

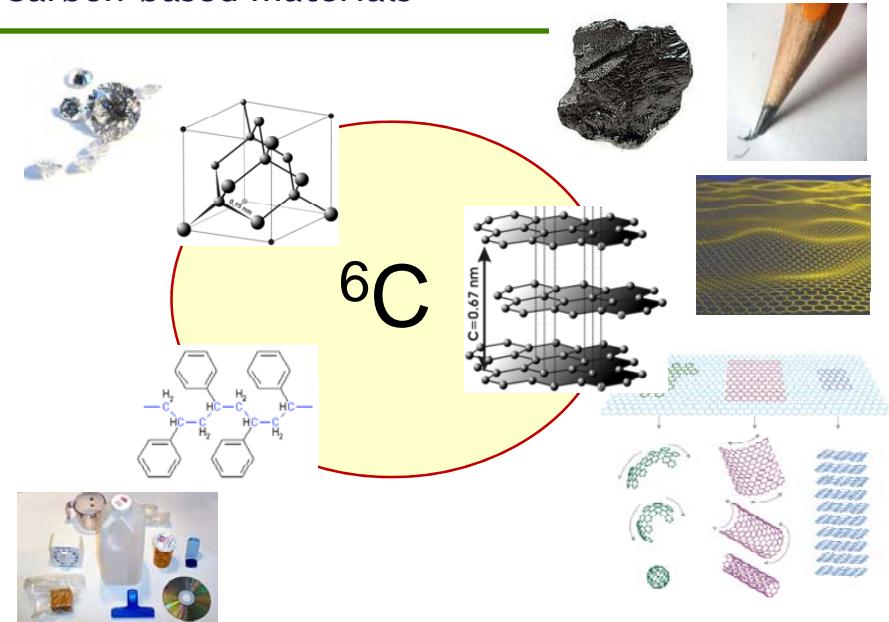


Ηλεκτρικές και οπτικές και ιδιότητες γραφενίου

Elefterios Lidorikis

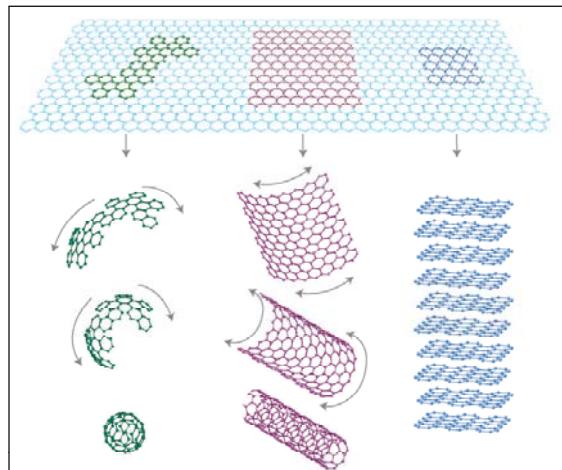
Materials Science & Engineering, University of Ioannina, Greece

Carbon-based materials



Graphene

- a one-atom-thick planar sheet of sp²-bonded carbon atoms

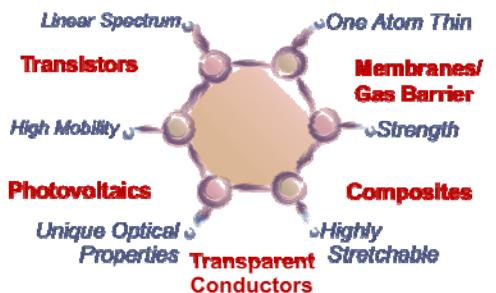


Picture from: A.K. Geim and K.S. Novoselov, "The rise of graphene", Nat. Mater. 6, 183 (2007)

Graphene applications

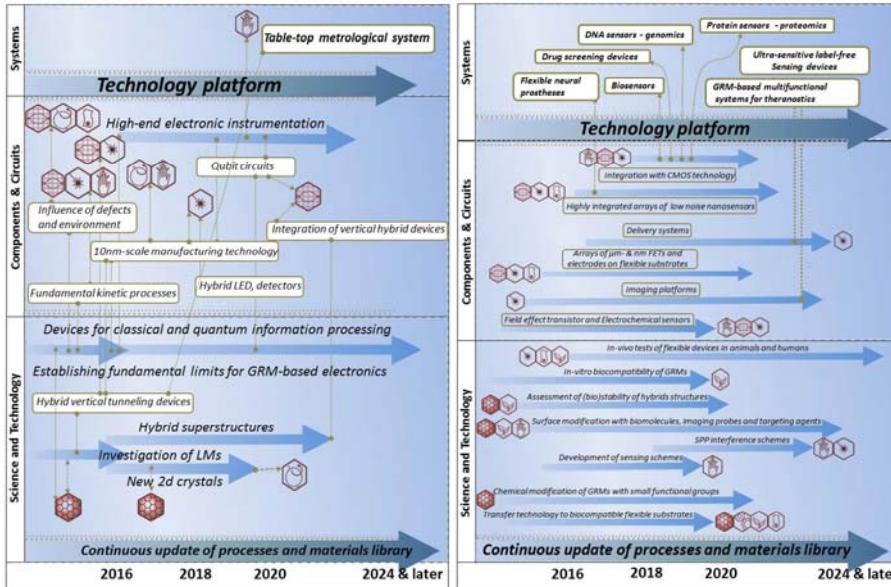
- Fundamental research
- Health and environment
- Production
- Electronic devices
- Spintronics
- Photonics and Optoelectronics
- Sensors
- Flexible electronics
- Energy storage and generation
- Composites
- Biomedical applications

Quantum Hall Effect



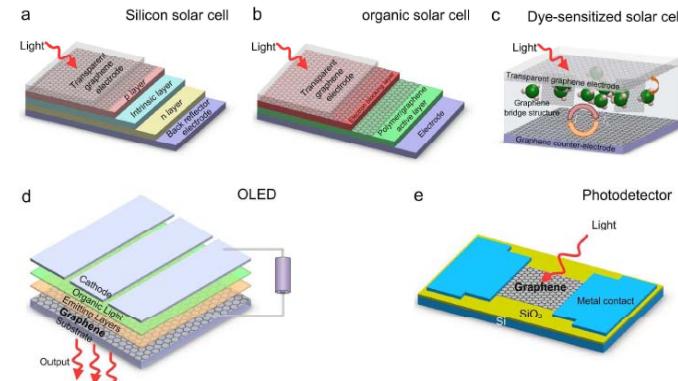
Graphene roadmap

http://graphene-flagship.eu/wp-content/uploads/2013/11/simpleshow_EN_Graphene_131004-640x360.mp4



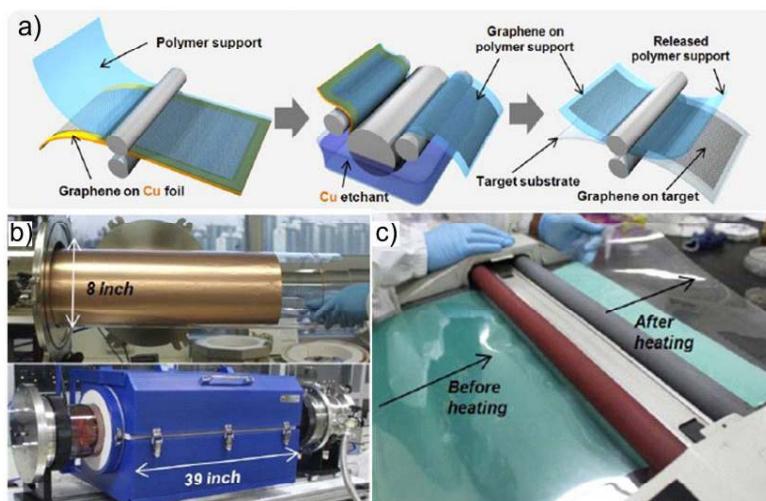
Some of graphene's optoelectronic applications

- Great properties for optoelectronics
 - High mobility - optical transparency - flexibility - environmental stability



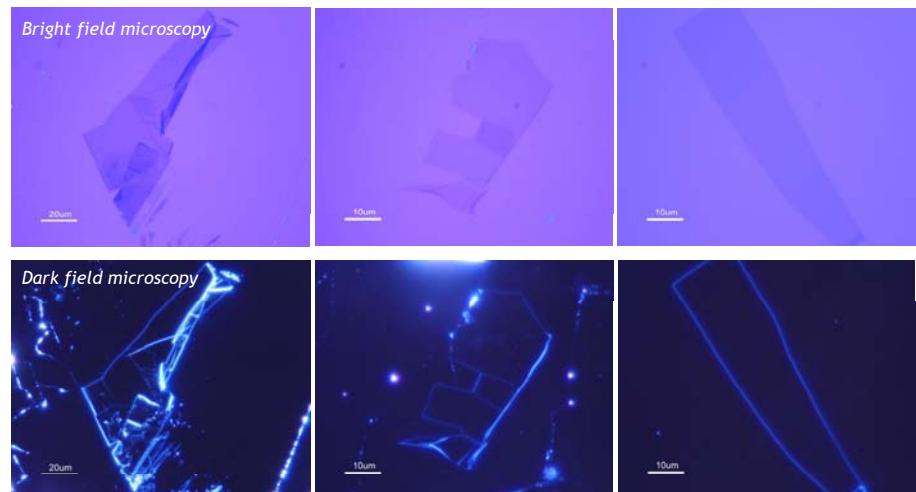
F. Bonaccorso, et al., Nat. Photonics 4, 611 (2010)

Growing graphene

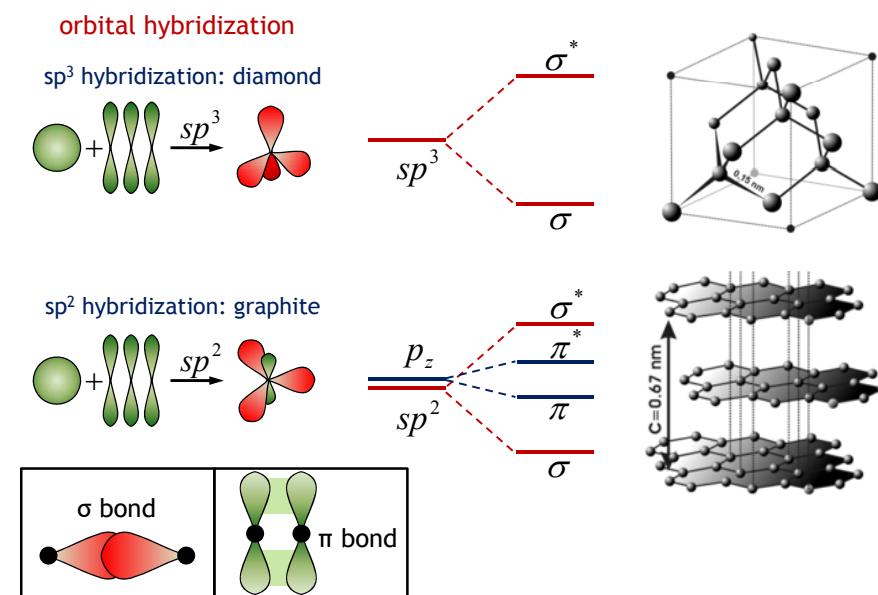


How does graphene look like?

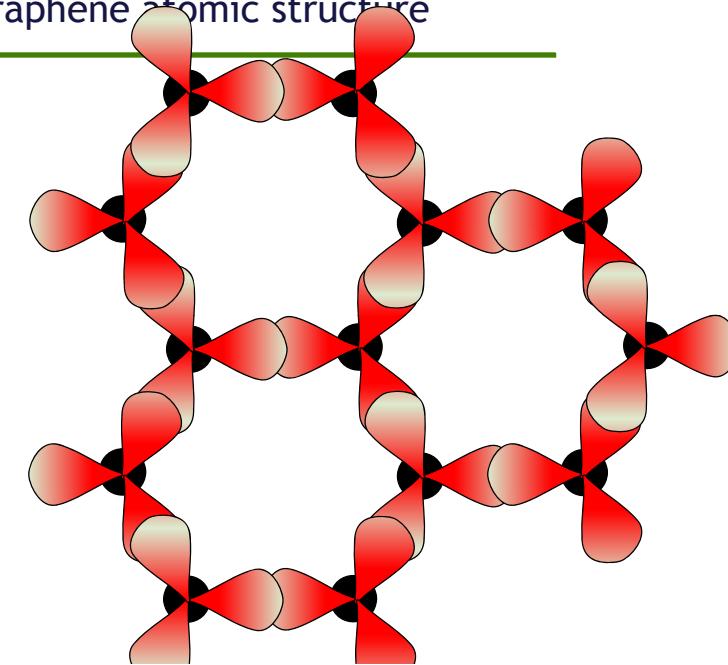
A single graphene layer of thickness d=0.335 nm is visible to the naked eye!!



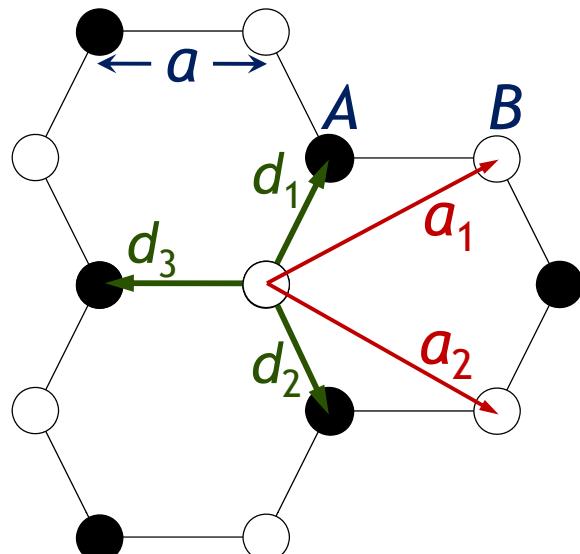
Carbon: ${}^6\text{C} = 1s^2 2s^2 2p^2$, group IV



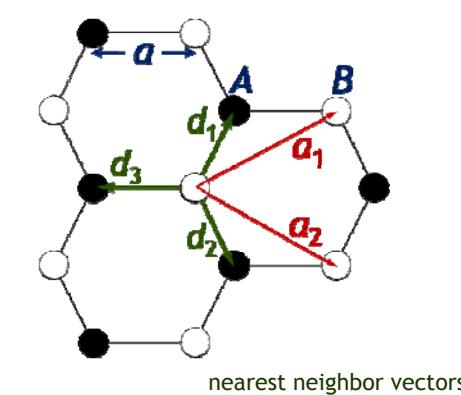
Graphene atomic structure



Graphene electronic structure: p_z orbitals



Graphene: a 2D hexagonal lattice with a basis



lattice vectors

$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3})$$

$$\mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3})$$

$$\mathbf{d}_3 = \frac{a}{2}(-1, 0)$$

$$\mathbf{d}_1 = \frac{a}{2}(1, \sqrt{3})$$

$$\mathbf{d}_2 = \frac{a}{2}(1, -\sqrt{3})$$

Schrödinger equation

$$\hat{H} \cdot \Psi(\mathbf{r}) = E \cdot \Psi(\mathbf{r})$$

wavefunction

$$\Psi(\mathbf{r}) = c_A \Phi_A(\mathbf{r}) + c_B \Phi_B(\mathbf{r})$$

$$\Phi_A(\mathbf{r}) = \sum_{\mathbf{r}_A} e^{i\mathbf{k} \cdot \mathbf{r}_A} \phi(\mathbf{r} - \mathbf{r}_A)$$

$$\Phi_B(\mathbf{r}) = \sum_{\mathbf{r}_B} e^{i\mathbf{k} \cdot \mathbf{r}_B} \phi(\mathbf{r} - \mathbf{r}_B)$$

unknowns are the c_A and c_B as function of k

eigenvalue problem

$$\langle \Phi_A | \hat{H} | \Psi \rangle = E \langle \Phi_A | \Psi \rangle$$

$$\langle \Phi_B | \hat{H} | \Psi \rangle = E \langle \Phi_B | \Psi \rangle$$

Tight-binding approach

- Eigenvalue problem

$$\langle \Phi_B | \hat{H} | \Psi \rangle = E \langle \Phi_B | \Psi \rangle$$

$$\langle \Phi_A | \hat{H} | \Psi \rangle = E \langle \Phi_A | \Psi \rangle$$

$$\Psi(\mathbf{r}) = c_A \Phi_A(\mathbf{r}) + c_B \Phi_B(\mathbf{r})$$

$$\Phi_A(\mathbf{r}) = \sum_{\mathbf{r}_A} e^{i\mathbf{k}\cdot\mathbf{r}_A} \phi(\mathbf{r} - \mathbf{r}_A)$$

$$\Phi_B(\mathbf{r}) = \sum_{\mathbf{r}_B} e^{i\mathbf{k}\cdot\mathbf{r}_B} \phi(\mathbf{r} - \mathbf{r}_B)$$

- Integrals

$$\langle \phi_{\mathbf{r}_A} | \hat{H} | \phi_{\mathbf{r}_B} \rangle e^{i\mathbf{k}\cdot(\mathbf{r}_A - \mathbf{r}_B)} = t \cdot e^{i\mathbf{k}\cdot\mathbf{d}} \quad \text{if } \mathbf{r}_A \text{ and } \mathbf{r}_B \text{ are neighbors, otherwise} = 0$$

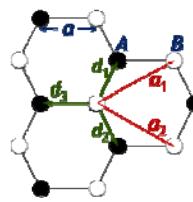
$$\langle \phi_{\mathbf{r}_A} | \hat{H} | \phi_{\mathbf{r}_{A'}} \rangle e^{i\mathbf{k}\cdot(\mathbf{r}_A - \mathbf{r}_{A'})} = t' \cdot e^{i\mathbf{k}\cdot\mathbf{a}} \quad \text{if } \mathbf{r}_A \text{ and } \mathbf{r}_{A'} \text{ are neighbors, otherwise} = 0$$

$$\langle \phi_{\mathbf{r}_A} | \phi_{\mathbf{r}_B} \rangle e^{i\mathbf{k}\cdot(\mathbf{r}_A - \mathbf{r}_B)} = 0$$

$$\langle \phi_{\mathbf{r}_A} | \phi_{\mathbf{r}_{A'}} \rangle e^{i\mathbf{k}\cdot(\mathbf{r}_A - \mathbf{r}_{A'})} = 1 \quad \text{if } \mathbf{r}_A = \mathbf{r}_{A'}, \text{ otherwise} = 0$$

- We get t , t' from experiment

$$t \approx 3 \text{ eV} \quad t' \ll t, \text{ thus we only assume } \mathbf{r}_A \leftrightarrow \mathbf{r}_B \text{ hopping}$$



Tight-binding approach

- Eigenvalue problem

$$\langle \Phi_A | \hat{H} | \Psi \rangle = E \langle \Phi_A | \Psi \rangle$$

$$\Psi(\mathbf{r}) = c_A \Phi_A(\mathbf{r}) + c_B \Phi_B(\mathbf{r})$$

$$\langle \Phi_B | \hat{H} | \Psi \rangle = E \langle \Phi_B | \Psi \rangle$$

$$\Phi_A(\mathbf{r}) = \sum_{\mathbf{r}_A} e^{i\mathbf{k}\cdot\mathbf{r}_A} \phi(\mathbf{r} - \mathbf{r}_A)$$

$$\Phi_B(\mathbf{r}) = \sum_{\mathbf{r}_B} e^{i\mathbf{k}\cdot\mathbf{r}_B} \phi(\mathbf{r} - \mathbf{r}_B)$$

$$t \cdot (e^{i\mathbf{k}\cdot\mathbf{d}_1} + e^{i\mathbf{k}\cdot\mathbf{d}_2} + e^{i\mathbf{k}\cdot\mathbf{d}_3}) \cdot c_B = E \cdot c_A$$

$$t \cdot (e^{-i\mathbf{k}\cdot\mathbf{d}_1} + e^{-i\mathbf{k}\cdot\mathbf{d}_2} + e^{-i\mathbf{k}\cdot\mathbf{d}_3}) \cdot c_A = E \cdot c_B$$

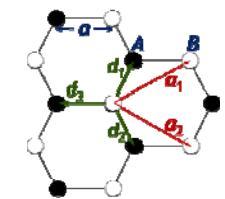
$$\text{set } f(\mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{d}_1} + e^{i\mathbf{k}\cdot\mathbf{d}_2} + e^{i\mathbf{k}\cdot\mathbf{d}_3}$$

$$\begin{pmatrix} 0 & t \cdot f(\mathbf{k}) \\ t \cdot f^*(\mathbf{k}) & 0 \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = E \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

- Solution to the eigenvalue problem

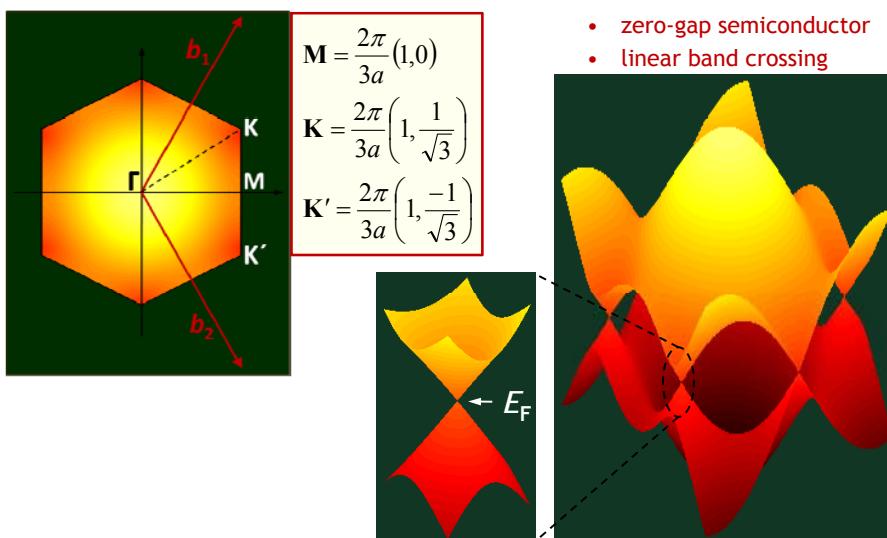
$$\begin{vmatrix} -E & t \cdot f(\mathbf{k}) \\ t \cdot f^*(\mathbf{k}) & -E \end{vmatrix} = 0 \Rightarrow E = \pm t \cdot |f(\mathbf{k})|$$

$$|f(\mathbf{k})| = \sqrt{3 + 2\cos(\sqrt{3}k_y a) + 4\cos\left(\frac{\sqrt{3}}{2}k_x a\right)\cos\left(\frac{3}{2}k_x a\right)}$$



Graphene band structure

- Relation between wavevector \mathbf{k} (momentum) and energy E



Dirac point

- Expand around \mathbf{K} -point

$$\mathbf{k} \rightarrow \mathbf{K} + \mathbf{q} \quad \mathbf{K} = \frac{2\pi}{3a}\left(1, \frac{1}{\sqrt{3}}\right)$$

$$k_x = \frac{2\pi}{3a} + q_x \quad k_y = \frac{2\pi}{3\sqrt{3}a} + q_y$$

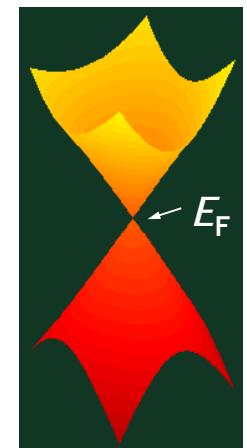
$$|f(\mathbf{k})| \equiv \frac{3}{2}a|\mathbf{q}|$$

- Energy around \mathbf{K} -point

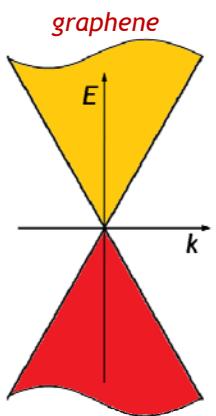
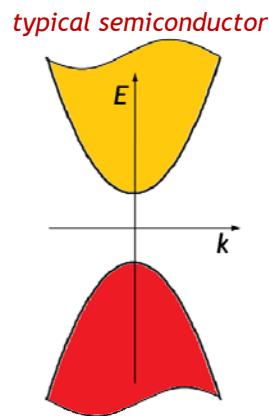
$$E \cong \pm \frac{3}{2}t \cdot a |\mathbf{q}| = \pm \hbar v_F |\mathbf{q}|$$

$$v_F = \frac{3}{2} \frac{t \cdot a}{\hbar} \approx 10^6 \text{ m/s}$$

$$E = \sqrt{p^2 c^2 + m^2 c^4} \quad \begin{cases} m = 0 \\ c = v_F \end{cases}$$



Massless Dirac fermions



$$f(\mathbf{k}) \equiv \frac{3}{2}a(q_x + iq_y) \quad \hat{H} \equiv \begin{pmatrix} 0 & \hbar v_F(\partial_x + i\partial_y) \\ \hbar v_F(\partial_x - i\partial_y) & 0 \end{pmatrix} = \hbar v_F \boldsymbol{\sigma} \cdot \mathbf{p}$$

Dirac density of states

- 2D density of states

$$D(k)dk = 4 \frac{2\pi k \cdot dk}{(2\pi)^2}$$

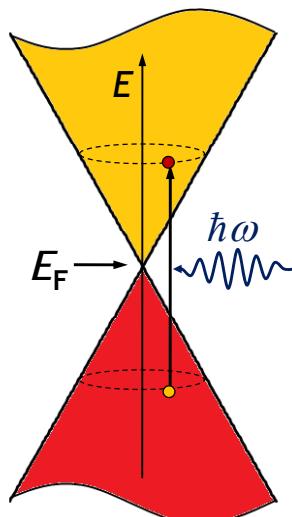
- Change into energy

$$E = \hbar v_F k$$

$$D(E)dE = \frac{2E \cdot dE}{\pi \hbar^2 v_F^2}$$

- The joint density of states is DOS at $\hbar\omega/2$

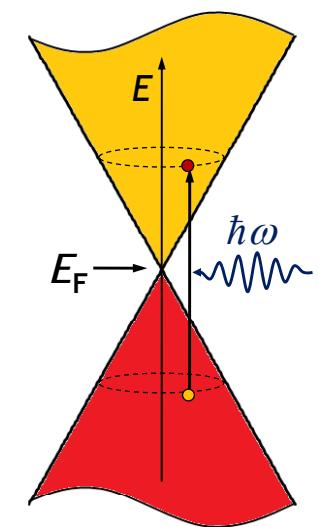
$$D\left(\frac{\hbar\omega}{2}\right) = \frac{\hbar\omega}{\pi \hbar^2 v_F^2} = \frac{\omega}{\pi \hbar v_F^2}$$



Optical properties

- Direct optical transitions
 - transition rate (Fermi's golden rule)

$$\eta = \frac{2\pi}{\hbar} |M|^2 D\left(\frac{\hbar\omega}{2}\right)$$



Transition matrix element

- Hamiltonian with minimal coupling

$$\hat{H} = v_F \boldsymbol{\sigma} \cdot \left(\mathbf{p} - \frac{e}{c} \mathbf{A} \right) = \hat{H}_0 + \hat{H}'$$

- Vector potential as a function of electric field

$$\mathbf{E} = \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \Rightarrow \mathbf{A} = i \frac{c \mathbf{E}}{\omega}$$

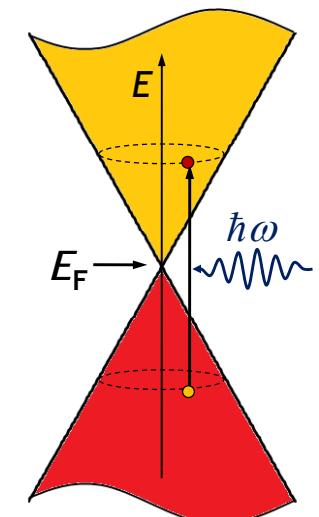
$$\hat{H}' = -i v_F \frac{e}{\omega} \boldsymbol{\sigma} \cdot \mathbf{E}$$

- Matrix element

$$|M|^2 = |\langle f | \hat{H}' | i \rangle|^2 = \frac{1}{16} v_F^2 \frac{e^2}{\omega^2} |\mathbf{E}|^2$$

- Electric field as a function of incident power

$$|M|^2 = I \frac{\pi e^2 v_F^2}{2c\omega^2}$$



Optical properties

- Direct optical transitions

- transition rate (Fermi's golden rule)

$$\eta = \frac{2\pi}{\hbar} |M|^2 D\left(\frac{\hbar\omega}{2}\right)$$

- transition matrix element

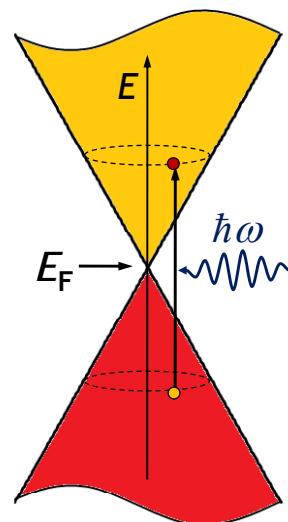
$$|M|^2 = I \frac{\pi e^2 v_F^2}{2c\omega^2}$$

- Dirac density of states

$$D\left(\frac{\hbar\omega}{2}\right) = \frac{\omega}{\pi\hbar v_F^2}$$

- absorption coefficient

$$A = \frac{\eta\hbar\omega}{I} = \pi \frac{e^2}{\hbar c} = \pi\alpha$$



Universal optical conductance

- Real part of conductivity

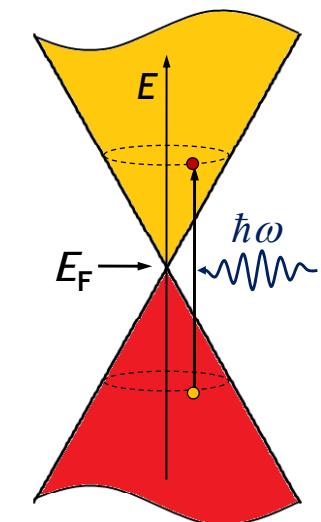
$$\Re\sigma(\omega) = \frac{\pi e^2}{\omega} |\mathbf{v}(\omega)|^2 D(\omega)$$

$$|\mathbf{v}(\omega)|^2 \propto v_F^2 \quad D(\omega) \propto \frac{\omega}{\pi\hbar v_F^2}$$

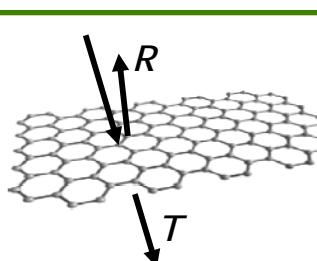
$$\boxed{\Re\sigma(\omega) = \frac{e^2}{4\hbar}}$$

- Dielectric constant

$$\epsilon(\omega) = 1 + i \frac{4\pi\sigma(\omega)}{\omega d}$$



Graphene optical transmission



Light transmission in the thin film limit

$$T = |t|^2 \approx 1 - \frac{4\pi}{c} \Re\sigma = 1 - \pi \frac{e^2}{\hbar c} = 1 - \pi\alpha$$

Light reflection in the thin film limit

$$R \propto \omega^2 d^2 \approx 0$$

Light absorption = 1-R-T = $\pi\alpha$

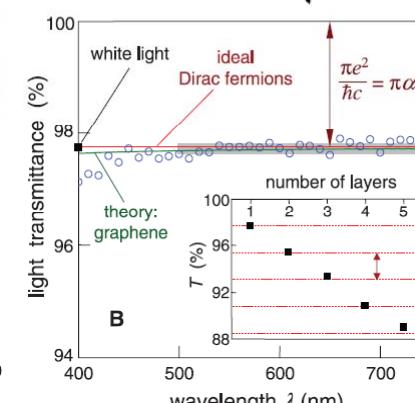
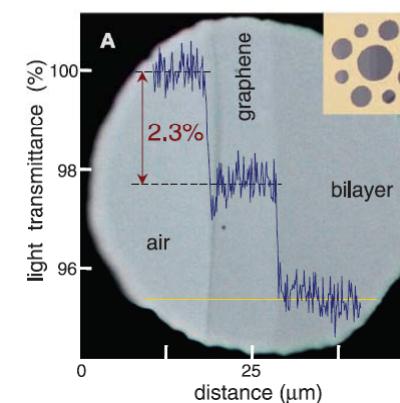
- universal absorption $\pi\alpha$ per graphene layer

$$\pi\alpha = \frac{3.14159...}{137.035...} \approx 0.023 = 2.3\%$$

Graphene optical transmission

- Experimental verification of $\pi\alpha$ absorption per layer

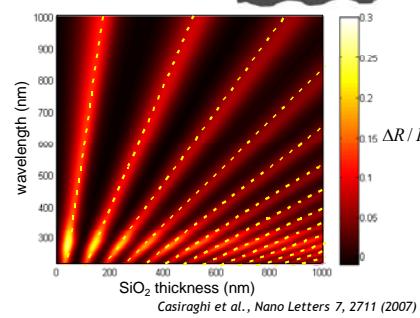
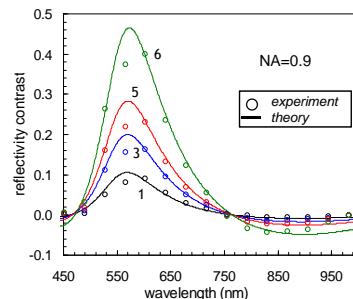
- experiments on graphene suspended in air



Nair et al., Science 320, 1308 (2008)

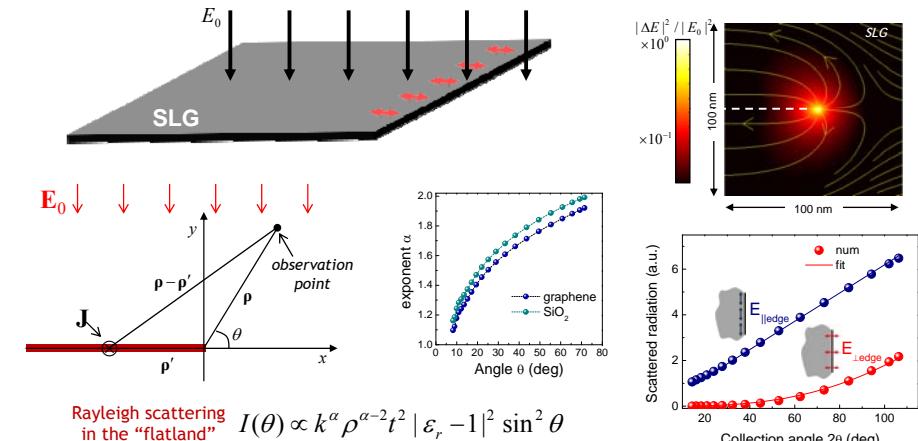
Graphene visibility

- If graphene does not reflect, how come it is visible?
 - only in specific substrates due to interference
 - choose a substrate with small initial reflection
 - graphene's effect is then maximal
- Condition for small reflection: antireflection
 - spacer thickness = $\lambda/4$
 - spacer index = $\sqrt{\text{substrate index}}$
- Experimental verification



Dark field visibility

- In dark field mode, only the edges of graphene "light up"
 - Numerical simulations and theory predict this behavior

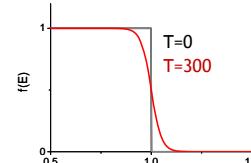


Conductance at finite temperature and doping

- Fermi-Dirac distribution function

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

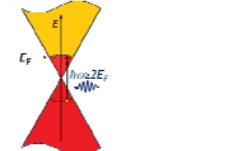
μ : chemical potential (due to doping)
 T : temperature (K)
 k_B : Boltzmann constant



- Interband transitions in the Dirac cone

$$\Re \sigma_{\text{inter}}(\omega) = \frac{\pi e^2}{\omega} |\mathbf{v}(\omega)|^2 D(\omega) \left[f\left(-\frac{\hbar\omega}{2}\right) - f\left(\frac{\hbar\omega}{2}\right) \right]$$

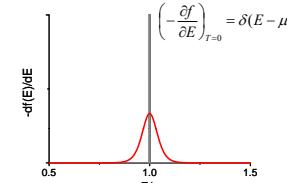
$$\approx \frac{e^2}{8\hbar} \left[\tanh\left(\frac{\hbar\omega+2\mu}{4k_B T}\right) + \tanh\left(\frac{\hbar\omega-2\mu}{4k_B T}\right) \right]$$



- Intraband transitions of free carriers

$$\sigma_{\text{intra}}(\omega) = e^2 \int \frac{d\mathbf{k}}{4\pi^2} \frac{\mathbf{v}(\mathbf{k}) \cdot \mathbf{v}(\mathbf{k})}{1/\tau - i\omega} \left(-\frac{\partial f}{\partial E} \right)_{E=E(\mathbf{k})}$$

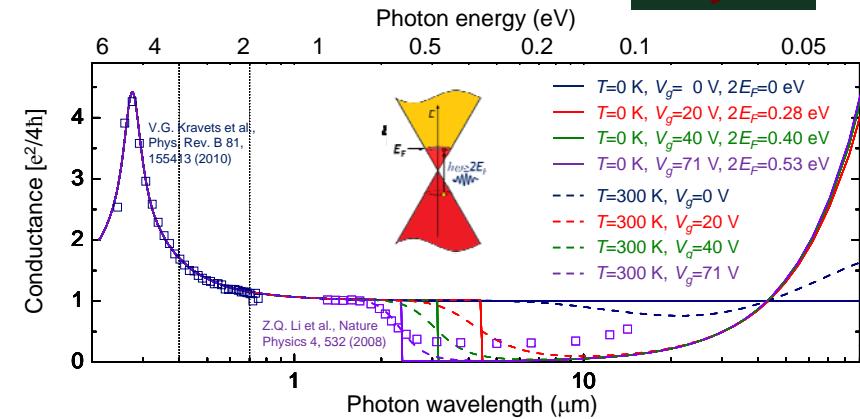
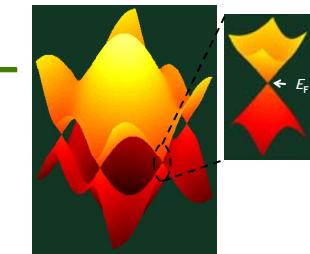
$$= e^2 \frac{2k_B T}{\pi\hbar^2} \ln\left(2 \cosh \frac{\mu}{2k_B T}\right) \frac{1}{1/\tau - i\omega}$$



Graphene conductance

- The full spectrum of graphene

- Van Hove peak in UV
- Universal conductance in VIS
- Pauli blocking due to doping in NIR
- Drude free electron conductance in IR



Electric field effect: doping by gating

- Graphene/oxide/semiconductor system

- Conductor/dielectric/conductor \Rightarrow capacitor
- Field applied by bottom gating with voltage V_g

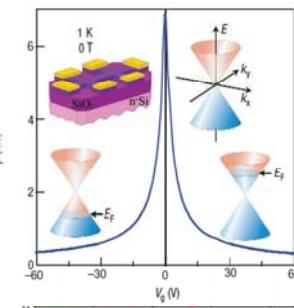
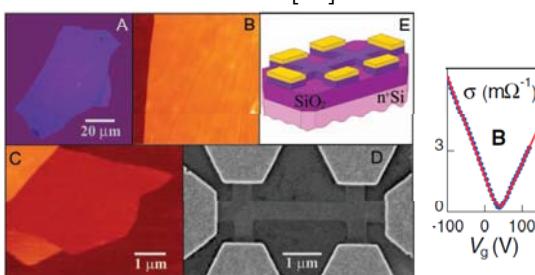
$$Q = C_g \cdot V_g \Rightarrow n = C_g \cdot V_g / e$$

- The scaled capacitance C_g/e was measured for graphene

$$C_g / e_{(300\text{nmSiO}_2/\text{Si})} = 7.2 \times 10^{10} \text{ cm}^{-1}\text{V}^{-1}$$

- So we can use

$$n[10^{10} \text{ cm}^{-2}] = 7.2 \times \frac{300}{t[\text{nm}]} \frac{\epsilon_r}{3.9} V_g [\text{V}]$$



K.S. Novoselov et al., Science 306, 666 (2004)
A.K. Geim and K.S. Novoselov, Nat. Mater. 6 (2007)

Electric field effect: Fermi level shift

- Number of charges in Fermi level (at T=0)

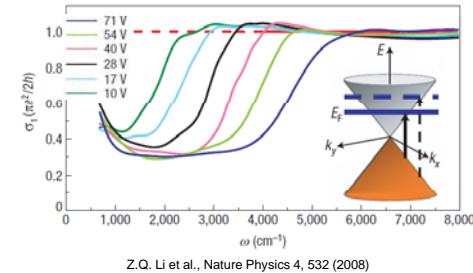
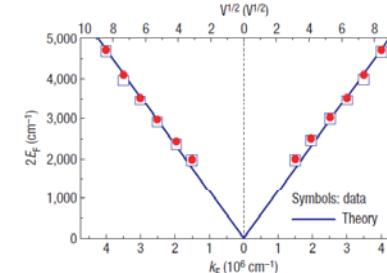
$$n = g_s g_v \int_0^{k_F} \frac{d\mathbf{k}}{4\pi^2} = \frac{4}{4\pi^2} \int_0^{k_F} 2\pi k dk = \frac{k_F^2}{\pi}$$

- So we can relate the Fermi energy to doping (at T=0)

$$n = k_F^2 / \pi = C_g \cdot V_g / e \Rightarrow n \propto V_g$$

$$k_F = \sqrt{\pi n} = \sqrt{\pi C_g V_g / e} \Rightarrow k_F \propto \sqrt{V_g}$$

$$E_F = \hbar v_F \sqrt{\pi n} = \hbar v_F \sqrt{\pi C_g V_g / e} \Rightarrow E_F \propto \sqrt{V_g}$$

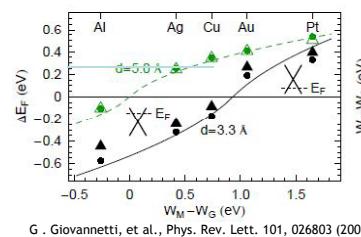
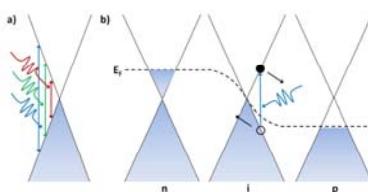


Z.Q. Li et al., Nature Physics 4, 532 (2008)

Doping by direct contact

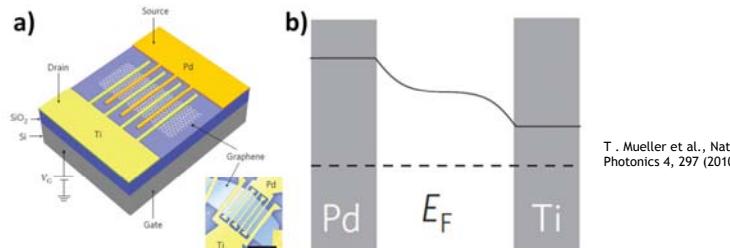
- Graphene contacted by a metal with different Fermi level

- Local shift of graphene's Fermi level
- Creation of a lateral "Schottky" junction



G. Giovannetti, et al., Phys. Rev. Lett. 101, 026803 (2008)

- Graphene photodetectors



T. Mueller et al., Nat. Photonics 4, 297 (2010)

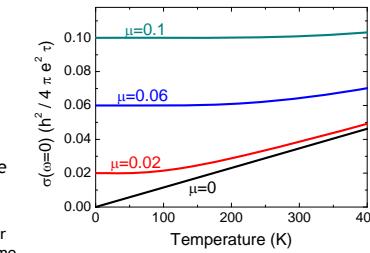
Graphene's free charges

- The free carrier conductance

$$\sigma_{\text{intra}} = e^2 \frac{2k_B T}{\pi \hbar^2} \ln \left(2 \cosh \frac{\mu}{2k_B T} \right) \frac{1}{1/\tau - i\omega}$$

- At high doping (large Fermi energy E_F or chemical potential μ), the free carrier conductance becomes temperature independent. So we use the $T=0$ approximation:

$$\sigma_{\text{intra}}(\omega) \approx \frac{e^2 E_F}{\pi \hbar^2} \frac{1}{1/\tau - i\omega} \quad \text{t: free carrier relaxation time}$$



- These carriers have an effective mass $E_F = v_F p_F = m^* v_F^2 \Rightarrow m^* = E_F / v_F^2$

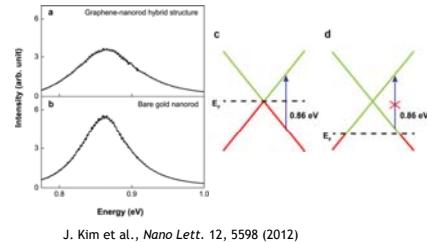
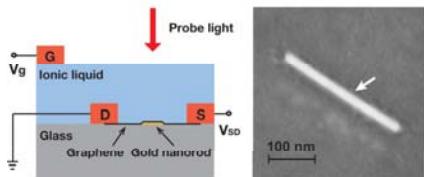
- The mobility μ^* is related to the relaxation time τ from the Drude formula: $\mu^* = \frac{e\tau}{m^*} \Rightarrow \tau = \frac{\mu^* E_F}{e v_F^2}$

- Typical mobility values $\mu^* > 10000 \text{ cm}^2 / \text{V} \cdot \text{s}$ or higher. For $E_F=0.1 \text{ eV}$ we get $\tau > 10^{-13} \text{ s}$
typical values for noble metals are $\tau \approx 10^{-14} \text{ s}$

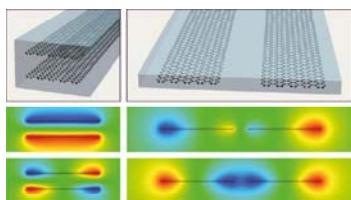
- Graphene very promising for IR plasmonics!!

Graphene plasmonic applications

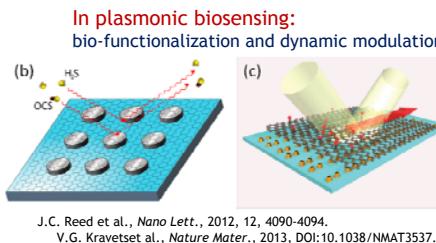
Active plasmonics:
dynamically modulated metal plasmonic



Graphene plasmonics:
Waveguides and circuits



J. Christensen et al., *ACS Nano* 6, 431 (2012)



Surface Plasmon Polaritons

- Charge density oscillations coupled with light

- Bound to propagate along the metal surface

- General form of all fields

- above the interface (insulator with dielectric function ϵ)
 $E_z, E_x, H_y \propto e^{i(k_{\parallel}x-\omega t)} e^{-\kappa z}$ $\kappa = \sqrt{k_{\parallel}^2 - \epsilon \omega^2 / c^2}$

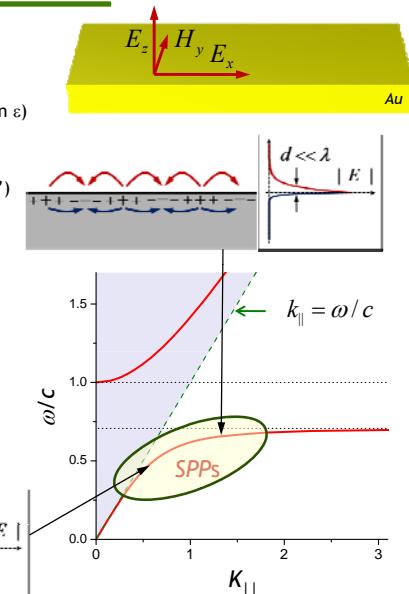
- below the interface (metal with dielectric function ϵ')
 $E'_z, E'_x, H'_y \propto e^{i(k_{\parallel}x-\omega t)} e^{+\kappa' z}$ $\kappa' = \sqrt{k_{\parallel}^2 - \epsilon' \omega^2 / c^2}$

- Boundary conditions

$$E'_x = E_x \quad H'_x = H_x$$

- Surface Plasmon Polariton (SPP)

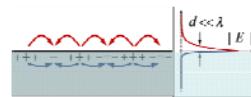
$$\left. \begin{aligned} \frac{\kappa}{\epsilon} + \frac{\kappa'}{\epsilon'} &= 0 \\ k_{\parallel} &= \frac{\omega}{c} \sqrt{\frac{\epsilon \epsilon'}{\epsilon + \epsilon'}} \end{aligned} \right\} \begin{aligned} \epsilon' &< -\epsilon \\ \text{SPPs} \end{aligned}$$



Plasmons on graphene

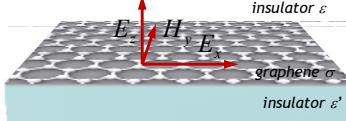
- Light coupled with Dirac charge density oscillations

- Bound to propagate along the graphene surface



- General form of all fields

- above graphene (insulator with dielectric function ϵ)
 $E_z, E_x, H_y \propto e^{i(k_{\parallel}x-\omega t)} e^{-\kappa z}$ $\kappa = \sqrt{k_{\parallel}^2 - \epsilon \omega^2 / c^2}$



- below graphene (insulator with dielectric function ϵ')
 $E'_z, E'_x, H'_y \propto e^{i(k_{\parallel}x-\omega t)} e^{+\kappa' z}$ $\kappa' = \sqrt{k_{\parallel}^2 - \epsilon' \omega^2 / c^2}$

- inside graphene (which has conductance σ) we have a current

$$I_x = \sigma E_x$$

- Boundary conditions

$$E'_x = E_x \quad H'_x = H_x + I_x$$

- General SPP condition

$$\frac{\kappa}{\epsilon} + \frac{\kappa'}{\epsilon'} = \frac{-i\sigma}{\epsilon_0 \omega}$$

- If $k_{\parallel} \gg \epsilon \omega^2 / c^2 \Rightarrow \kappa = \kappa' \approx k_{\parallel}$ then $k_{\parallel} \approx \epsilon_0 \frac{\epsilon + \epsilon'}{2} \frac{2i\omega}{\sigma}$

$$\text{using } \epsilon_g \approx 1 + \frac{i\sigma}{d\epsilon_0 \omega}$$

we also get

$$\frac{\kappa}{\epsilon} + \frac{\kappa'}{\epsilon'} = \frac{1 - \epsilon_g}{d}$$

$$k_{\parallel} \approx \frac{\epsilon + \epsilon'}{d(1 - \epsilon_g)}$$

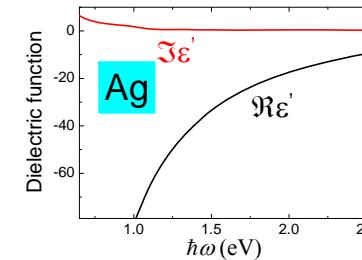
SPP conditions

- We get two different SPP relations

typical metal/dielectric SPP

$$\frac{\kappa}{\epsilon} + \frac{\kappa'}{\epsilon'} = 0$$

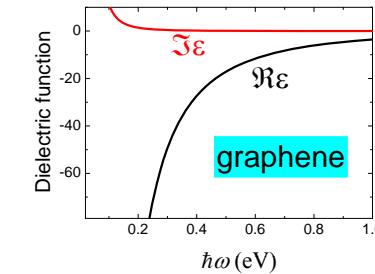
$$k_{\parallel} = \frac{\omega}{c} \sqrt{\frac{\epsilon \epsilon'}{\epsilon + \epsilon'}}$$



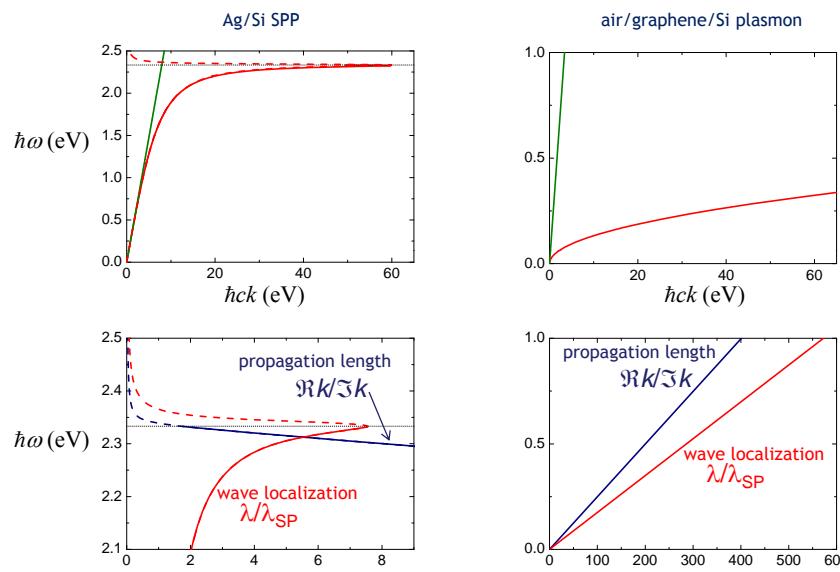
typical dielectric/graphene/dielectric plasmon

$$\frac{\kappa}{\epsilon} + \frac{\kappa'}{\epsilon'} = \frac{1 - \epsilon_g}{d}$$

$$k_{\parallel} \approx \frac{\epsilon + \epsilon'}{d(1 - \epsilon_g)}$$

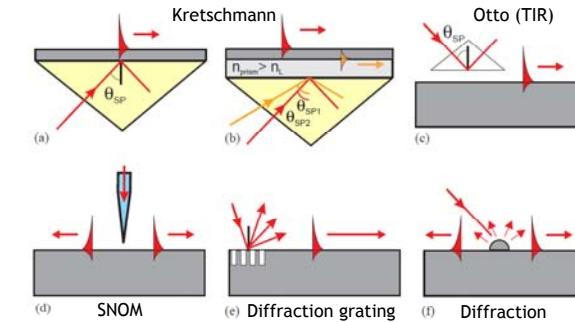


Camparison between SPPs



Excitation of SPPs

- Surface plasmon polaritons exist below the light-cone
 - momentum conservation does not allow direct excitation
 - special care is needed to excite them

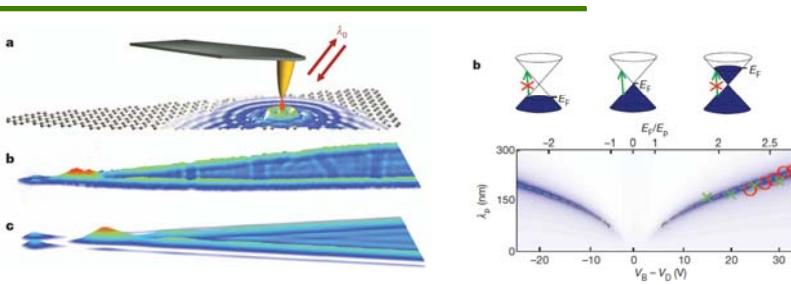


Zayats, Smolyaninov and Maradudin, Phys. Rep. 408, 131 (2005)

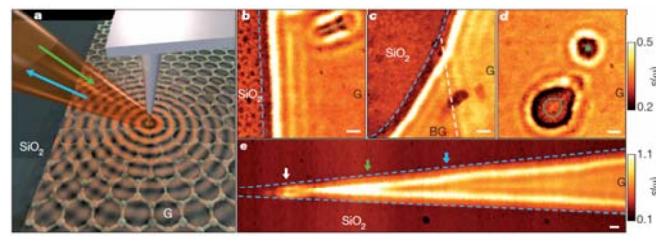
- In grating excitation:

$$k_{\parallel} \rightarrow k_{\parallel} + m \frac{2\pi}{a}, \quad m = 0, \pm 1, \pm 2, \dots$$

Measuring graphene plasmons



J. Chen et al., Nature 487, 77 (2012)



Z. Fei et al., Nature 487, 82 (2012)