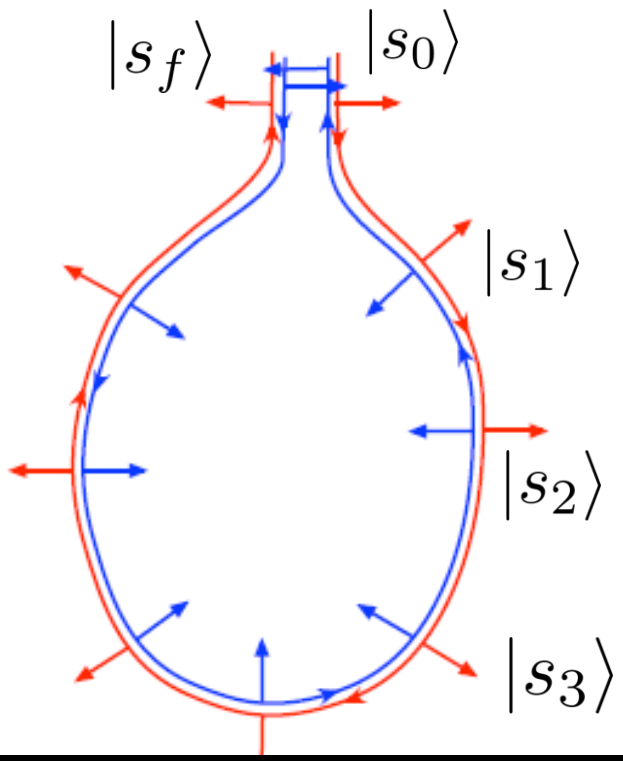
Cooperon (spin/pseudospin driven effect)

Original prediction (cooperon equation)
S. Hikami, A.I. Larkin, Y. Nagaoka, Prog. Theor. Phys. 63, 707 (1980)

The spin of electrons rotate (adiabatically) as it moves around the classical path

$$\sigma = \sigma_{\text{Drude}} + \delta\sigma$$

$$\delta\sigma = -\frac{2e^2 D}{\pi\hbar\Omega}\int_0^\infty dt\mathcal{Z}(t)\langle\mathcal{Q}_{s.o}(t)\rangle(e^{-t/\tau_\varphi} - e^{-t/\tau_e})$$



$$|s_{n+1}\rangle = e^{-i\Delta\theta S_z/\hbar}|s_n\rangle$$

$$\mathcal{R}_t = \mathcal{T}e^{-\frac{i}{\hbar}\int_0^t \mathcal{H}_{s.o}dt}$$

$$\mathcal{H}_{s.o} = \frac{\hbar}{4m^2c^2}\vec{\sigma}.(\vec{\nabla}V(\mathbf{r})\times\vec{p})$$

$$\boxed{\mathcal{Q}_{s.o}(t) = \sum_{\pm}\langle s_0|\mathcal{R}^\dagger_{-t}|s_f\rangle\langle s_f|\mathcal{R}_t|s_0\rangle}$$

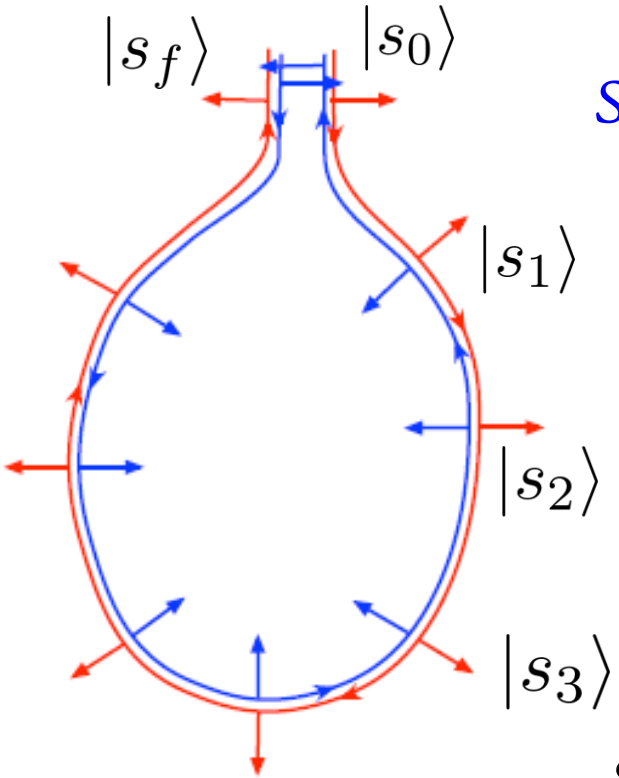
Cooperon (spin/pseudospin driven effect)

$$\sigma = \sigma_{\text{Drude}} + \delta\sigma$$

$$\langle \mathcal{Q}_{s.o}(t) \rangle = \sum_{\pm} \langle s_0 | \mathcal{R}^{\dagger}_{-t} | s_f \rangle \langle s_f | \mathcal{R}_t | s_0 \rangle$$

Spin rotates by an angle -π

Spin rotates by an angle +π



Because of the complex conjugation these two phases add up to a total rotation of **2π**

Total Berry s phase

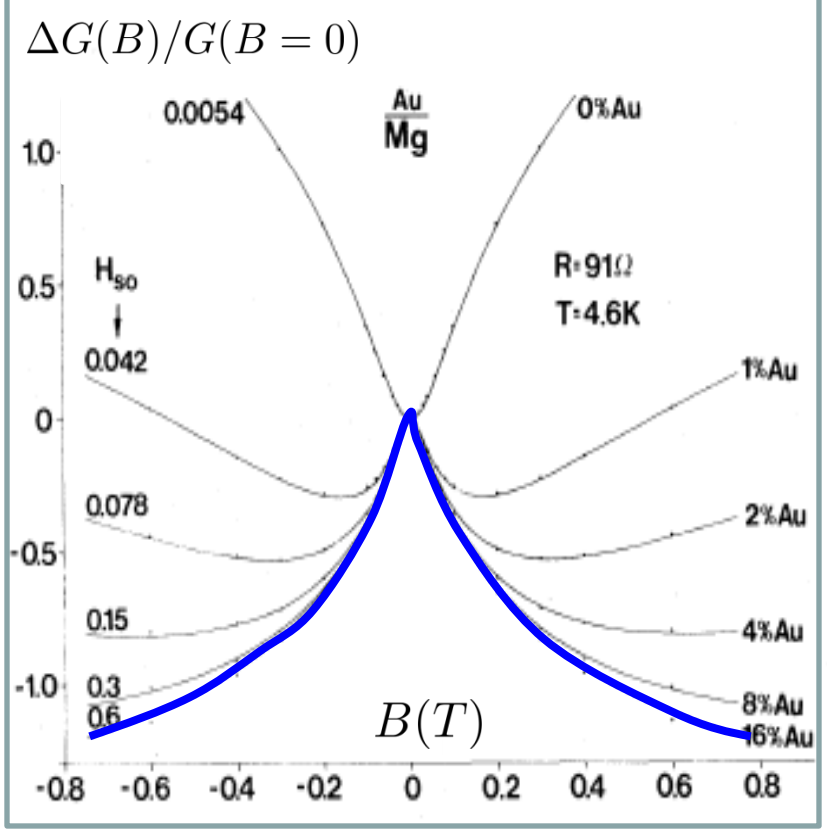
$$\langle \mathcal{Q}_{s.o}(t) \rangle = -1/2$$

S. Chakravarty & A. Schmid Phys. Rep- 140, 193 (1986)

Strong so-coupling-antilocalization

Original prediction (cooperon equation)
S. Hikami, A.I. Larkin, Y. Nagaoka, Prog. Theor. Phys. 63, 707 (1980)

Magnetoconductance



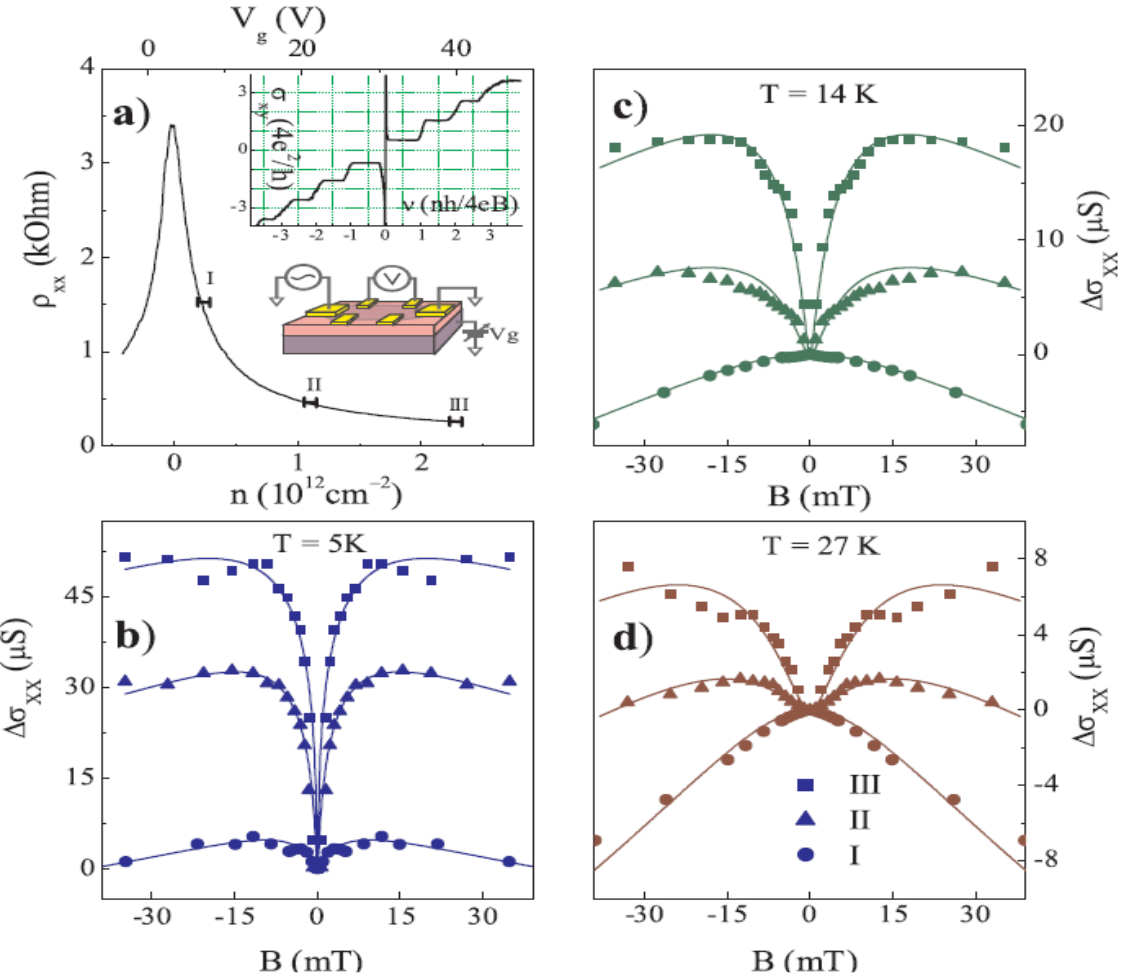
G. Bergmann,
Phys. Rev. Lett. 48, 1046 (1982)

Thin Mg disordered metallic film (9nm thickness!) –weak so-coupling with **Au impurities** (strong so coupling)

Experimental observation of Weak antilocalization

Weak antilocalization in graphene……

F.V. Tiknonenko et al, **Phys. Rev. Lett 97, 146805 (2007)**



No so-coupling…
no magnetic impurities

Strictly driven by
Berry s phase (pseudospin)

Weak localization in 2D graphene

E. McCann, K. Kechedzhi, V. I. Fal'ko, H.Suzuura, T. Ando, B.L. Altshuler,
Phys. Rev. Lett 97, 146805 (2007)

Quantum interferences correction (WL/WAL)

$$\Delta\sigma(B) = e^2/\pi h \left\{ \mathcal{F}\left(\frac{\tau_B^{-1}}{\tau_\varphi^{-1}}\right) - \mathcal{F}\left(\frac{\tau_B^{-1}}{\tau_\varphi^{-1}+2\tau_i^{-1}}\right) - 2\mathcal{F}\left(\frac{\tau_B^{-1}}{\tau_\varphi^{-1}+\tau_i^{-1}+\tau_*^{-1}}\right) \right\}$$

τ_i *intervalley scattering time*
τ_ω *trigonal warping scattering time*
τ_s *intravalley scattering time*
$\tau_B = \hbar/2eDB$

$$F(z) = \ln z + \Psi(1/2 + 1/z)$$

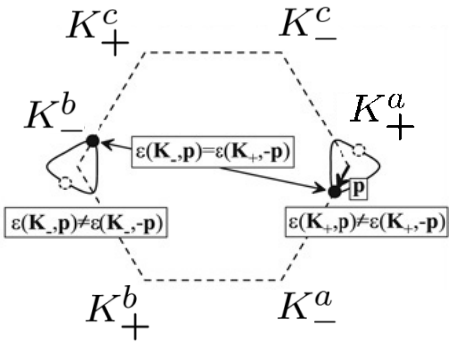
digamma function

Introduction of **several phenomenological parameters** which can not be computed analytically from a given disorder model

$$\tau_w^{-1} + \tau_z^{-1} + \tau_i^{-1} \equiv \tau_*^{-1}.$$

$$\tau_w^{-1} = 2\tau_0(\epsilon^2\mu/\hbar v^2)^2.$$

$$\tau_i^{-1} = 4\tau_{\perp\perp}^{-1} + 2\tau_{z\perp}^{-1}, \qquad \tau_z^{-1} = 4\tau_{\perp z}^{-1} + 2\tau_{zz}^{-1}.$$



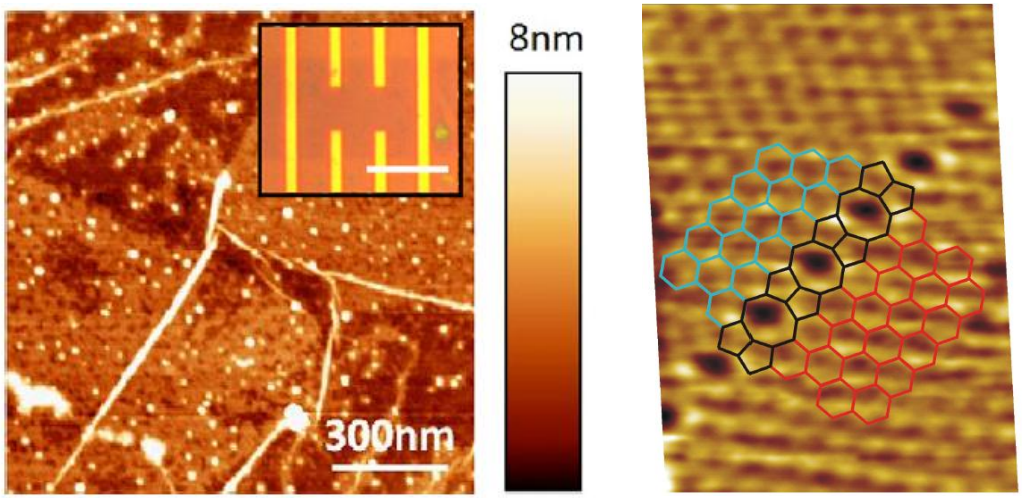
The real “dirty” graphene ?

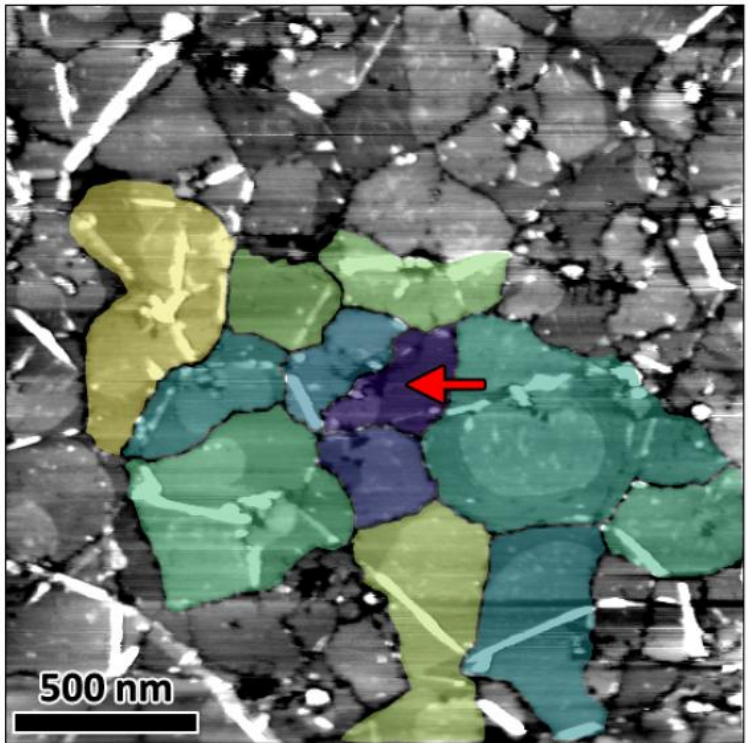
CVD graphene film transferred on SiO_2
How does it looks like ?

Mesoscopic scale

AFM image

EPL, 94 (2011) 28003





"Different thermal expansion of the Cu foil and the graphene sheet result in the formation of a few nm high ripples. Locally cracks can form during the transfer process and occasionally one is left with PMMA residues"

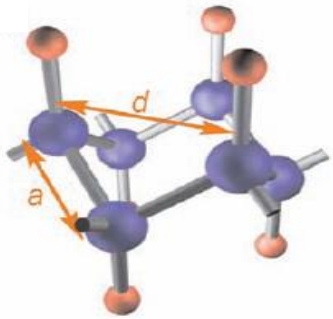
Graphene Chemical Derivatives

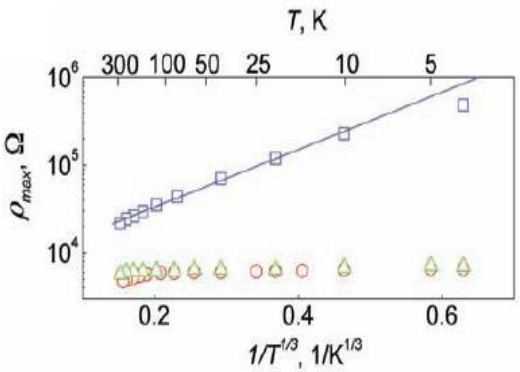
Turning graphene to a
true band insulator vs mobility gap material

Hydrogenation of Graphene

Band insulator
(towards **GRAPHANE**)

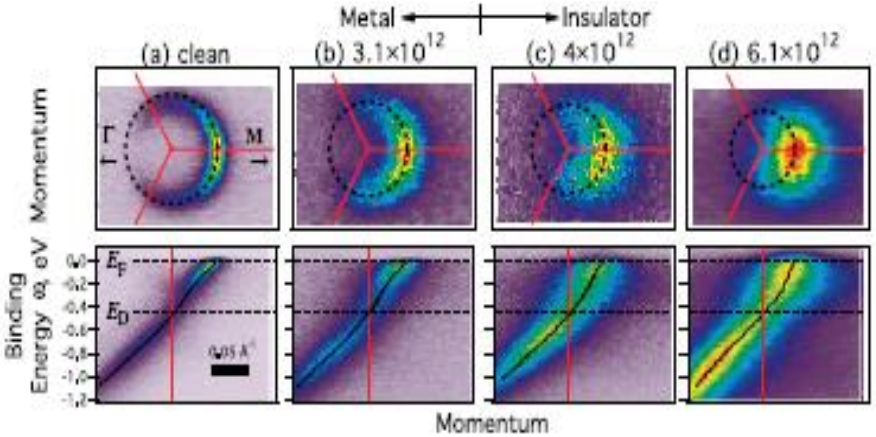
D.C. Elias et al.,
Science 323, 610 (2009)





Anderson insulator
(*low hydrogen coverage*)

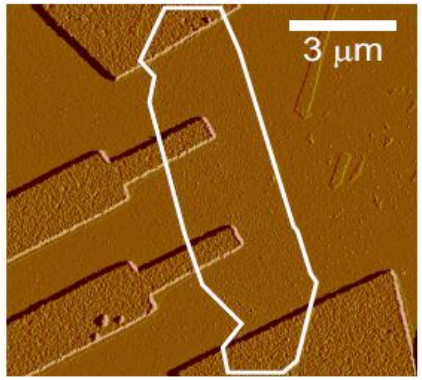
A. Bostwick et al.,
Phys. Rev. Lett. 103, 056404 (2009)

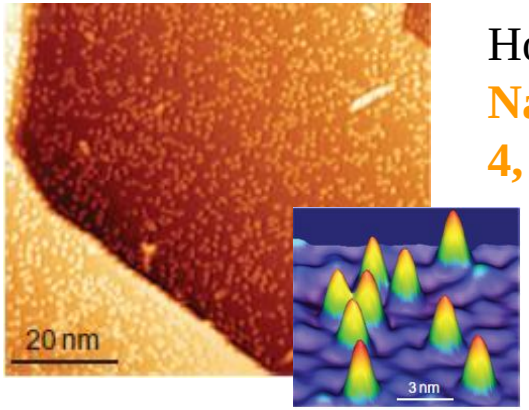


Ozone treatment of Graphene

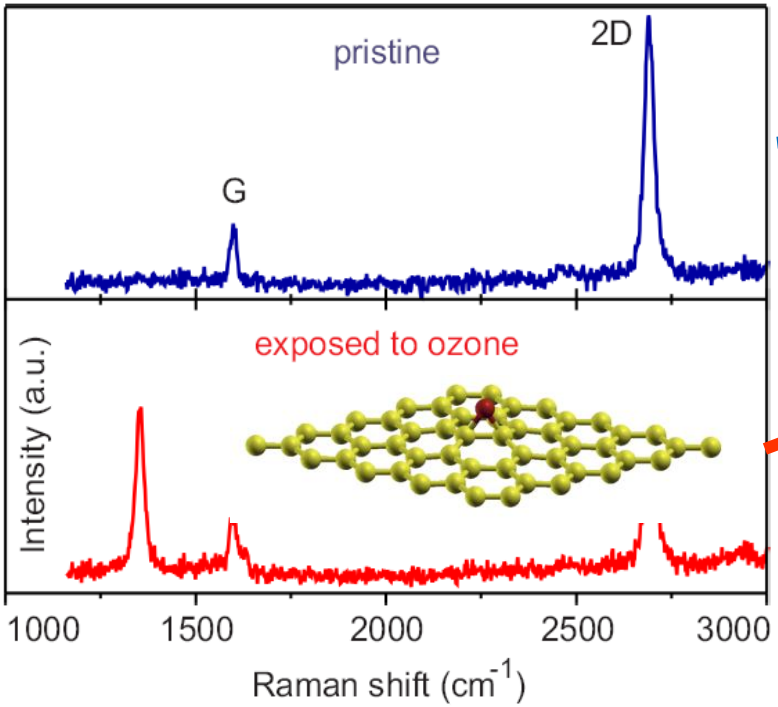
J. Moser et al.,
PRB 81, 205445 (2010)

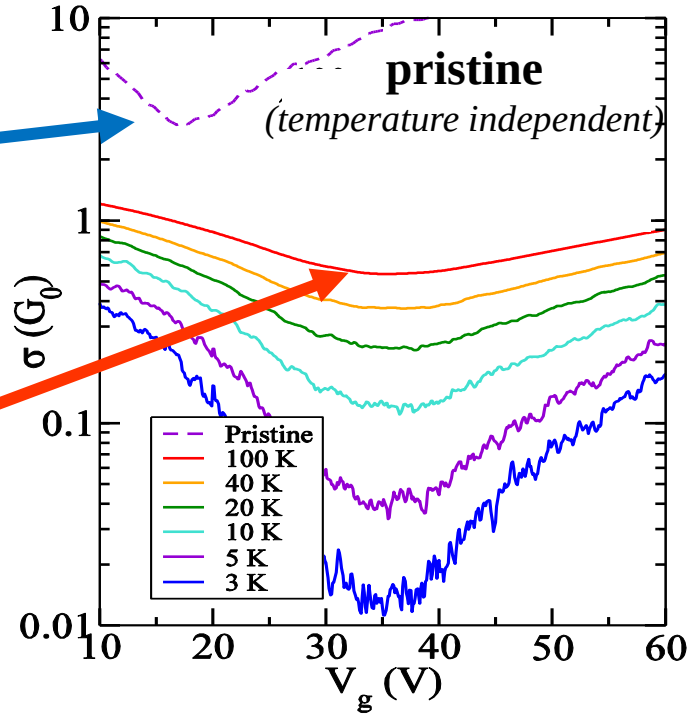
Ozone flux → O_3





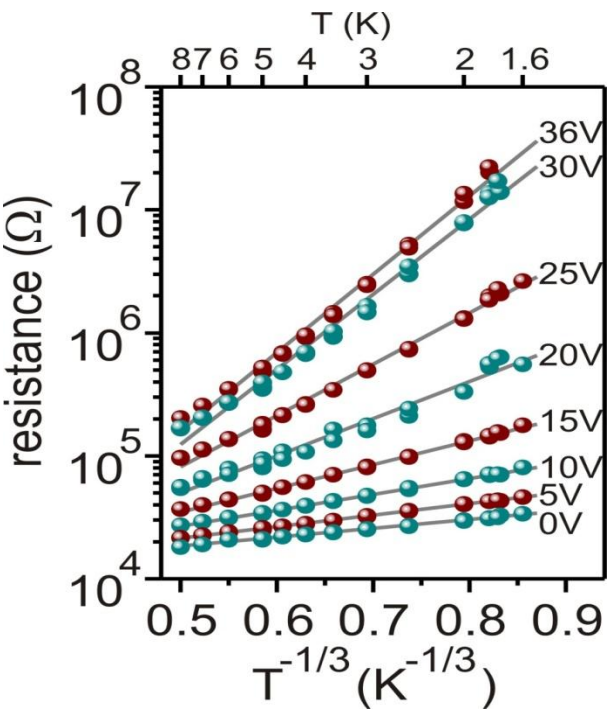
Hossain et al,
Nature Chemistry 4, 305 (2012)





Gate-dependent Transport

Low temperature transport
(variable range hopping)



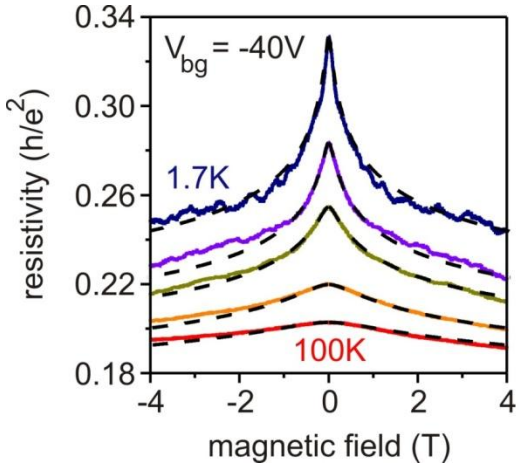
$$\sigma(T) = \exp(-(T_0/T)^{1/3})$$

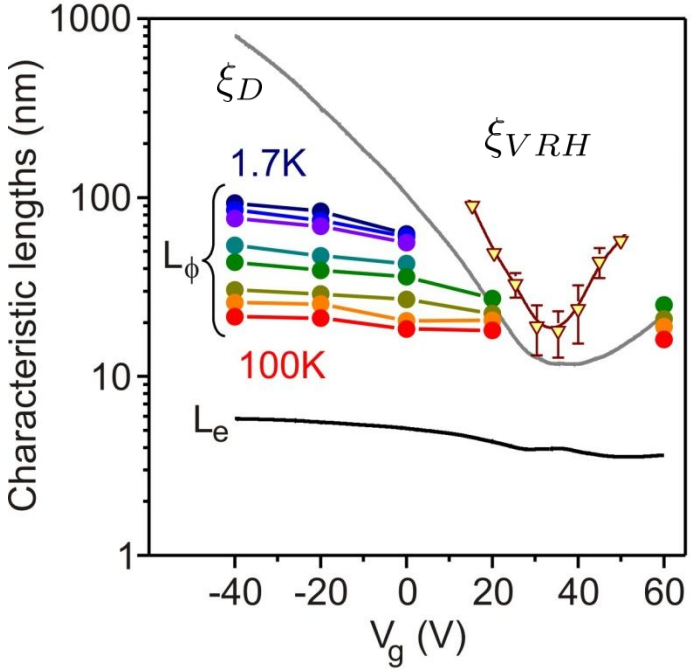
Localization length

$$\xi_{VRH} = \sqrt{13.8/k_B \rho T_0}$$

$$\xi_D = \ell_e \exp(\sigma_D/(e^2/h))$$

Magnetotransport fingerprints
(weak localization-coherence length-)



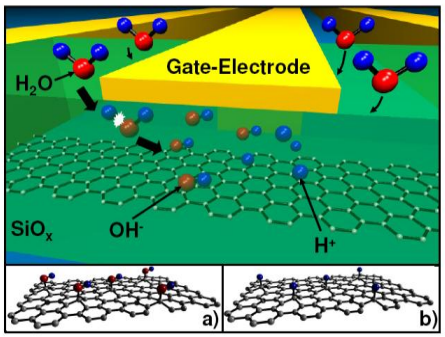


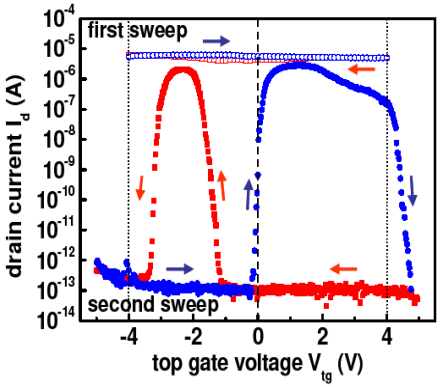
J. Moser, H. Tao, S.R., F. Alsina, C. M. Sotomayor Torres, A. Bachtold, **Phys. Rev B 81, 205445 (2010)**

Disorder Engineering of new functionality...

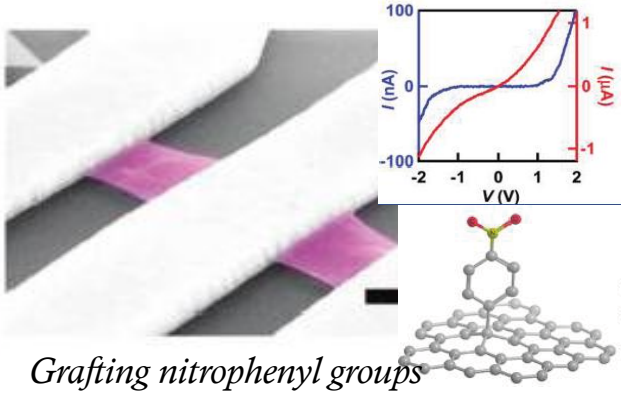
Bandgap engineering (chemical functionalization)

Electrochemical switch





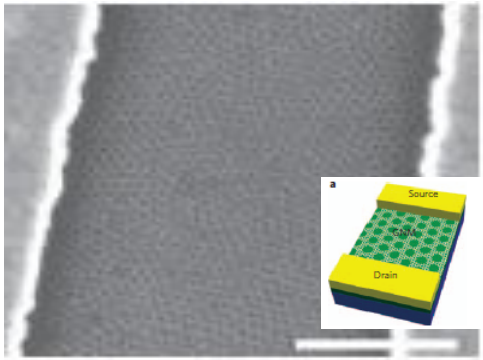
T. Echtermeyer et al, Elec. Dev. Lett. (2008)



Grafting nitrophenyl groups

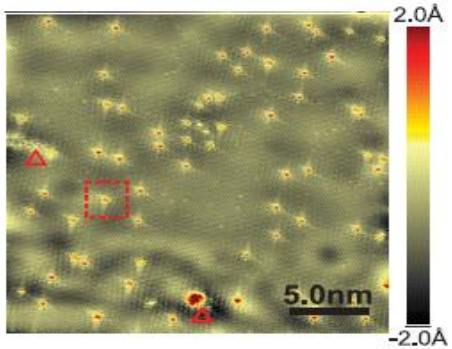
H. Zhang Nano Lett. (in press)

Graphene Nanomesh



J. Bai et al., Nature Nanotech 2010

Nitrogen doped graphene



J.C. Meyer et al., Nat. Mat. 10, 209 (2011)

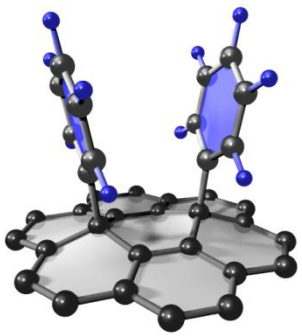
L. Zhao et al., Science 333,999 (2011)

Complexity & Computational challenges

- Enhanced structural & electronic complexity at the nanoscale driven by disorder (defects, deformations,chemical reactivity,…)
- Randomness of defects distribution
- *If quantitative prediction is targeted*

Simulation of **very large system size**

$1\mu m^2$ - 10 Millions carbon atoms



Theoretical modelling & simulation

- **First-principles calculations** - *accurate predictions of structures, electronic properties, description of impurity states,…*
- **Reduced Hamiltonian (tight-binding,..)**
- **Order N implementation of transport methodologies** *(Landauer, Kubo)*

Kubo formula in a nutshell

Electronic system is described by $\hat{\mathcal{H}}_0 = \frac{\hat{\mathbf{P}}^2}{2m} + \hat{\mathcal{V}}$ with spectrum $\varepsilon_k, |\Psi_k\rangle$

Perturbation : applying an electric field

$$\vec{\mathcal{E}} = \mathcal{E}_0 \cos \omega t \vec{u}_x$$

Transition between states of the system at equilibrium
(*to the first order of time-dependent perturbation theory*)

$$\hat{\mathcal{H}}_0 = \frac{(\hat{\mathbf{P}}+e\mathbf{A})^2}{2m} + \hat{\mathcal{V}} = \hat{\mathcal{H}}_0 + \delta\hat{\mathcal{H}}$$

Perturbation $\delta\hat{\mathcal{H}} = \frac{e}{m}\mathbf{A}\hat{\mathbf{P}} = -\frac{e\mathcal{E}_0}{2i\omega}(e^{i\omega t} - e^{-i\omega t})\hat{V}_x$ (Coulomb gauge)

Transition rate from k to q reads

$$p(t) = \frac{1}{\hbar^2}\left|\int_0^t e^{i(\varepsilon_k - \varepsilon_q)\tau/\hbar}\langle\mathbf{k}|\delta\hat{\mathcal{H}}|\mathbf{q}\rangle\right|^2$$

$$= \frac{2\pi}{\hbar}\left(\frac{e\mathcal{E}_0}{2\omega}\right)^2\left|\langle\mathbf{k}|\hat{V}_x|\mathbf{q}\rangle\right|^2\left(\delta(\varepsilon_k - \varepsilon_q + \hbar\omega) + \delta(\varepsilon_k - \varepsilon_q - \hbar\omega)\right)$$

Transition induced energy loss (emission)

Transition induced energy gain (absorption)

Kubo formula in a nutshell

Total absorbed power by the system is computed by evaluating
Allpossible transitions, accounting for state occupancies

$$= \frac{\pi e^2 \mathcal{E}_0}{\hbar\omega^2}\left[-\hbar\omega\sum_{kq} f_q(1-f_k)\left|\langle \mathbf{k}|\hat{V}_x|\mathbf{q}\rangle\right|^2\delta(\varepsilon_k-\varepsilon_q-\hbar\omega)+\hbar\omega\sum_{kq} f_q(1-f_k)\left|\langle \mathbf{k}|\hat{V}_x|\mathbf{q}\rangle\right|^2\delta(\varepsilon_k-\varepsilon_q+\hbar\omega)\right]$$

$$\Re e\sigma(\omega) = \frac{\mathcal{P}}{\mathcal{E}_0^2\Omega/2} = \frac{2\pi e^2\hbar}{\Omega}\sum_{kq}\frac{f_q-f_k}{\hbar\omega}\left|\langle \mathbf{k}|\hat{V}_x|\mathbf{q}\rangle\right|^2\delta(\varepsilon_k-\varepsilon_q-\hbar\omega)$$

Kubo-Greenwood formula of quantum conductivity

$$\Re e\sigma(\omega) = \frac{2\pi e^2\hbar}{\Omega}\int_{-\infty}^{+\infty} dE\,\frac{f(E)-f(E+\hbar\omega)}{\hbar\omega}\mathrm{Tr}[\hat{V}_x\delta(E-\hat{\mathcal{H}})\hat{V}_x\delta(E-\hat{\mathcal{H}})]$$

R Kubo, Rep. Prog. Phys. 29 255-284 (1966)

Real Space Order N Kubo Transport

$$\Re e\sigma(\omega) = \frac{2\pi e^2\hbar}{\Omega}\int_{-\infty}^{+\infty} dE\,\frac{f(E)-f(E+\hbar\omega)}{\hbar\omega}\mathrm{Tr}[\hat{V}_x\delta(E-\hat{\mathcal{H}})\hat{V}_x\delta(E-\hat{\mathcal{H}})]$$

$$\boxed{\sigma_{dc} = e^2 n(E_F)\lim_{t\to\infty}\frac{d}{dt}\Delta X^2(E_F,t)}$$

$$\Delta X^2(E_F,t) = \langle|\,\hat{X}(t)-\hat{X}(0)\,|^2\rangle_{E_F} \longrightarrow \frac{\mathrm{Tr}\big[[\hat{X},\hat{U}(t)]^\dagger\delta(E-\mathcal{H})[\hat{X},\hat{U}(t)]\big]}{\mathrm{Tr}[\delta(E-\mathcal{H})]}$$

$$\downarrow$$

$$\frac{\langle\widetilde{\varphi}_{RP}(t)|\delta(E-\mathcal{H})|\widetilde{\varphi}_{RP}(t)\rangle}{\langle\varphi_{RP}|\delta(E-\mathcal{H})|\varphi_{RP}\rangle}$$

$$\begin{cases} \hat{U}(t) = e^{\frac{-i\hat{\mathcal{H}}t}{\hbar}} \\ \hat{X}(t) = e^{\frac{i\hat{\mathcal{H}}t}{\hbar}}\hat{X}(0)e^{\frac{-i\hat{\mathcal{H}}t}{\hbar}} \\ \hat{X}(t)-\hat{X}(0) = \hat{U}^\dagger(t)[\hat{X},\hat{U}(t)] \end{cases}$$

$$|\varphi_{RP}\rangle = \frac{1}{\sqrt{N_{sites}}}\sum_{j=1}^{N_{sites}} e^{i\theta_j}|j\rangle$$

$$|\widetilde{\varphi}_{RP}(t)\rangle \simeq \sum_{n=0}^{N_{pol}} c_n(t)[\hat{X},\mathcal{Q}_n(\hat{\mathcal{H}})]|\varphi_{RP}\rangle$$

$$\langle\varphi_{RP}|\delta(E-\hat{\mathcal{H}})|\varphi_{RP}\rangle = -\frac{1}{\pi}\lim_{\eta\to 0}\Im m\langle\varphi_{RP}|\frac{1}{E+i\eta-\hat{\mathcal{H}}}|\varphi_{RP}\rangle,$$

$$\cfrac{1}{E+i\eta-a_1-\cfrac{b_1^2}{E+i\eta-a_2-\cfrac{b_2^2}{\ddots\,\cfrac{}{E+i\eta-a_N-b_N^2\Sigma(\omega)}}}}$$

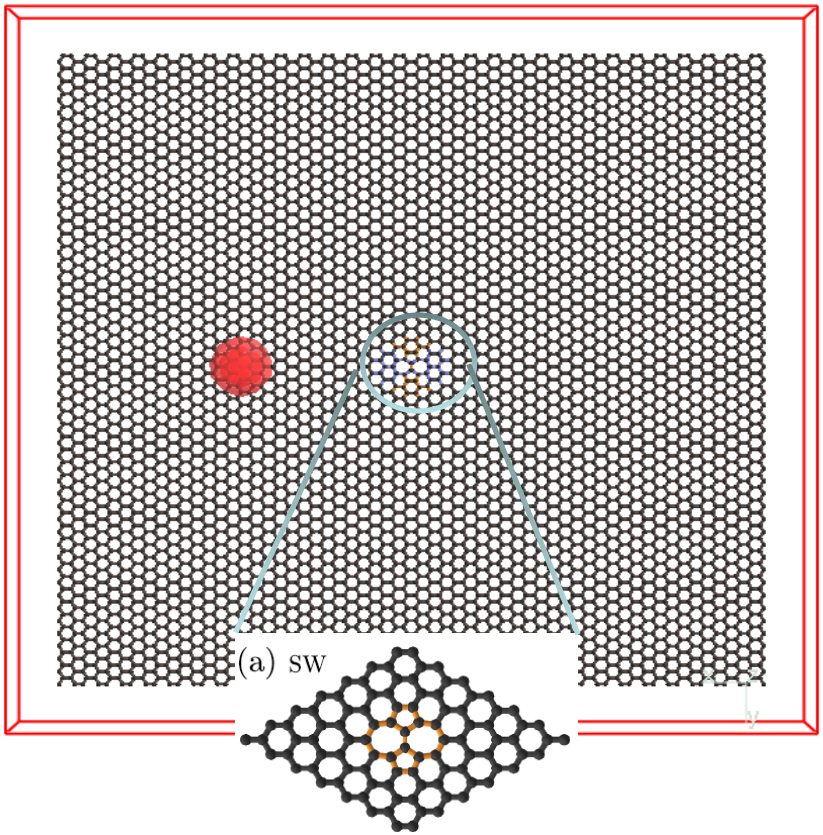
S.R. et al **PRL 79, 2518 (1997); PRL 87, 246803 (2001)**

Quantum Transport Methodology

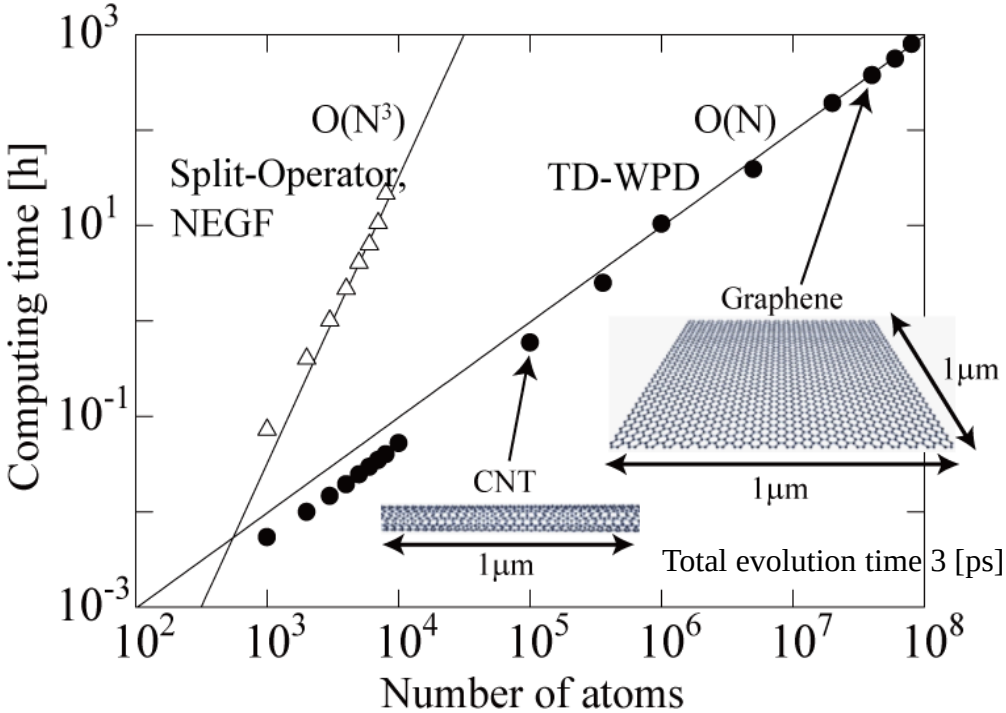
Time-evolution of wavepackets dynamics

$$D(E,t) = \frac{\langle (\hat{X}(t) - \hat{X}(0))^2 \rangle}{t}$$ **Diffusion coefficient**

Conductivity using Kubo approach



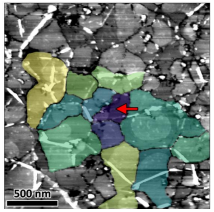
$$\sigma_{dc} = e^2 \rho(E) \lim_{t \to \infty} \frac{d}{dt} \Delta X^2(E,t)$$



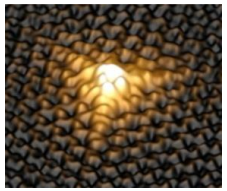
H. Ishii, F. Triozon, K. Hirose, S.R., **C.R. Physique 10, 283-296 (2009)**

OUTLINE

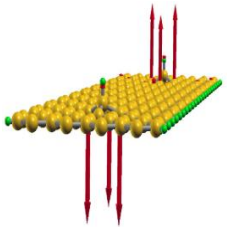
1. *"Clean versus dirty graphene ?"*



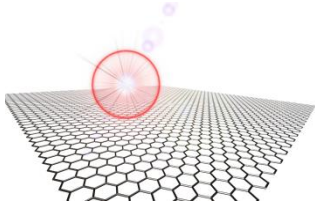
2. *From long range to short range disorder*
   Towards amorphous sp2 carbon membrane



3. *Local magnetic ordering (hydrogenation) and metal-insulator transition*



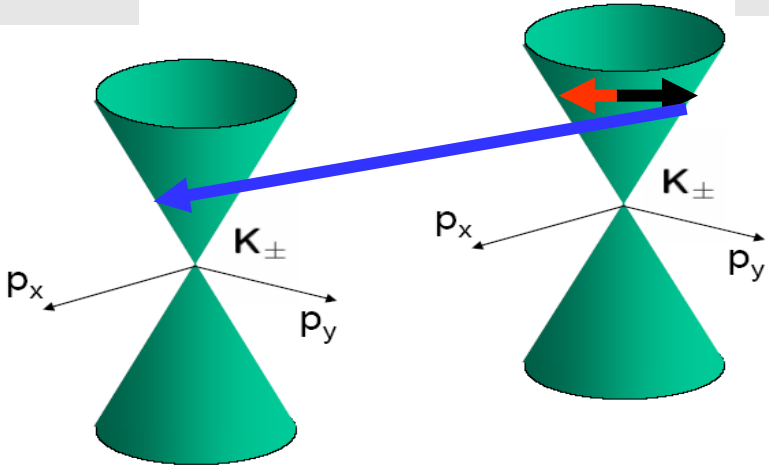
4. *Band gap tunability using a mid-infrared laser field*

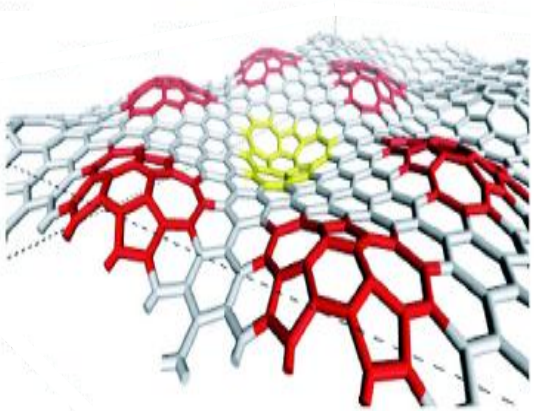


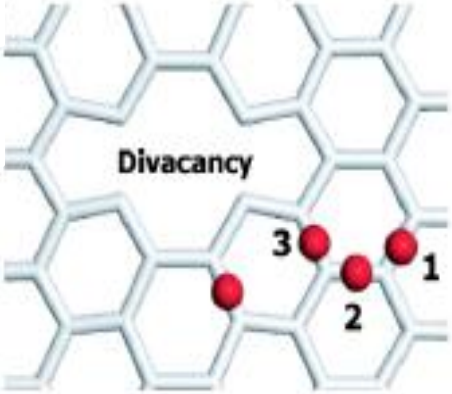
Long range versus short range potential

Long range potential
Intravalley scattering
(short momentum transfer)

Short range potential
Intervalley scattering
(large momentum transfer)

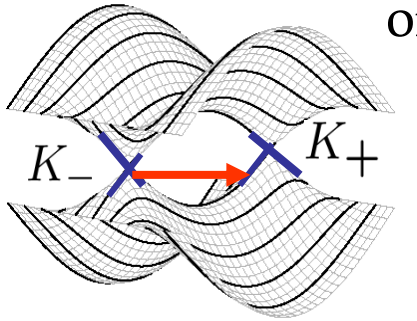






* Mean free path (el density)
* Quantum interferences
& Localization phenomena
* Anomalous vs conventional QHE
(Mirlin)

Breaking all symmetries (Anderson)

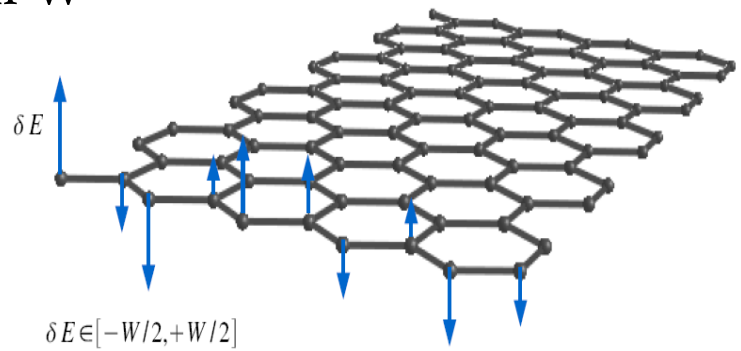


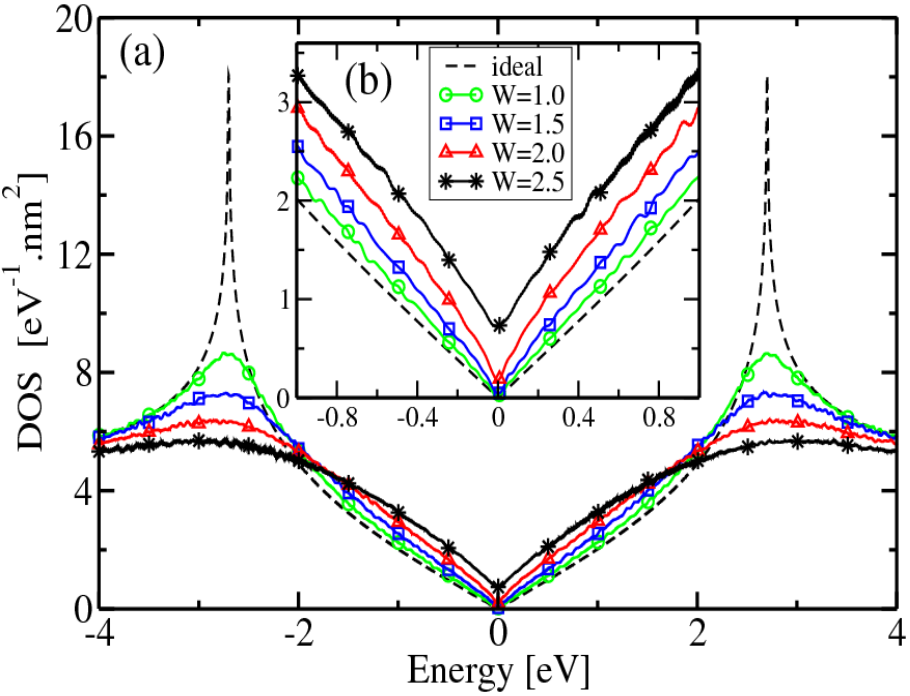
onsite energy fluctuations within W

$$\varepsilon_i \in [-\frac{W}{2}, +\frac{W}{2}]$$

Uniform probability

(short-range potential)





Density of states

No disorder

Agrees with analytical result

With Disorder

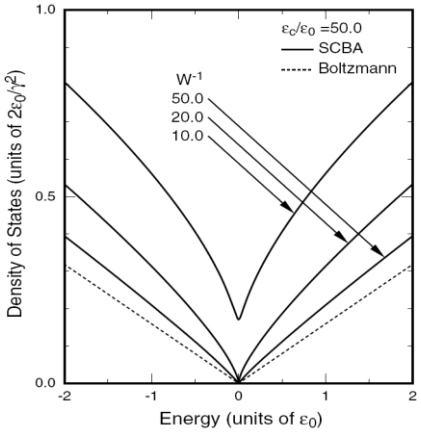
*) As W is enhanced

, DoS increases close to CNP

*) Close to VHs

Smoothening

(disorder-enhanced Scattering)



Note : no shift of Fermi level

N. H. Shon and T. Ando,

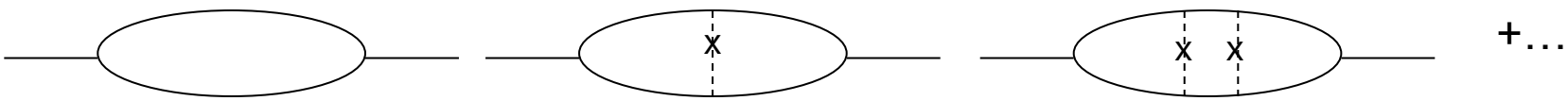
J. Phys. Soc. Jpn. 67, 2421 (1998)

Self Consistent Born Approximation

Conductivity (Kubo)

$$\sigma_{xx} \sim \mathrm{Tr}\langle v_x \Im m G(E+i\eta) v_x \Im m G(E+i\eta)\rangle_{\mathrm{conf.}}$$

$$\langle G(E)G(E')\rangle \sim \langle G(E)\rangle\langle G(E')\rangle \quad \text{(semiclassical approximation)}$$

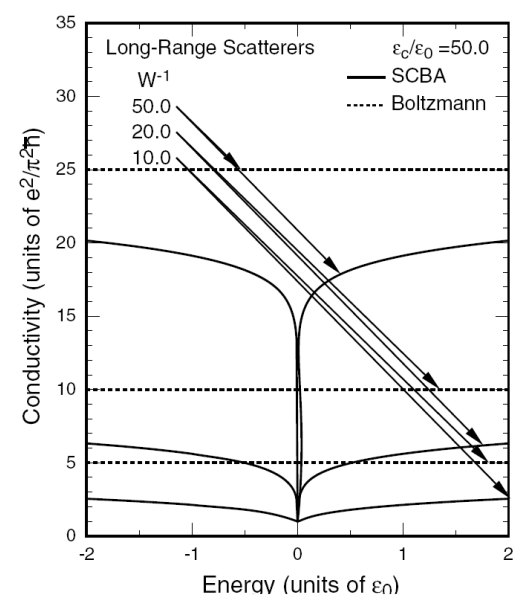


$$\boxed{\sigma(E) = \frac{e^2}{\pi h}\left[1 + \left(\frac{E-\Delta}{\Gamma} + \frac{\Gamma}{E-\Delta}\right)\mathrm{Atan}\left(\frac{E-\Delta}{\Gamma}\right)\right]}$$

$$\Sigma(E+i\eta) = \Delta(E) - i\Gamma(E)$$

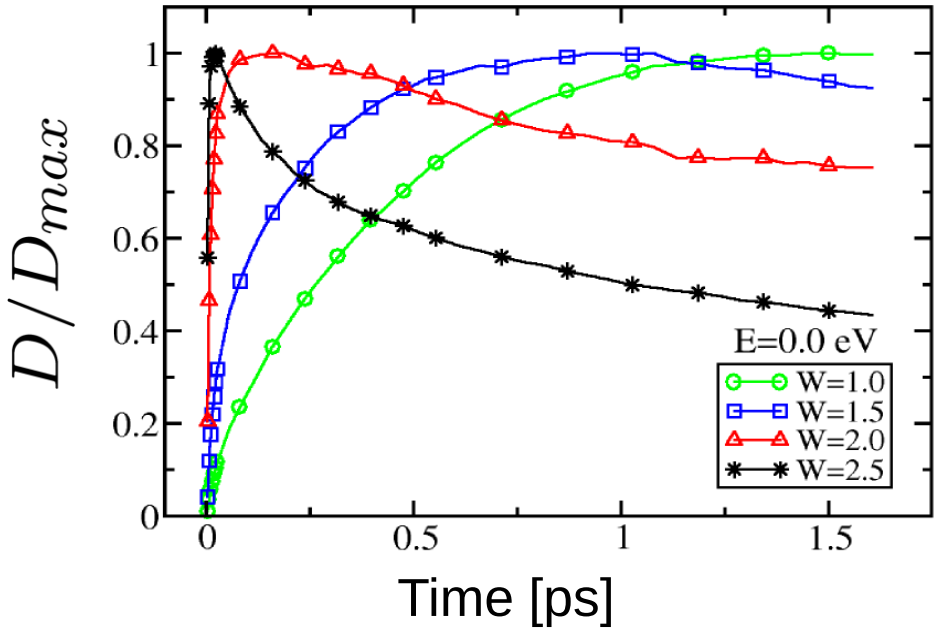
$$\boxed{\sigma(E=0) = \frac{4e^2}{\pi h}}$$

*(2 spin * 2 valley degeneracy)*



N. H. Shon and T. Ando, J. Phys. Soc. Jpn. 67, 2421 (1998)

Quantum Diffusion



From the maximum of diffusivity

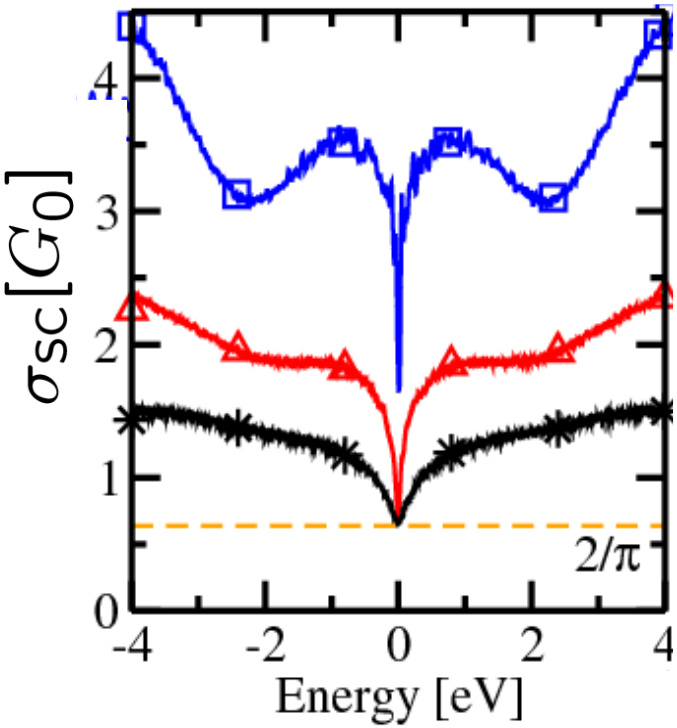
$$D \sim v_F \ell_e$$

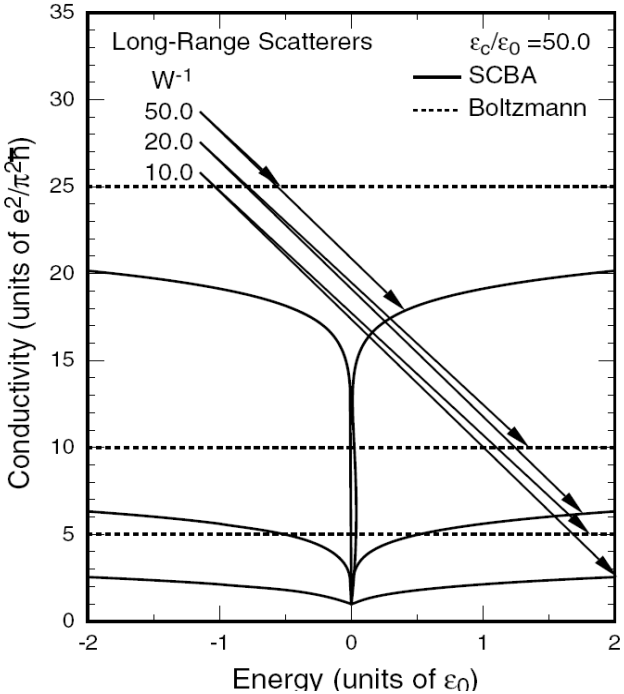
$$\sigma_{SC} = e^2 \rho(E) v(E) \ell_e$$

$$\mu(E) = \sigma_{sc}(E)/en(E)$$

Kubo conductivity (at D_{max})

Semiclassical part of the conductivity-from Kubo approach-
(short range scattering)





$$\sigma_{SC}(E_F = 0) = 4e^2/(h\pi)$$

agrees with SCBA

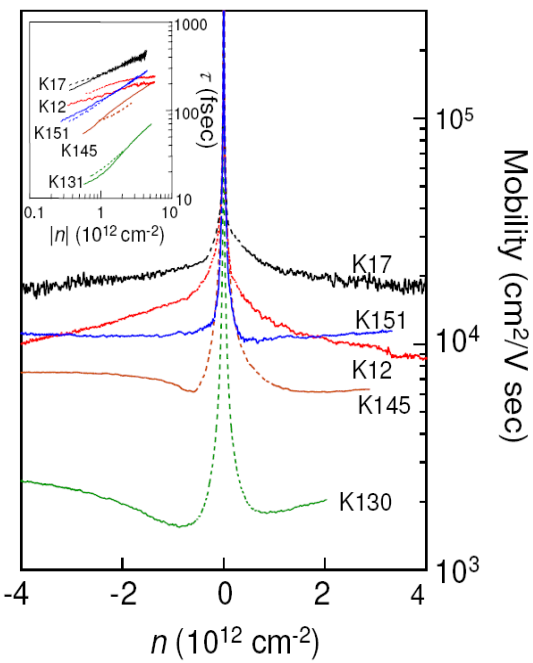
N. H. Shon and T. Ando,
J. Phys. Soc. Jpn. 67, 2421 (1998)
P. M. Ostrovsky, I.V. Gornyi, A. D. Mirlin,
Phys. Rev. B 74, 235443 (2006)

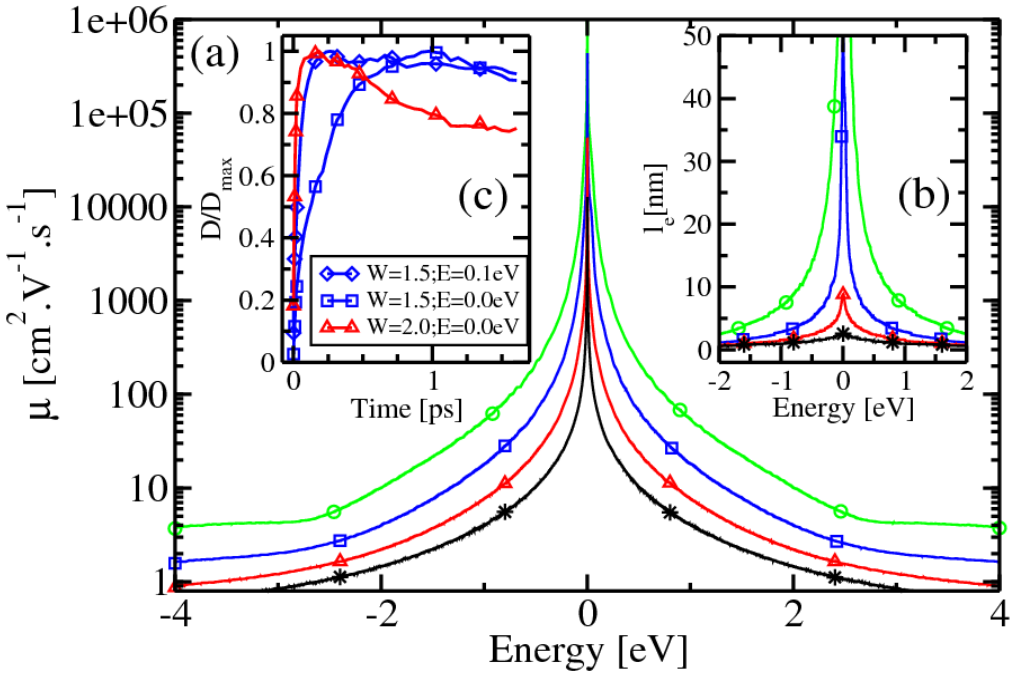
Charge mobilities in 2D graphene

$$D \sim v_F \ell_e$$

$$\sigma_{SC} = e^2 \rho(E) v(E) \ell_e$$

$$\mu(E) = \sigma_{SC}(E)/en(E)$$

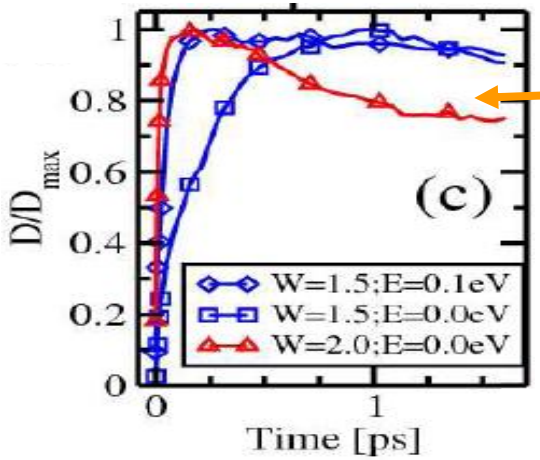




*) Divergence of mfp & mobility as E_F moves towards CNP
*) Mobility changes agrees with experimental data for poorer quality samples

Experimental data by Ph. Kim (columbia)
Y.W. Tan *et al.*, Phys. Rev. Lett. 99, 246803 (2007)

Quantum interferences effects



QIE

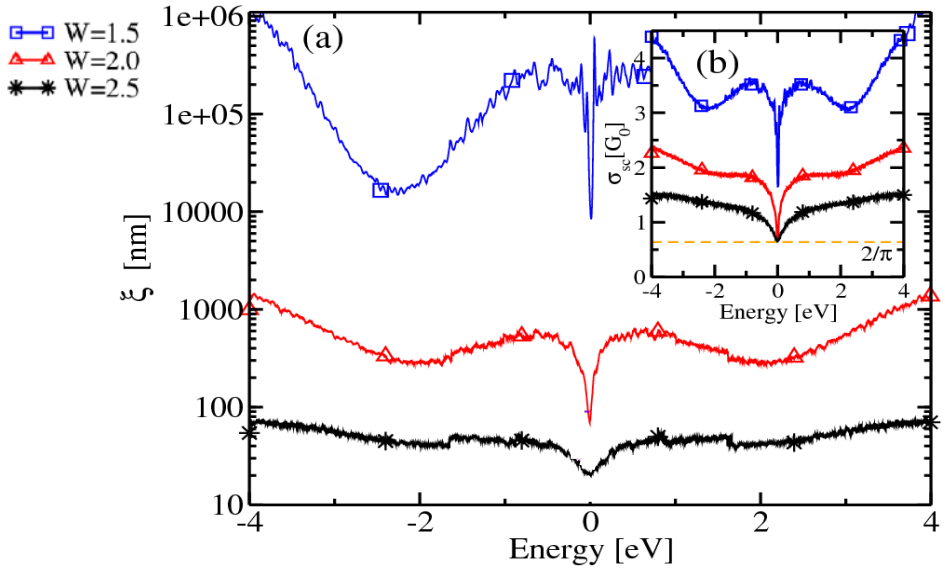
Localization effects –
-2D scaling theory of localization-

Lee & Fisher, PRL 47, 882 (81)

$$\sigma(L) = \sigma_{SC} - \Delta\sigma(L)$$

(quantum correction scaling)

$$\Delta\sigma(L) = (G_0/\pi)\ln(L/\ell_e)$$



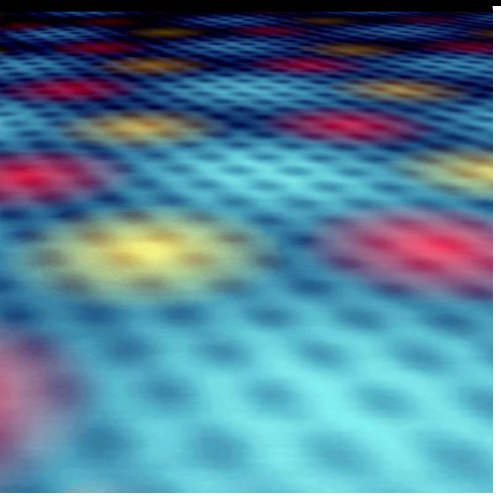
ξ (localization length) is defined by

$$\Delta\sigma(L = \xi) = \sigma_{sc}$$

$$\xi = \ell_e \exp(\pi\sigma_{sc}/G_0)$$

A. Lherbier, B. Biel, YM. Niquet, and SR, PRL 100, 036803 (2008)

Long range and pseudospin effects.



Charges trapped in the oxide

$$\mathcal{H} = \sum_{\alpha} V_\alpha |\alpha\rangle\langle\alpha| + \gamma_0 \sum_{\langle\alpha,\beta\rangle} e^{-i\varphi_{\alpha\beta}} |\alpha\rangle\langle\beta|$$

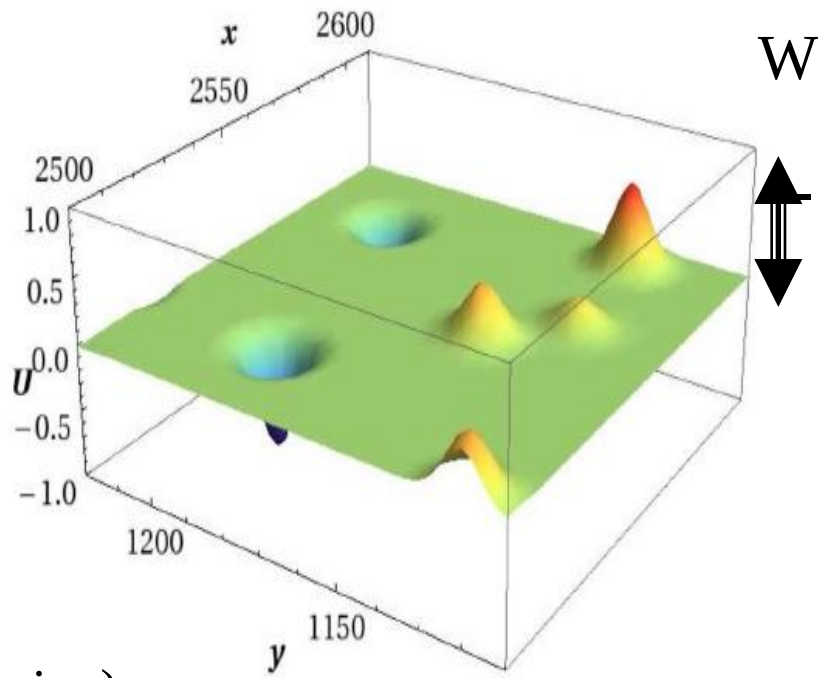
Long range (Gaussian) potential

$$V_\alpha = \sum_{i=1}^{N_I} \varepsilon_i \exp(-|\mathbf{r}_\alpha - \mathbf{r}_i|^2/(2\xi^2))$$

$$\varepsilon_i \in [-W/2, W/2](\gamma_0\text{-unit}),\ W = 0.5 - 2$$

$$\xi = 3a = 0.426\text{nm} \quad \gamma_0 = -2.7\text{eV}$$

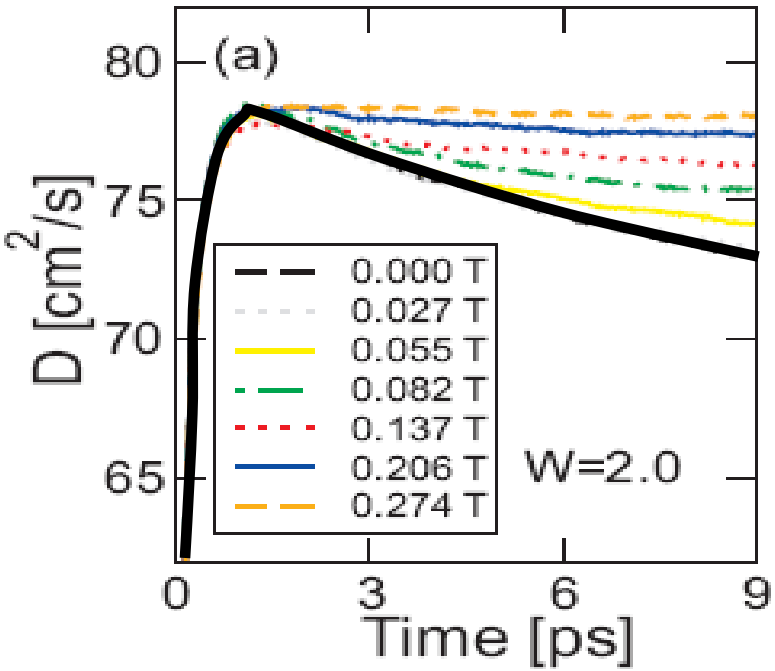
$$n_i = N_i/N = 0.125\%, 0.25\%, 0.5\%$$



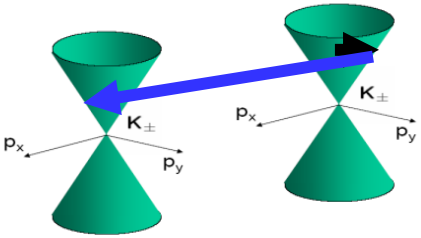
Sample size $S \sim 0.3\mu\text{m}^2$

W (depth of onsite potential ~screening)

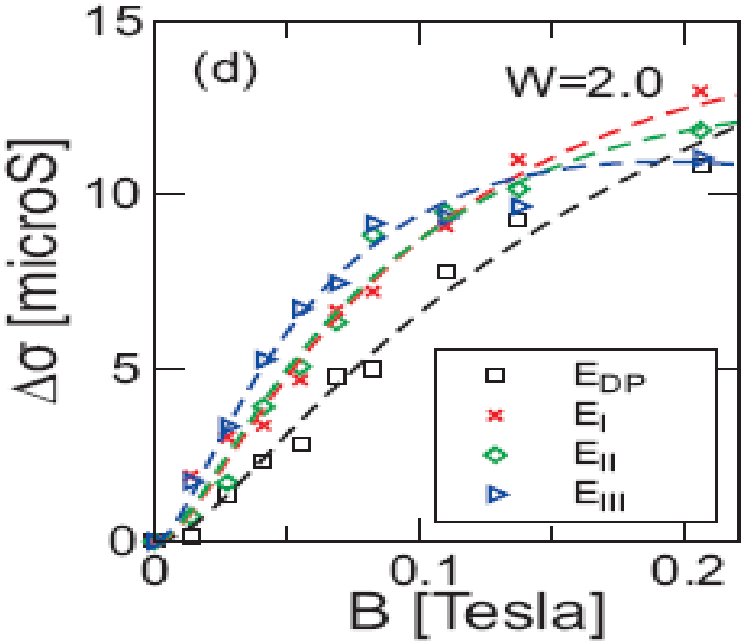
B-suppression of quantum interferences



At B=0 the Diffusion shows onset of localization (time-dependent decay)



$$\Delta\sigma(B) = \sigma(B) - \sigma(B=0)$$

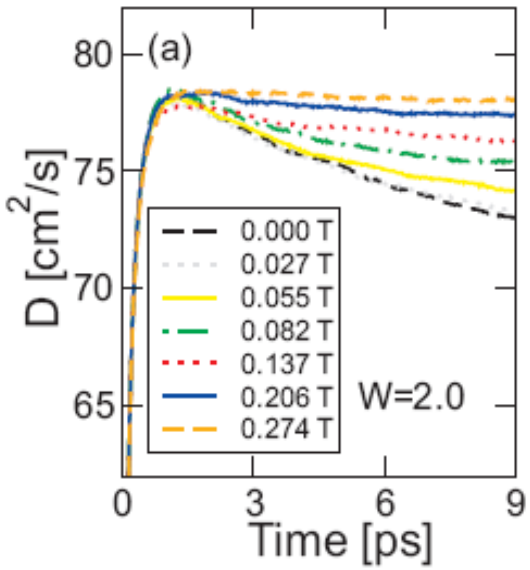


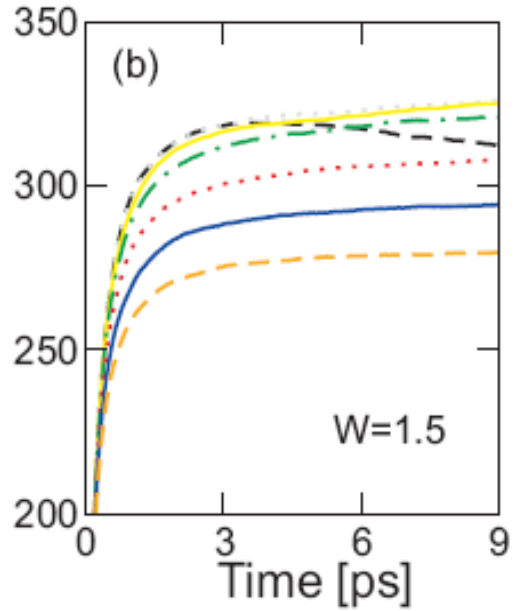
Quantum interferences
are suppressed by increasing magnetic field

Weak localization phenomenon

$$\ell_e \in [9, 20]\text{nm}$$

Tuning the disorder and valley mixing

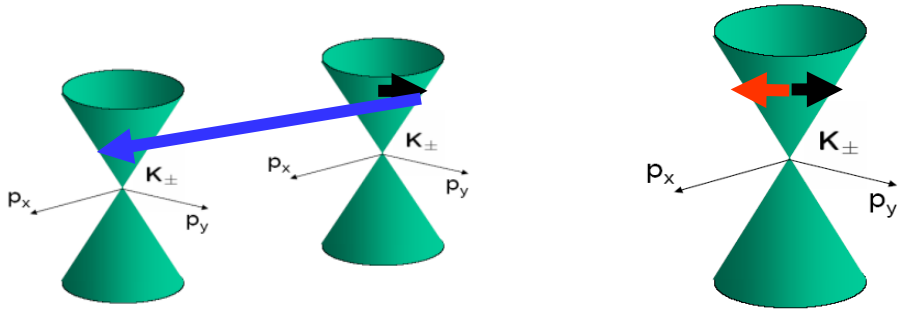


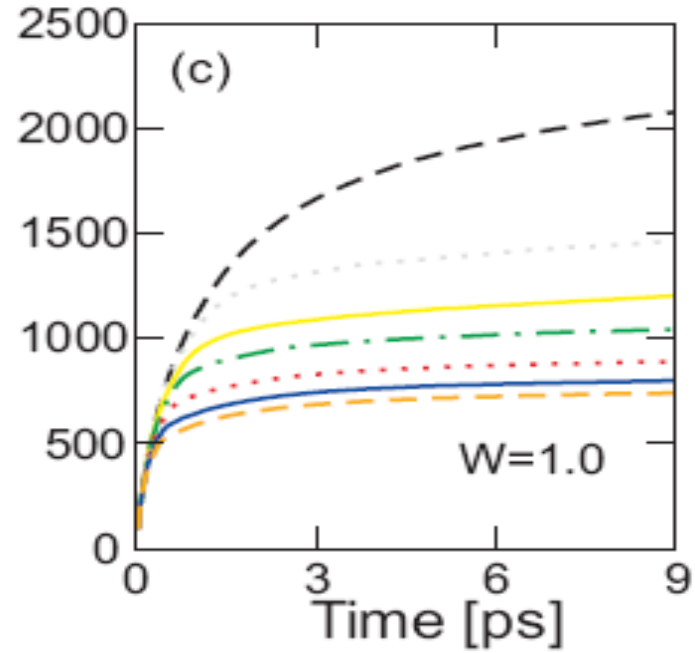


At W=1 the transport regime does not reach the diffusive regime within computational time

(~quasiballistic~)

At W=1.5 a crossover is observed On the Diffusion coefficient behavior

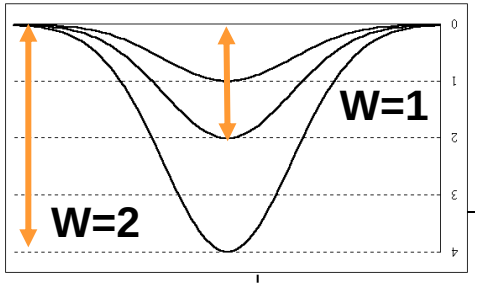


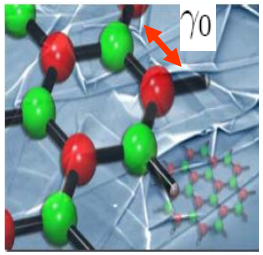


Crossover from WL to WAL

$$\sigma(E, t = N_t \Delta t) = e^2 \rho(E) D(E,t)/2$$

$$\Delta\sigma(B) = \sigma(B) - \sigma(B=0)$$

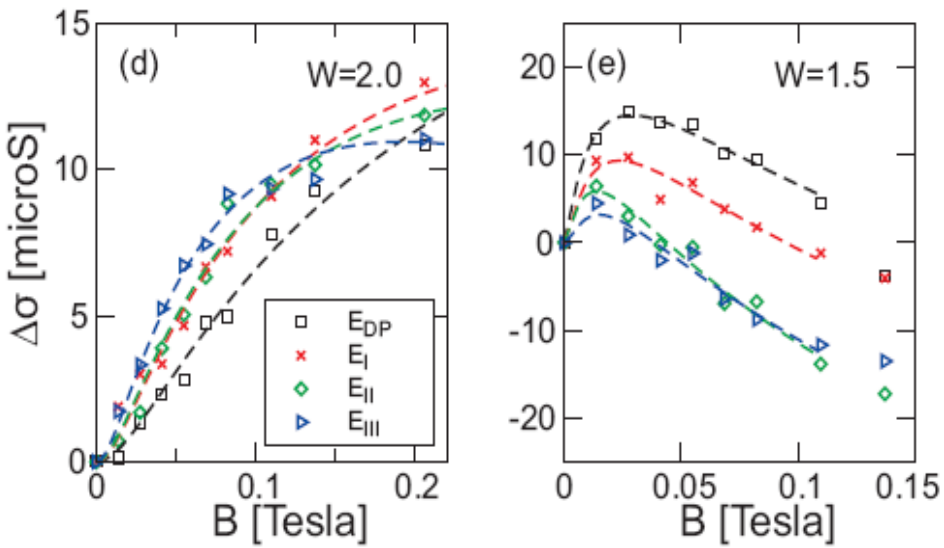




E_{DP}=0
E_I=0.049eV
E_{II}=0.097eV
E_{III}=0.146eV

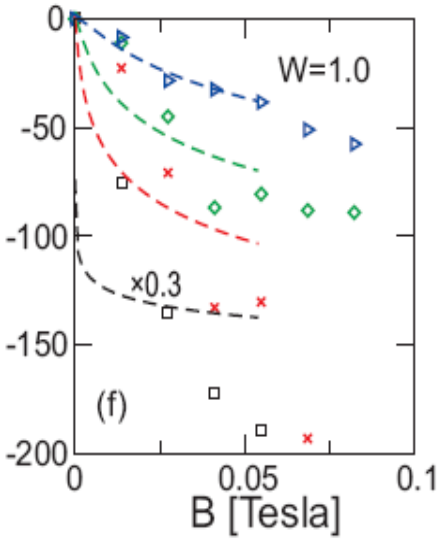
Weak localization

Crossover
Weak Antilocalization



Not WAL !!
(ballistic regime
Klein tunneling activated)

$$\Delta\sigma(B) < 0$$

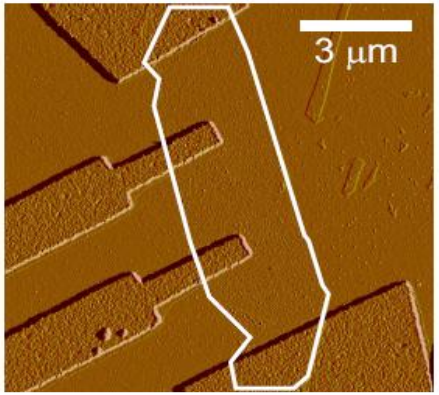


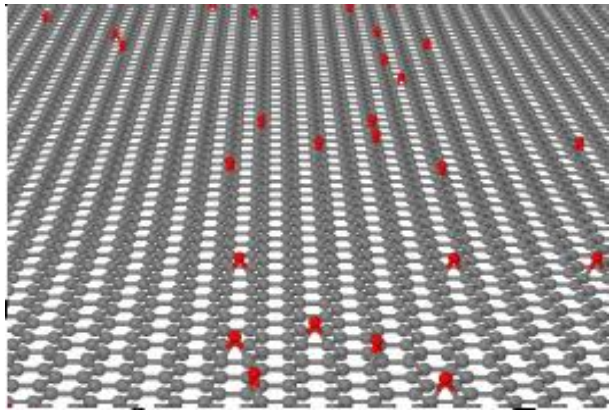
F. Ortmann, A. Cresti, G. Montambaux, SR. **Eur. Phys. Lett. 94, 47006 (2011)**

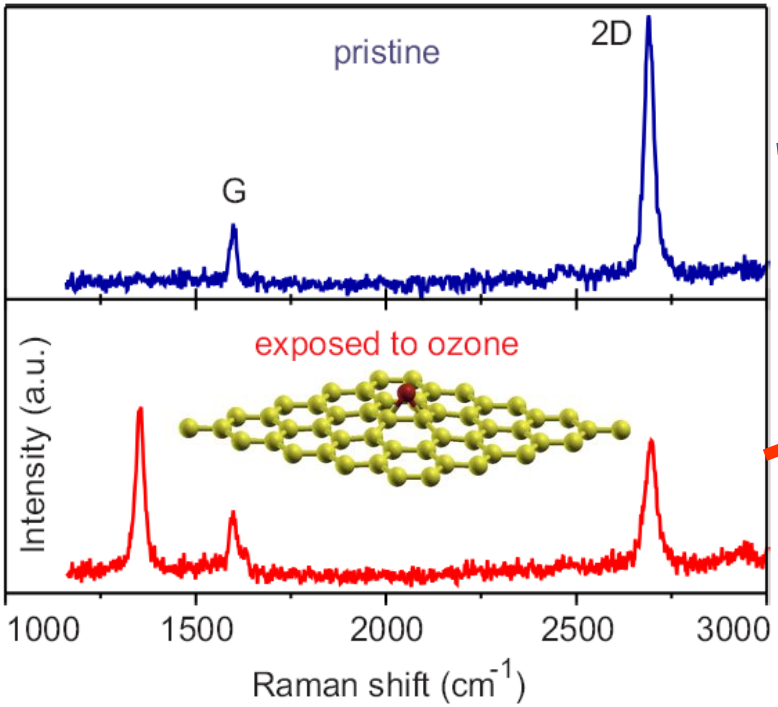
Quantifying the epoxide density ?

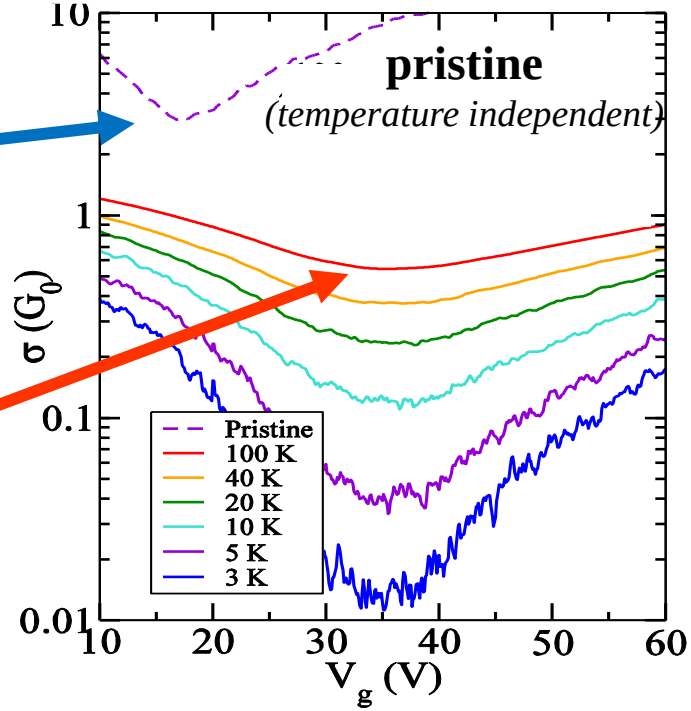
J. Moser et al.,
Phys. Rev. B 81, 205445 (2010)

Ozone flux → O_3







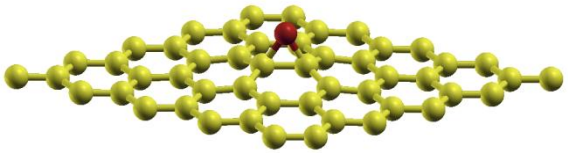


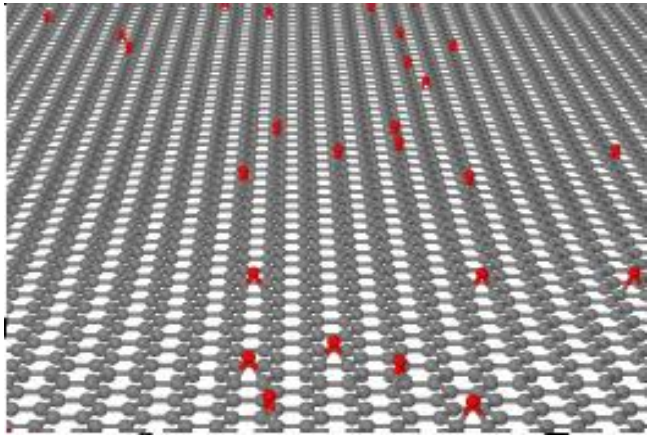
Epoxide defects

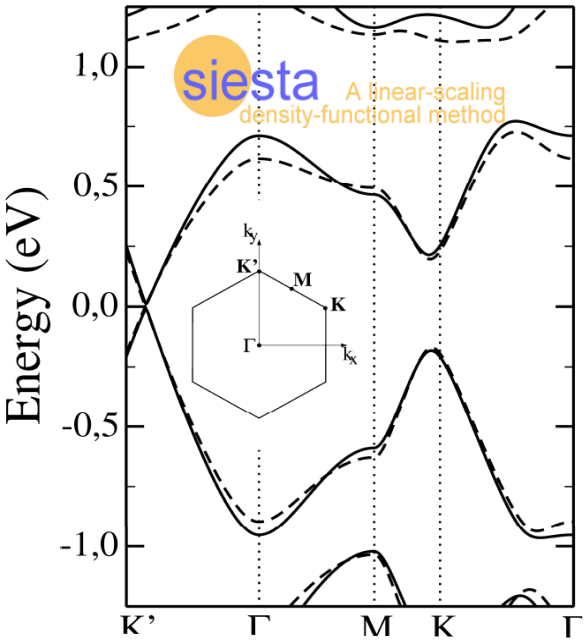
Ab-initio calculations +TB reparametrization

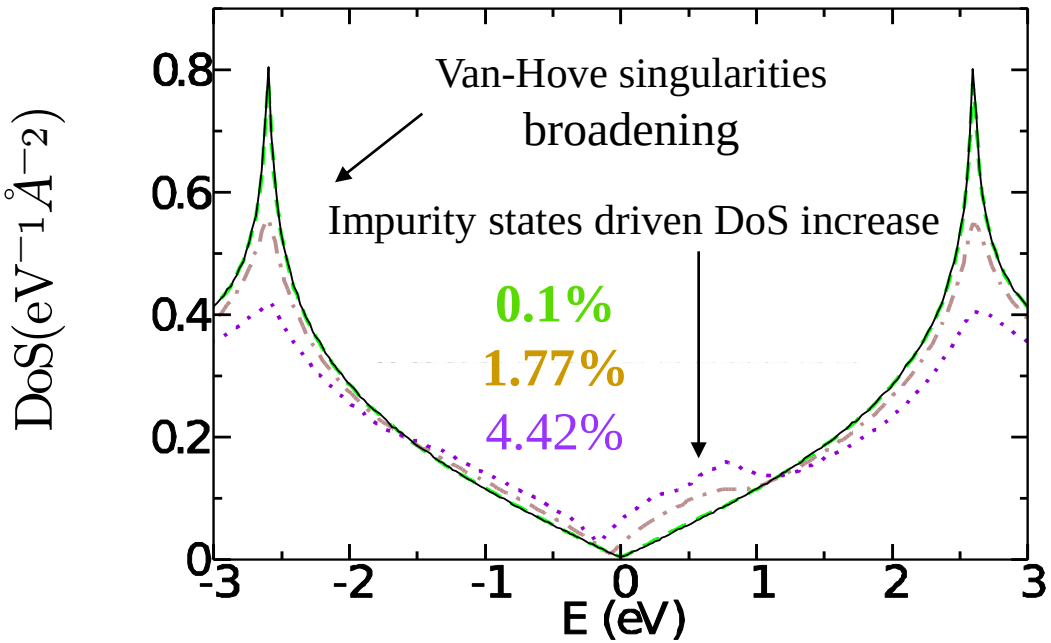
$O_3 \longrightarrow O_2 + C\text{-}O\text{-}C$

Epoxide defect









N. Leconte et al,
ACS Nano 4, 4033 (2010)

Does Boltzmann conductivity capture Dirac Point Physics?

$$\sigma^*_{\mathrm{Drude}}(E) = (4e^2/h) \times k\ell_e(E)/2$$

$$\rho(E) = 2|E|/(\pi \times (\hbar v_F)^2)$$

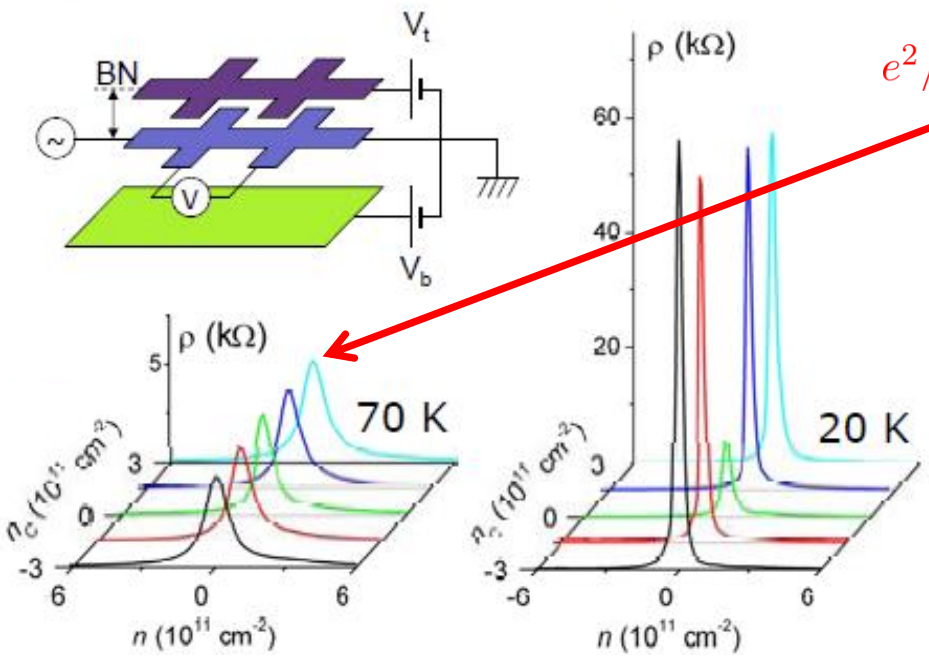
Fermi Golden Rule

Approximations

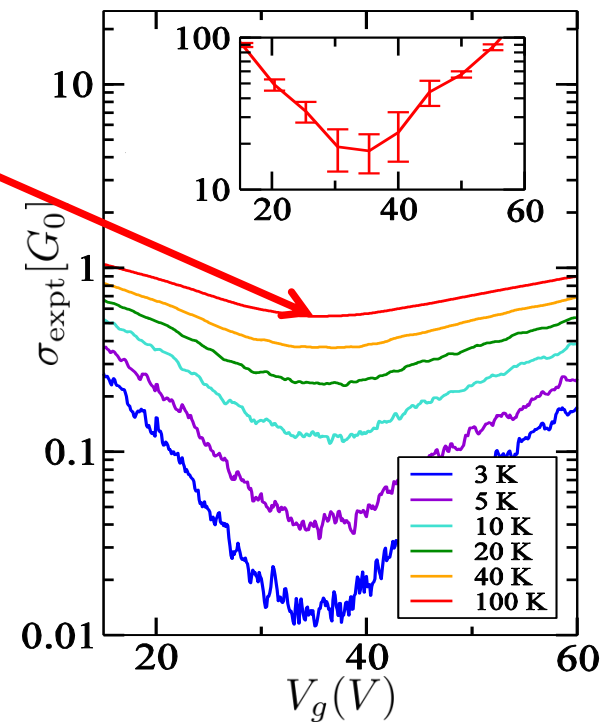
-all multiple scattering interferences

-DoS unchanged

$$\sigma^*_{\mathrm{Drude}} = 2e^2/h(\sqrt{\pi C_g V_g/e})\ell_e \qquad C_g \simeq 1.15 \times 10^{-4}\mathrm{Fm}^{-2}$$



$e^2/h \sim (6k\Omega)^{-1}$

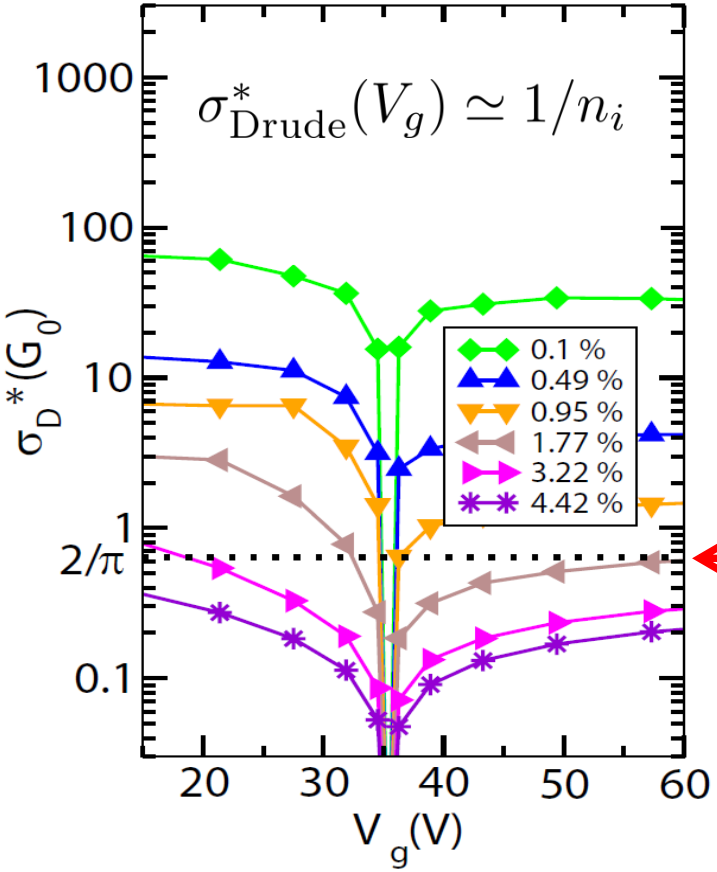


L. Ponomarenko et al: Nature Physics 7, 958, (2011)

Limit of Bloch Boltzmann approach….

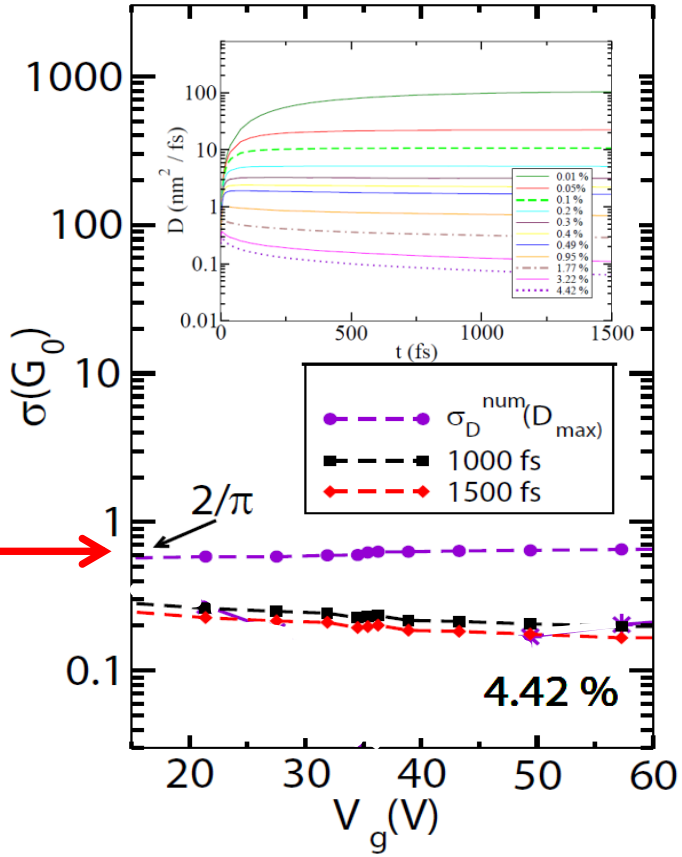
$$\sigma^*_{\mathrm{Drude}}(E) = (4e^2/h) \times k\ell_e(E)/2$$

$$\sigma(E,t) = (e^2/2)\mathrm{Tr}[\delta(E-\hat{H})]D(E,t)$$



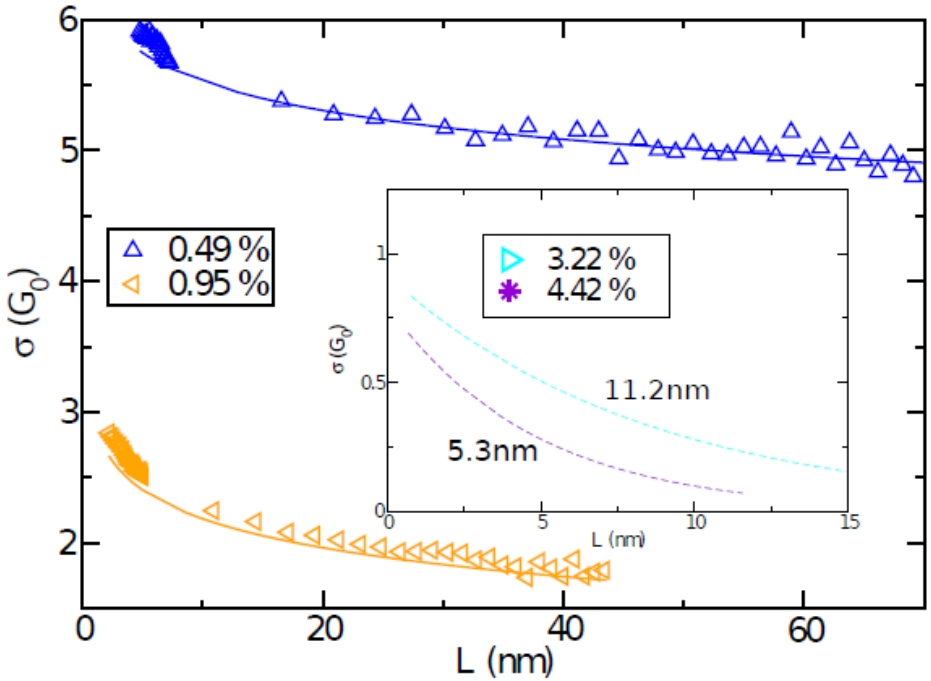
Minimum conductivity
(self-consistent Born approximation)

$$\frac{4e^2}{\pi h}$$



N. Leconte et al, **ACS Nano 4, 4033 (2010)**

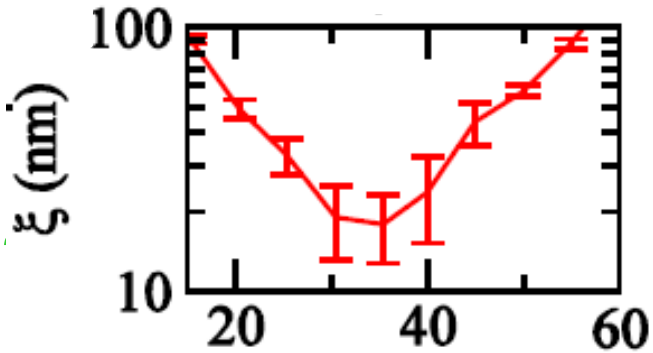
Scaling behavior of conductivity



$$\sigma(L) - \sigma\big|_{sc} = -\frac{e^2}{\hbar\pi^2}\ln\left(\frac{L}{\sqrt{2}\ell_e}\right)$$

$$\sigma(L) \sim \exp\left(-\frac{L(t)}{\xi}\right)$$

$$\xi(E) = \ell_e \exp(\pi\sigma_{\mathrm{Drude}}/2G_0)$$

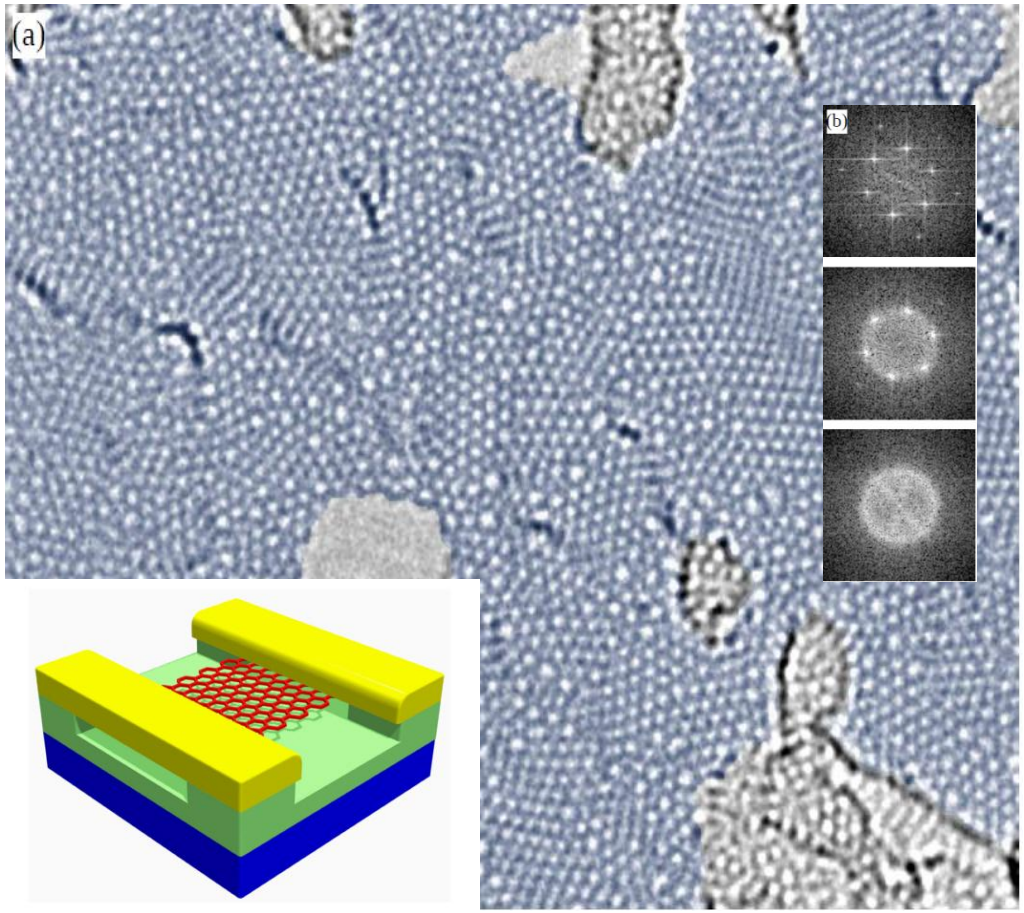


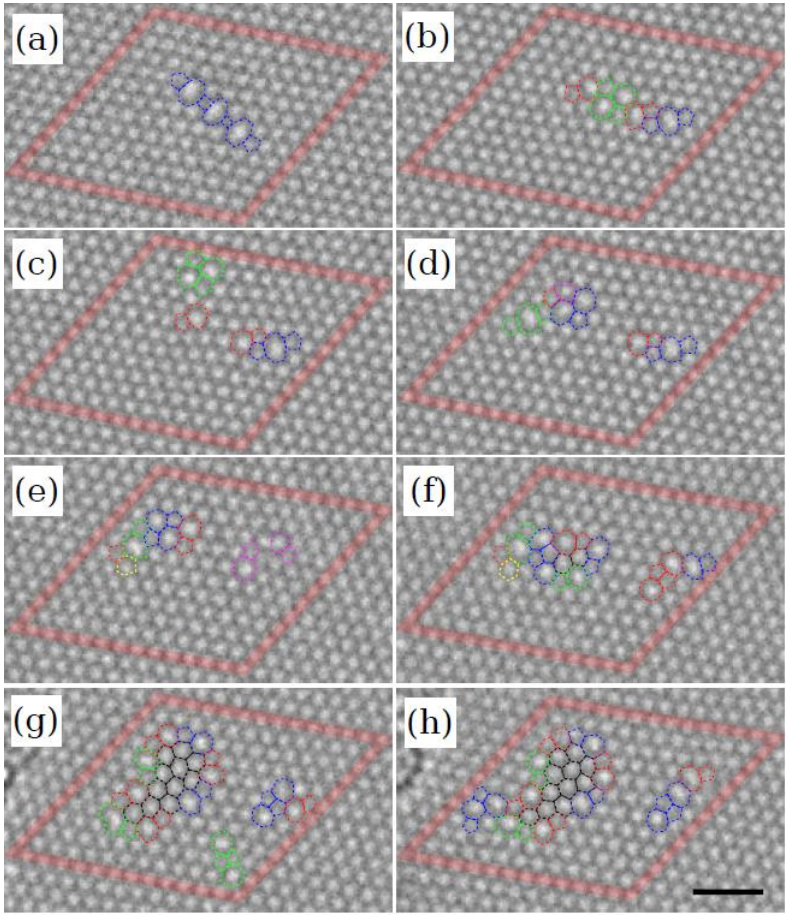
$$n_i = 2 - 4\%$$

N. Leconte et al., **PRB 84, 235420 (2011)**

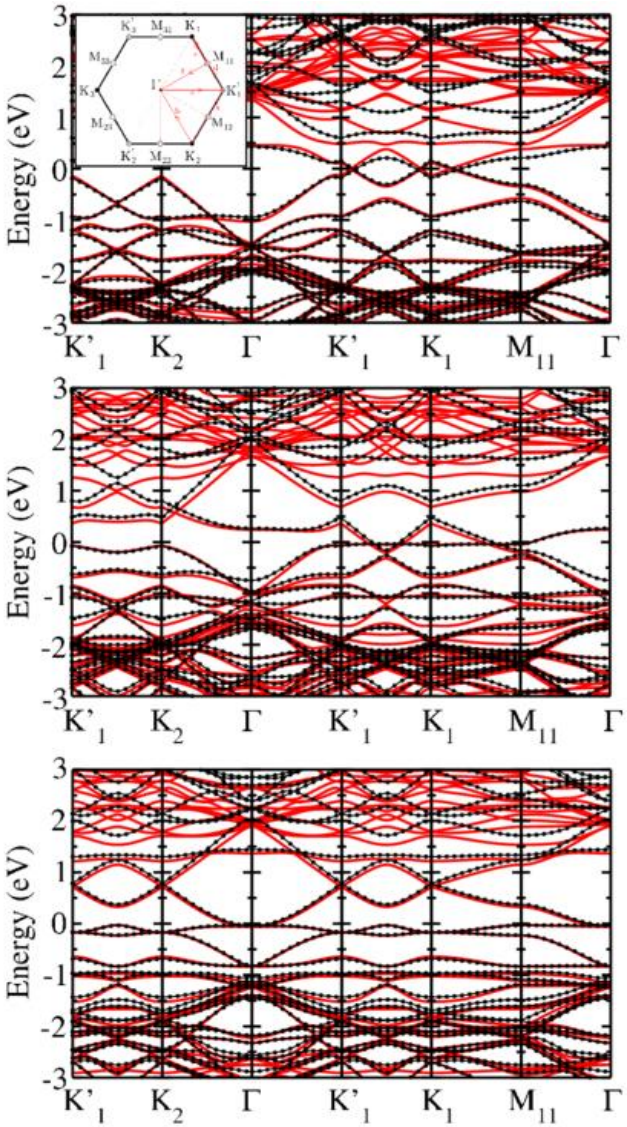
Towards Amorphous Graphene

J. Kotakoski, A. V. Krasheninnikov, U. Kaiser,J. C. Meyer,
Phys. Rev. Lett. 106, 105505 (2011)



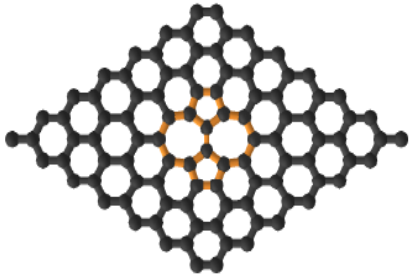


Non Magnetic Structural Defects

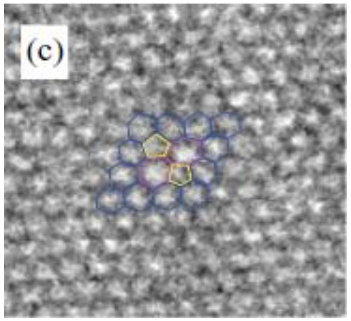


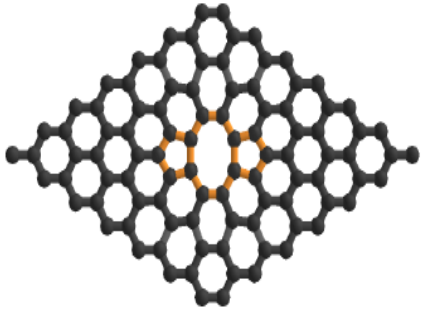
SIESTA ab initio calculations (red)

TB-third nearest neighbors (black)

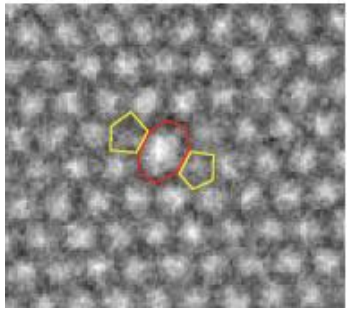


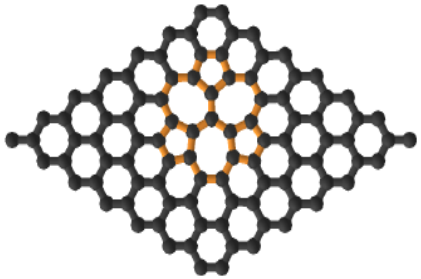
Stone-Wales





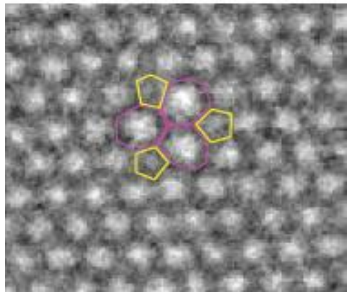
Divacancy 585





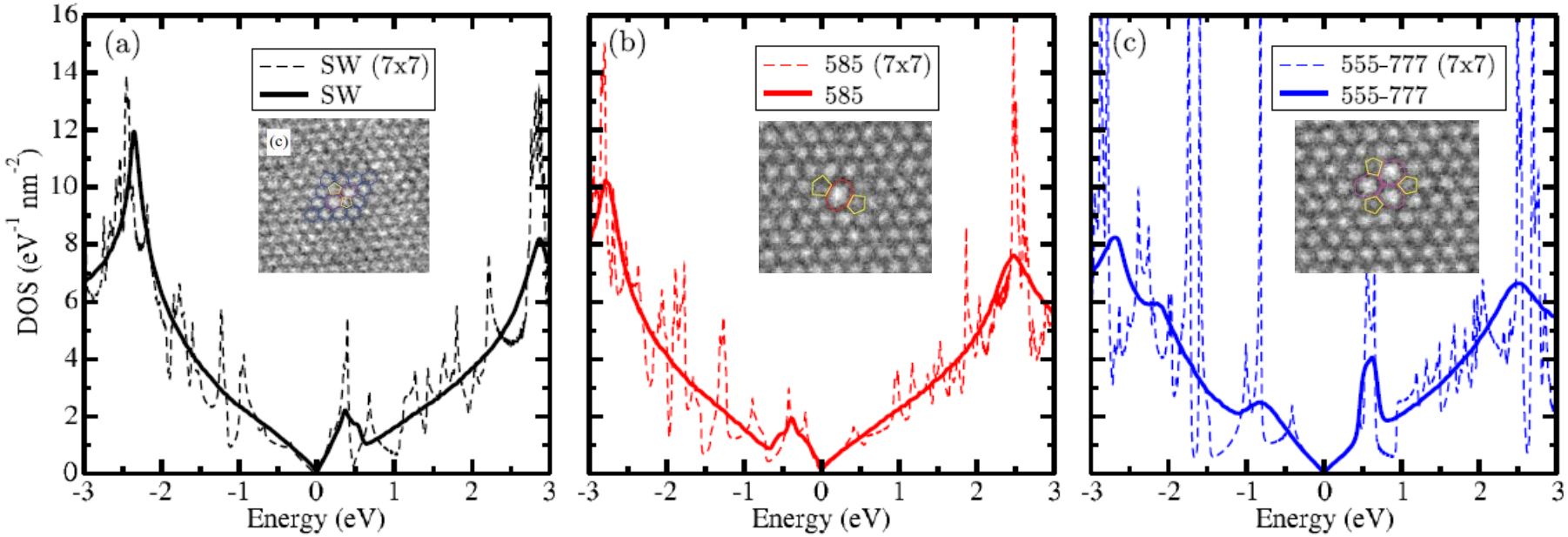
Divacancy 555777

3-fold symmetry axis

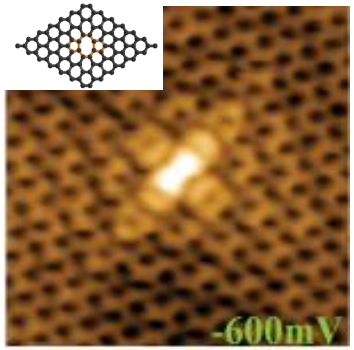


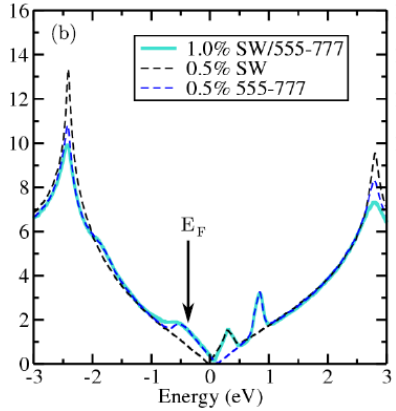
J. Kotakoski et al **PRB 83, 245420 (2011)**

Defect fingerprint



Each defect has a specific fingerprint,
from an experimental curve,
one could unravel the precise nature
and density defects





Ugeda et al, PRB 85, 121402(R) (2012)

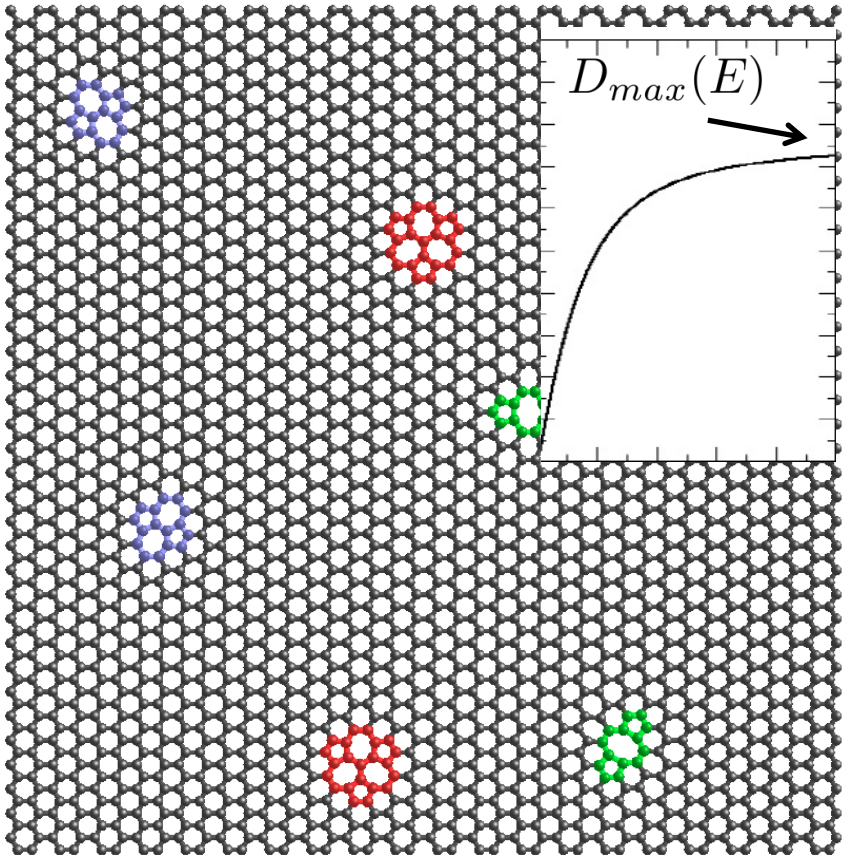
DoS, MFP and SC-Conductivities

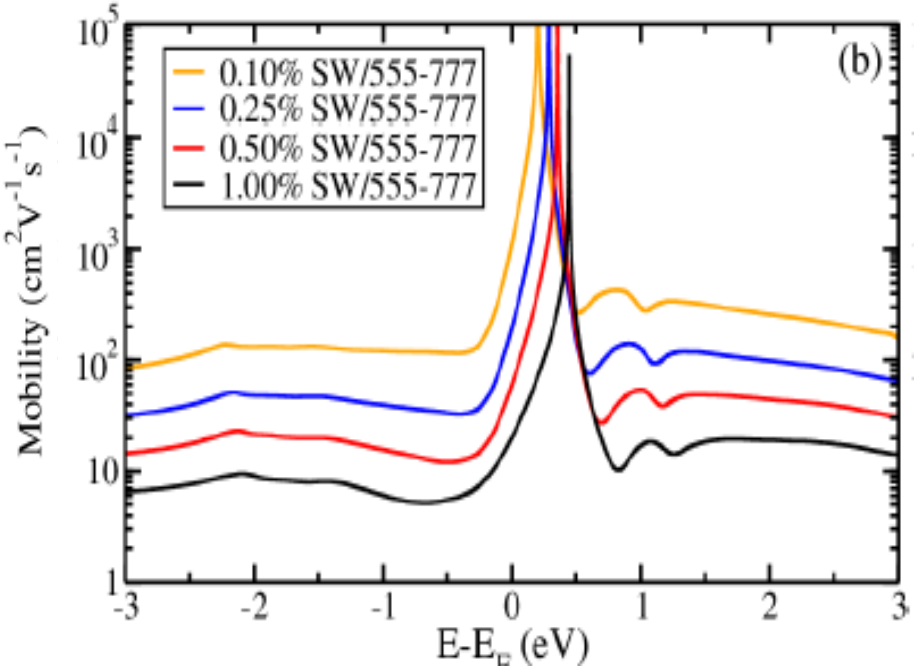
From dynamics of wavepackets

$$D_{max}(E) = v(E)\ell_e(E)$$

$$\sigma_{sc}(E) = e^2\rho(E)D_{max}(E)/2$$

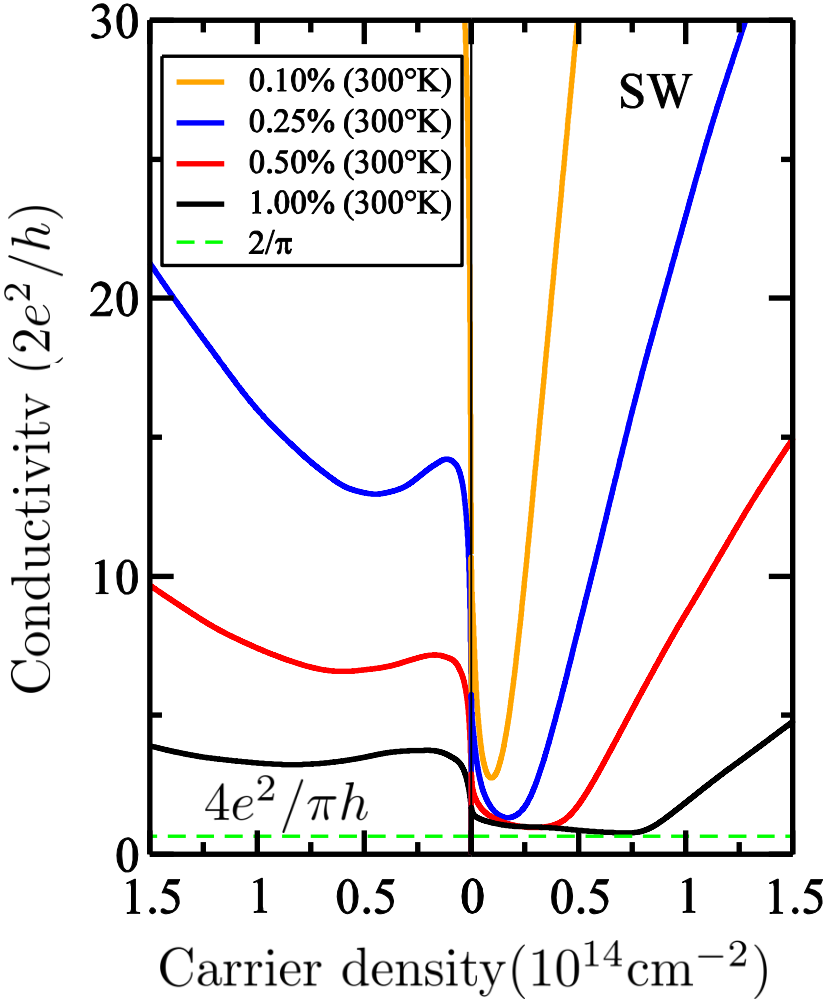
$$\mu = \sigma_{sc}(E)/ne$$





A. Lherbier et al., **Phys. Rev. Lett 106, 046803 (2011)**

Minimum (semiclassical) conductivity



Semiclassical conductivities

$$\sigma_{sc}(E) = e^2 \rho(E) D_{max}(E)/2$$

Upon increasing defect density
Drude conductivity decays until it reaches
its minimum value

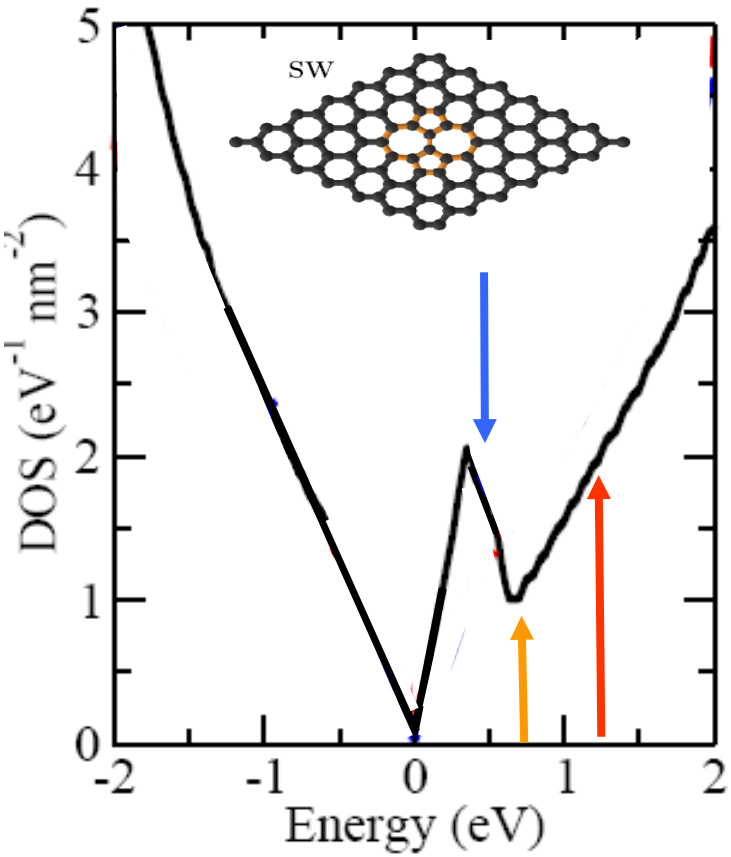
$$\sigma(E) = \frac{4e^2}{\pi h}$$

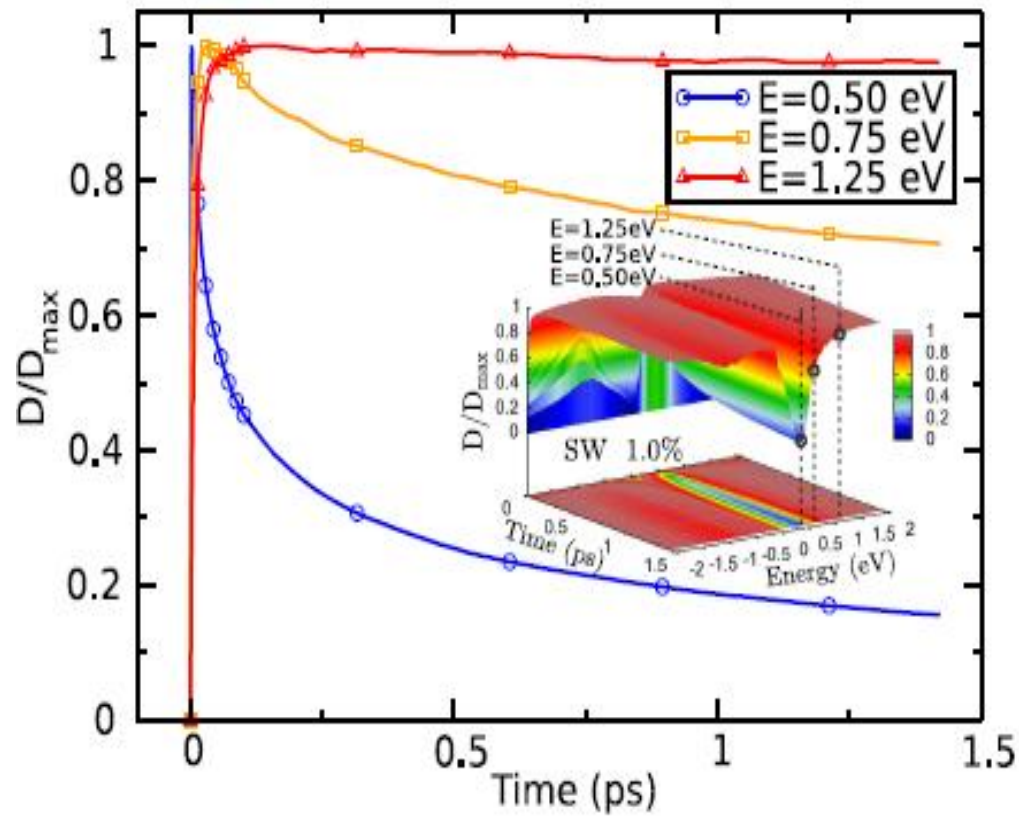
$$\sigma_{xx} \sim \mathrm{Tr}\langle v_x \Im m G(E+i\eta) v_x \Im m G(E+i\eta)\rangle_{\mathrm{conf.}}$$

$$\langle G(E)G(E')\rangle \sim \langle G(E)\rangle\langle G(E')\rangle$$

(semiclassical approximation)

Quantum interferences & localization





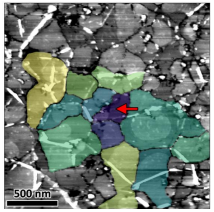
Transport regime tuning from diffusive to **Weak / Strong localization**

$$\xi(E) = \ell_e \exp(\pi\sigma_{\mathrm{Drude}}/2G_0)$$

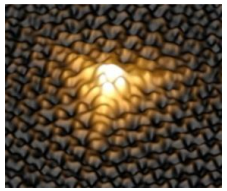
A. Lherbier et al., **Phys. Rev. Lett 106, 046803 (2011)**

OUTLINE

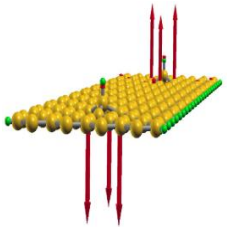
1. *"Clean versus dirty graphene ?"*



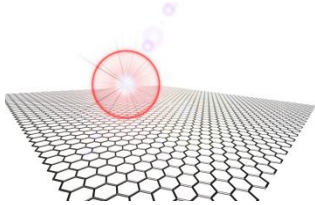
2. *From long range to short range disorder*
   Towards amorphous sp2 carbon membrane



3. *Local magnetic ordering (hydrogenation) and metal-insulator transition*



4. *Band gap tunability using a mid-infrared laser field*



Room temperature ferromagnetism

APPLIED PHYSICS LETTERS **98**, 193113 (2011)

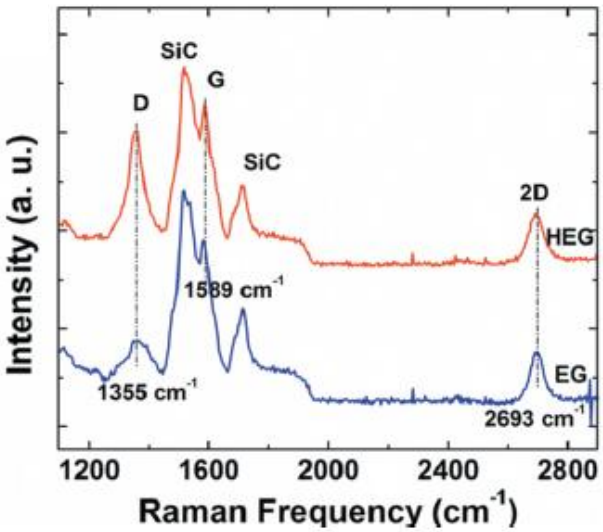
Room temperature ferromagnetism in partially hydrogenated epitaxial graphene

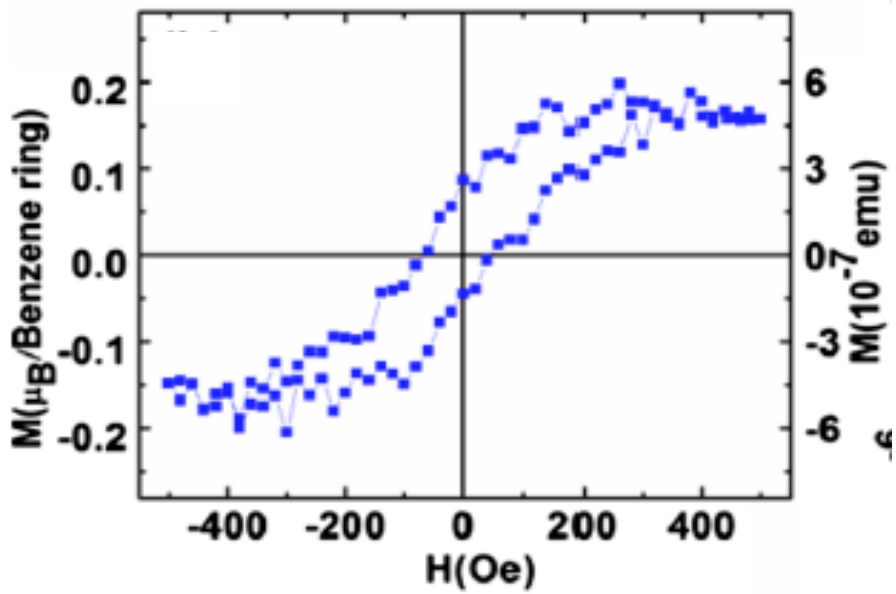
Lanfei Xie,[1] Xiao Wang,[1,2] Jiong Lu,[3] Zhenhua Ni,[4] Zhiqiang Luo,[4] Hongying Mao,[3] Rui Wang,[1] Yingying Wang,[4] Han Huang,[1] Dongchen Qi,[1] Rong Liu,[1] Ting Yu,[4] Zexiang Shen,[4] Tom Wu,[4] Haiyang Peng,[4] Barbaros Özyilmaz,[1] Kianping Loh,[3] Andrew T. S. Wee,[1] Ariando,[1,2,a)] and Wei Chen[1,3,a)]

[1]*Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542*
[2]*NUSNNI-Nanocore, National University of Singapore, 5A Engineering Drive 1, Singapore 117411*
[3]*Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543*
[4]*Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371*

(Received 12 March 2011; accepted 18 April 2011; published online 12 May 2011)

Magnetic hysterisis at room temperature



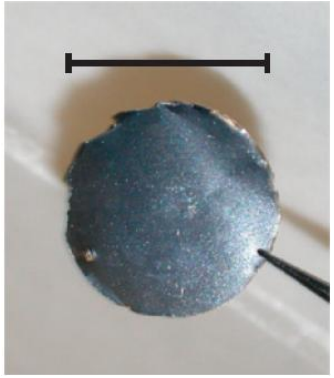


Absence of magnetic ordering

nature physics

LETTERS

PUBLISHED ONLINE: 10 JANUARY 2012 | DOI: 10.1038/NPHYS2183



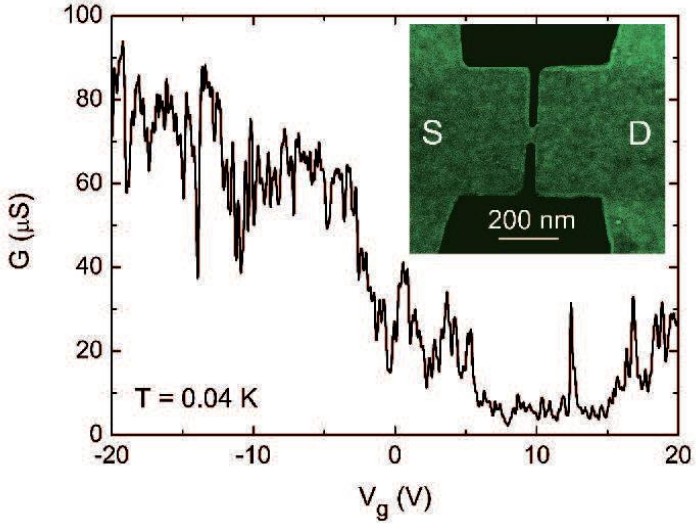
Spin-half paramagnetism in graphene induced by point defects

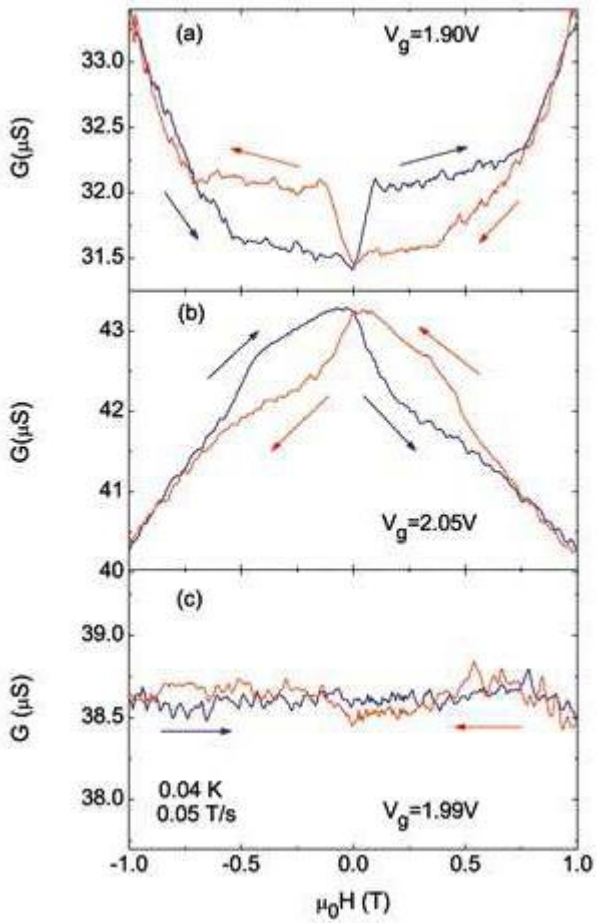
R. R. Nair[1], M. Sepioni[1], I-Ling Tsai[1], O. Lehtinen[2], J. Keinonen[2], A. V. Krasheninnikov[2,3], T. Thomson[1], A. K. Geim[1] and I. V. Grigorieva[1]*

Here we show that point defects in graphene—(1) fluorine adatoms in concentrations x gradually increasing to stoichiometric fluorographene $CF_{x=1.0}$ (ref. 17) and (2) irradiation defects (vacancies)—carry magnetic moments with spin 1/2. Both types of defect lead to notable paramagnetism but no magnetic ordering could be detected down to liquid helium temperatures.

Unexplained Magnetoconductance hysteresis

Observation of hysteresis loops of the magnetoconductance in graphene devices
A. Candini, C. Alvino, W. Wernsdorfer and M. Affronte,
Phys. Rev. B 83, 121401 (2011)





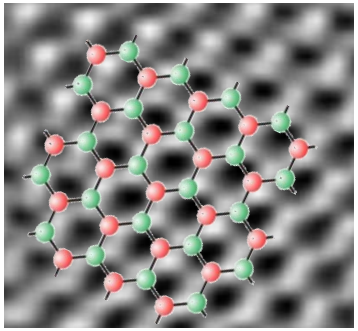
"*the hysteresis loops reflect* ***the magnetization reversal of the localized moments****, as the conducting graphene layer detects the magnetization behavior through its magnetoconductance.*"

Defects ? (vacancies….)

Lieb s Theorem

E.H. Lieb, **Phys. Rev. Lett** 62, 1201 (1989)

$$\mathcal{H} = \sum_{ij\sigma} t c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} (\hat{n}_{i\uparrow}\langle \hat{n}_{i\downarrow}\rangle + \hat{n}_{i\downarrow}\langle \hat{n}_{i\uparrow}\rangle - \langle \hat{n}_{i\uparrow}\rangle\langle \hat{n}_{i\downarrow}\rangle)$$

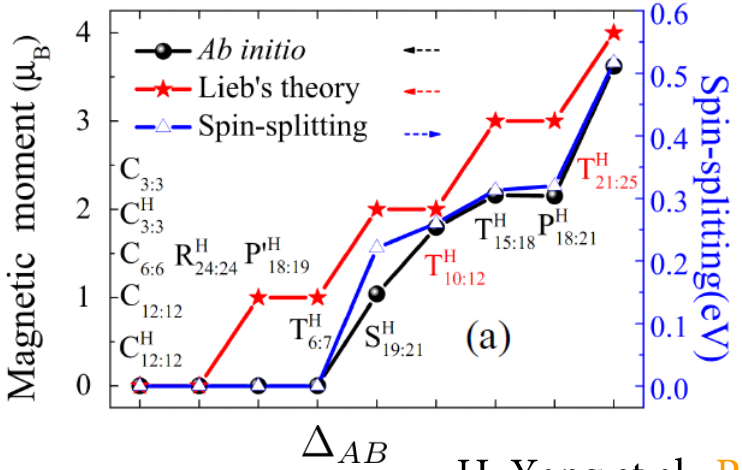


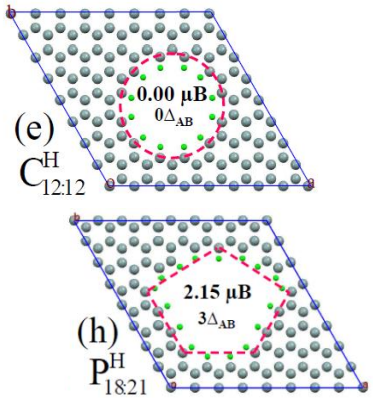
Theorem (repulsive case) : If the lattice is **bipartite** (t couple only A sites with B sites), Assuming number of B larger or equal to number of A sites (and number of electron =total number of sites (half-filled band), then the ground state of $\mathcal{H}$ is unique with spin $S = \frac{1}{2}(\mid B \mid - \mid A \mid) = \frac{1}{2}\Delta_{AB}$

Graphene Nanomesh

J. Bai et al.,

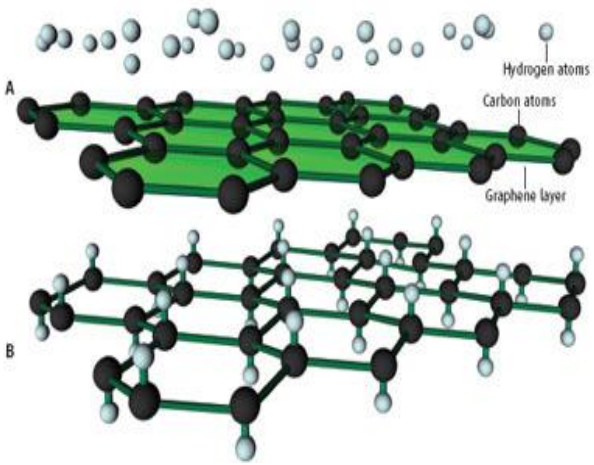
Nature Nanotech 2010





H. Yang et al., PRB 84, 214404 (2011)

Describing Hydrogenated Graphene



Hubbard Hamiltonian

*Single π band with a **repulsive Coulomb interaction** between electrons with opposite spin occupying the same orbital*

$$\sum_{ij\sigma} t c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_i (\hat{n}_{i\uparrow}\langle\hat{n}_{i\downarrow}\rangle + \hat{n}_{i\downarrow}\langle\hat{n}_{i\uparrow}\rangle - \langle\hat{n}_{i\uparrow}\rangle\langle\hat{n}_{i\downarrow}\rangle)$$

$U > 0$ *constant one-site coulomb repulsion raising energy by U when 2 electrons occupy the same orbital*

$$\langle\hat{n}_{i\uparrow}\rangle = \int dE f(E_F - E)\rho_{i\uparrow}(E) \qquad \hat{n}_{i,\uparrow} = c^{\dagger}_{i,\uparrow} c_{i,\uparrow}$$

$$\langle\hat{n}_{i\sigma}\rangle_0 \Rightarrow \mathcal{H} \Rightarrow \rho_{i\sigma} \Rightarrow \langle\hat{n}_{i\sigma}\rangle$$

$$\varepsilon_{i\uparrow} = U\langle\hat{n}_{i\uparrow}\rangle(1 - \langle\hat{n}_{i\downarrow}\rangle)$$

$$\varepsilon_{i\downarrow} = U\langle\hat{n}_{i\downarrow}\rangle(1 - \langle\hat{n}_{i\uparrow}\rangle)$$

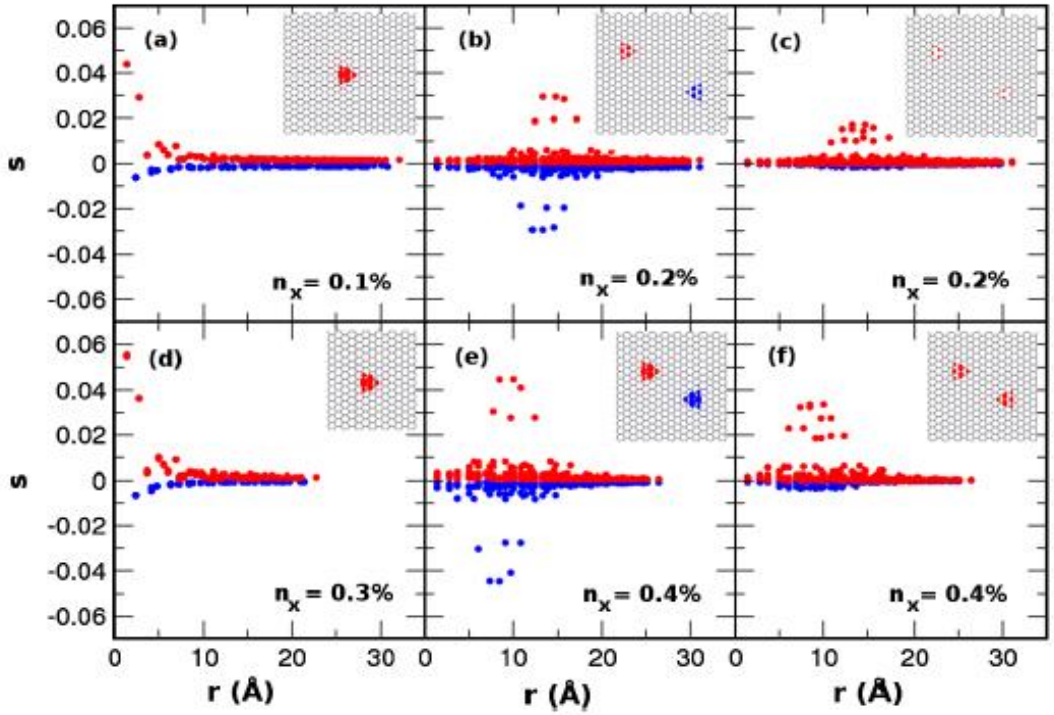
$$\mathcal{M}_i = \frac{\langle\hat{n}_{i\uparrow}\rangle - \langle\hat{n}_{i\downarrow}\rangle}{2}$$

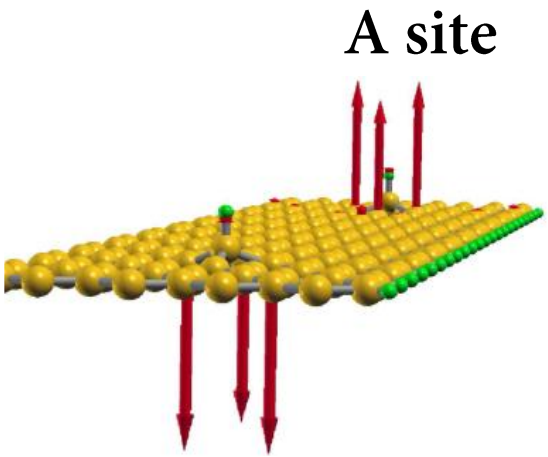
self-consistent occupation numbers *for spin-down and spin-up electrons*

Spin texture around Hydrogen defects

<u>Case studies</u> *low H- coverage*

Absence of any (local) magnetic ordering (1 H per unit cell)
Local Antiferromagnetism (2 H defects on sites A and B)
Local Ferromagnetism (2H grafted on the same sublattice A)
or applying magnetic field



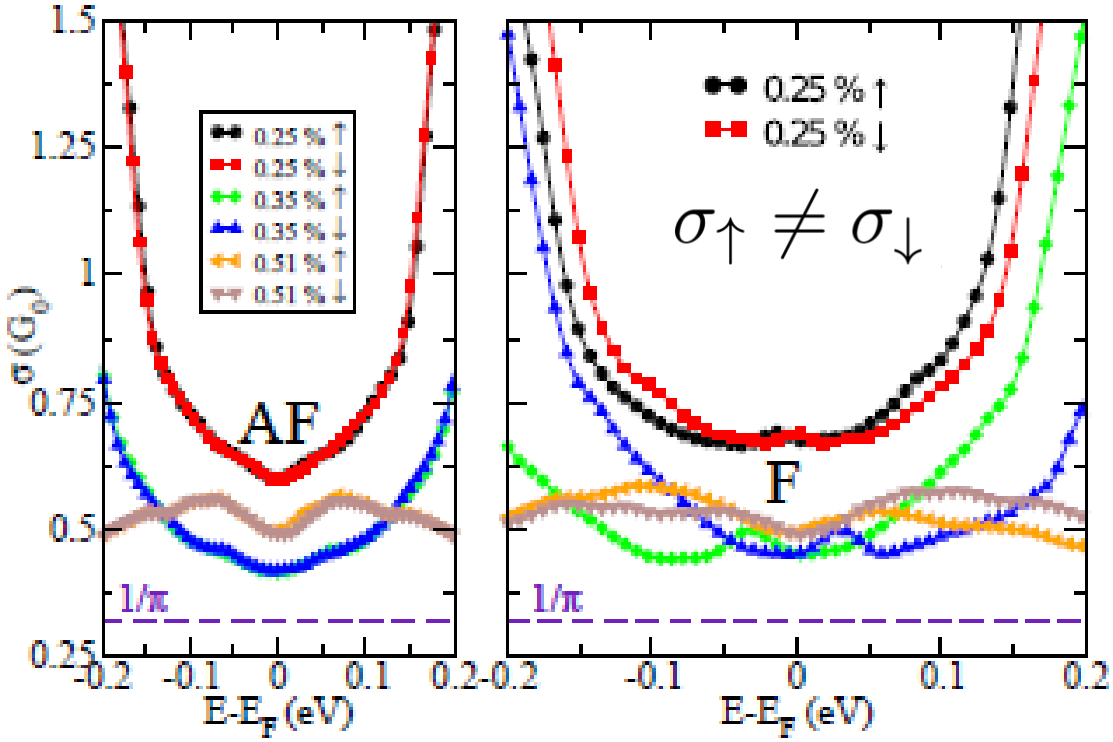


Local (site) spin (s) versus r (*the distance to the center of the supercell*)

Drude Conductivity – magnetic state

$$\sigma_{\uparrow,\downarrow}(E,t) = (e^2/2)\mathrm{Tr}[\delta_{\uparrow,\downarrow}(E-\hat{H})]D_{\uparrow,\downarrow}(E,t)$$

Spin-resolved DoS *Spin-r esolved diffusion coefficient*



Neglecting quantum interferences

$$\sigma^{\mathrm{Drude}}_{\uparrow,\downarrow}(E) \sim 1/n_x$$

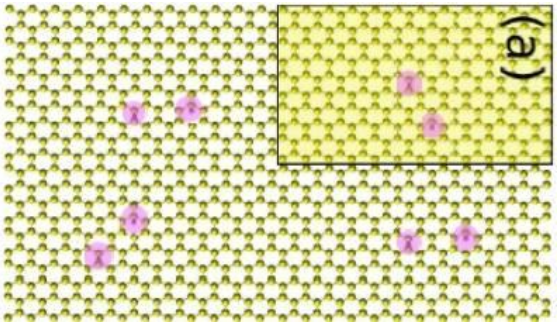
For the local ferromagnetic ordering spin splitting and $\sigma_\uparrow \neq \sigma_\downarrow$

$$\sigma^{\mathrm{Drude}}_{\uparrow}(E) + \sigma^{\mathrm{Drude}}_{\downarrow}(E) \geq 4e^2/\pi h$$

D. Soriano et al., **Phys. Rev. Lett. 107, 016602 (2011)**

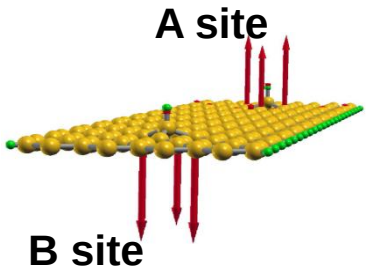
Magnetoresistance signal

$$\mathrm{MR} = (\sigma^F - \sigma^{AF})/(\sigma^F + \sigma^{AF})$$



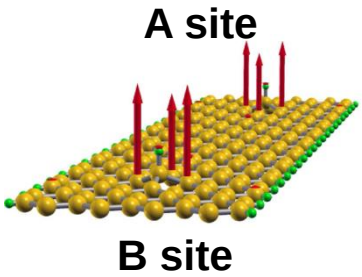
$$\sigma^{AF} = \sigma^{AF}_{\uparrow} + \sigma^{AF}_{\downarrow}$$

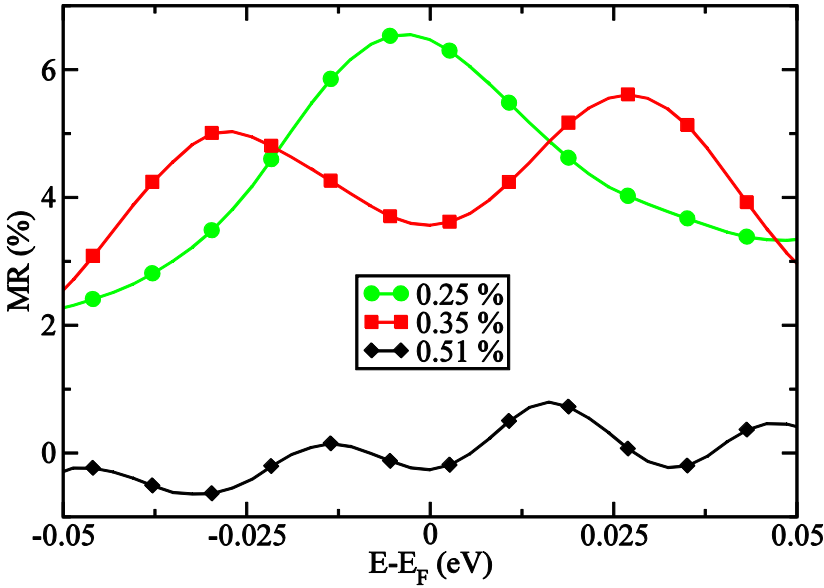
Ground state



$$\sigma^{F} = \sigma^{F}_{\uparrow} + \sigma^{F}_{\downarrow}$$

Excited state (applying B)

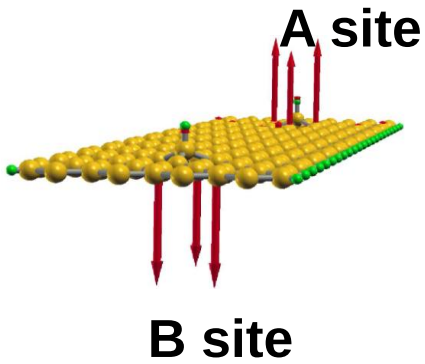


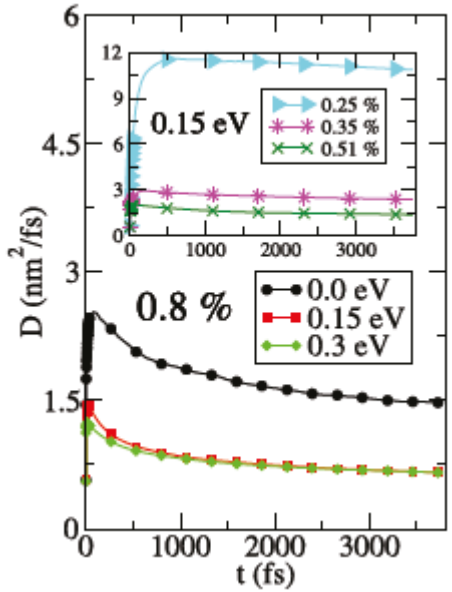


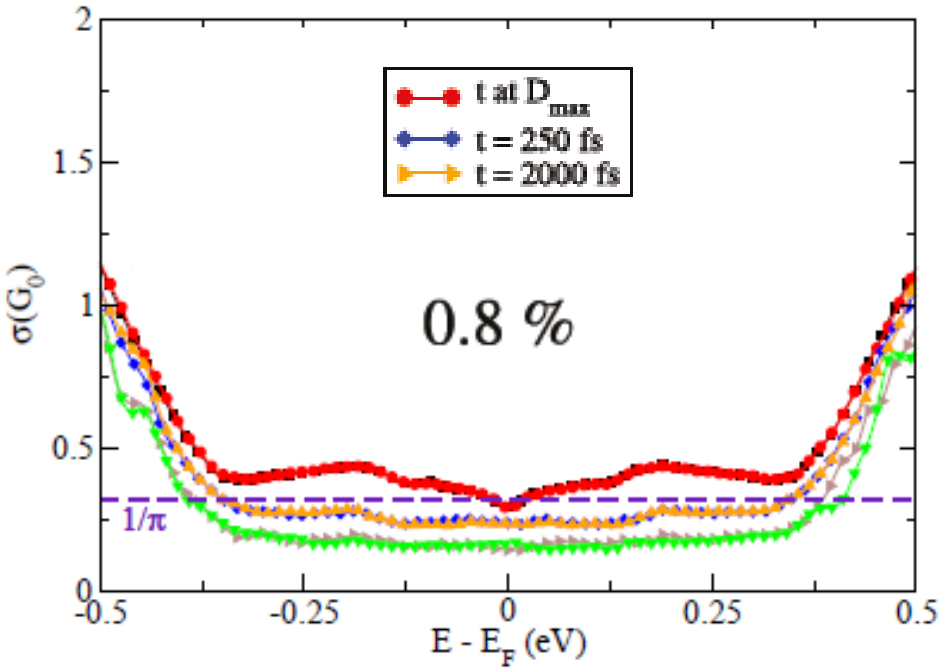
D. Soriano, N. leconte, P. Ordejon, J.C. Charlier, J. Palacios, S.R.

Phys. Rev. Lett. 107, 016602 (2011)

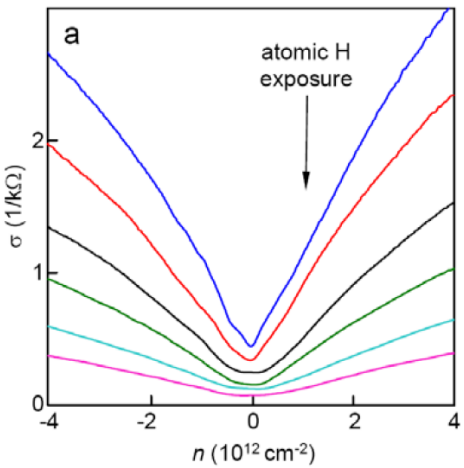
Local Antiferromagnetism / quantum regime







Manchester s group



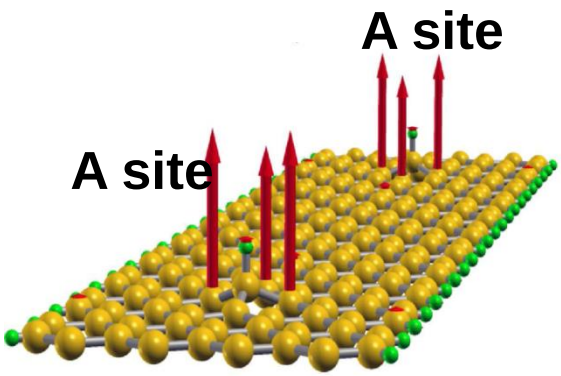
The disordered graphene turns to an insulator
Conductivity strongly decay at low temperatures

$$\xi(E) = \ell_e \exp(\pi\sigma_{\mathrm{Drude}}/2G_0)$$

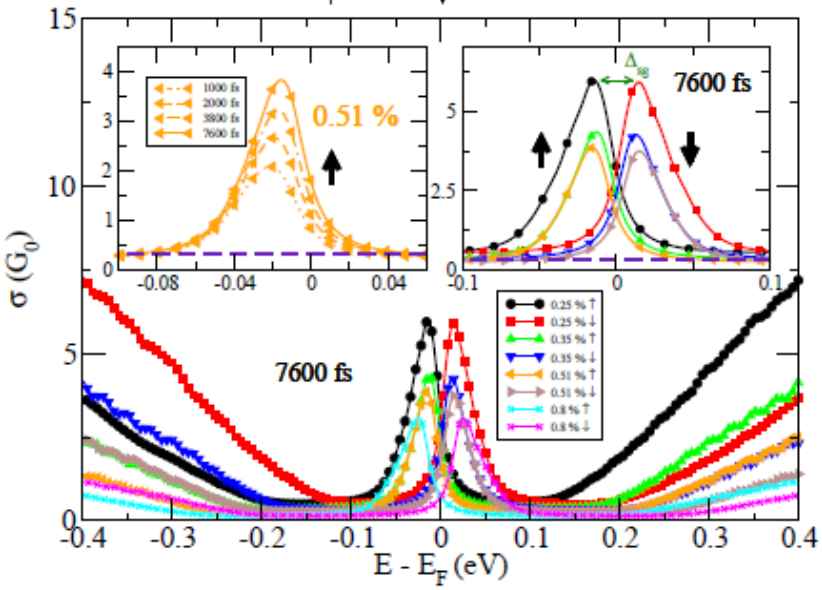
$$n_x = 0.25\% \text{ and } 0.8\%$$
$$\xi(E) \sim 8 - 15\mathrm{nm}$$

N. Leconte, D. Soriano, S. R. et al. **ACS Nano 5, 3987 (2011)**

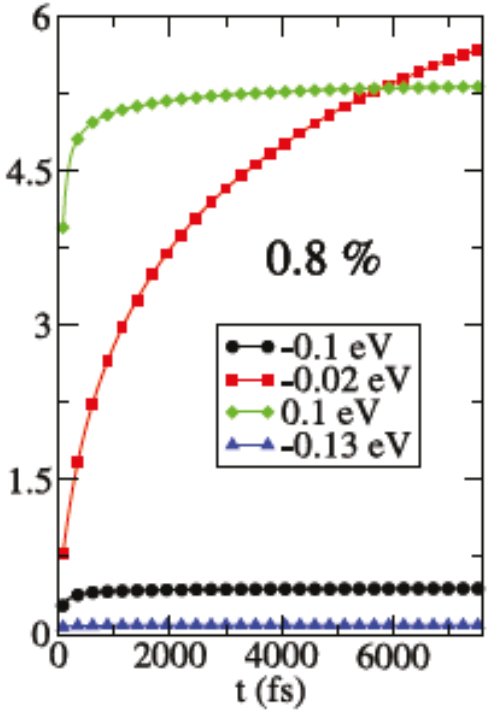
Local Ferromagnetic ordering



$$\Delta_{sg} = |\varepsilon^r_\uparrow - \varepsilon^r_\downarrow| \in [25, 30]\text{meV}$$



Spin Splitting



$\sigma_{Kubo} \geq 4e^2/\pi h$ Suppression of quantum interferences

The disordered graphene remains metallic
conductivity insensitive to localization
Effects at low temperatures

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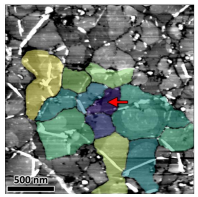
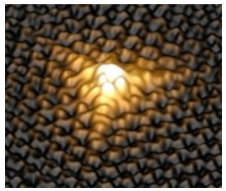
OUTLINE

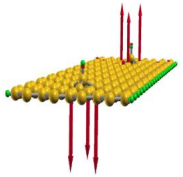
1. *Welcome to the world of "dirty graphene" ?*



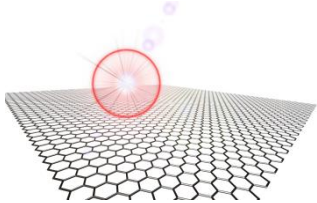
2. *From structural defects to amorphous sp^2 membrane (transparent electrodes ?)*



3. *Local magnetic ordering (hydrogenation) and metal-insulator transition*



4. *Band gap tunability using a mid-infrared laser field*



Acknowledgements

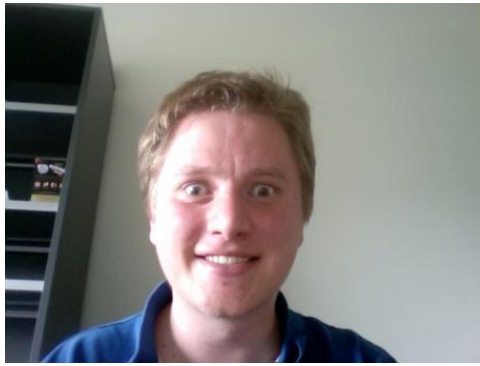
Ph.D students

Nicolas Leconte
Dinh Van Tuan



Postdocs

Frank Ortmann
David Soriano



Collaborations

Aurelien Lherbier
Jean-Christophe Charlier
Pablo Ordejon