Graphene: electrical and optical properties (tutorial)

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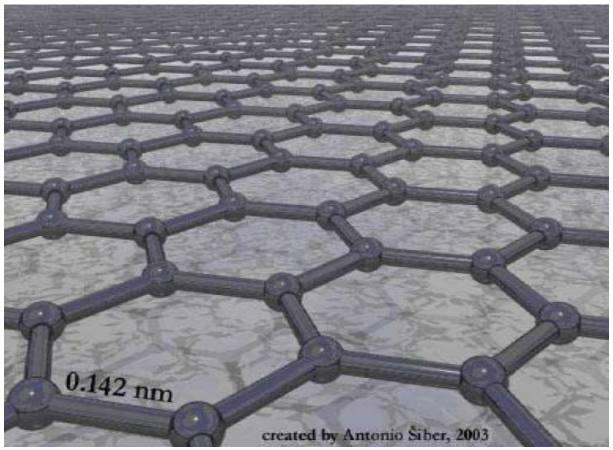
Outline:

- **Graphene** (existence/stability, atomic lattice, fabrication, band structure)
- **Electrical and optical properties of graphene**
- **Few-layer graphene stacks and bulk graphite**
- **Conclusions**

Graphene

2D



2D crystal made of carbon atoms organized in hexagonal lattice

Theoretically known over sixty years…

P. R. Wallace, Phys. Rev. 71, 622 (1947)

Isolated/fabricated in 2004

K. S. Novoselov et al., Science 306, 666 (2004)

Diamond

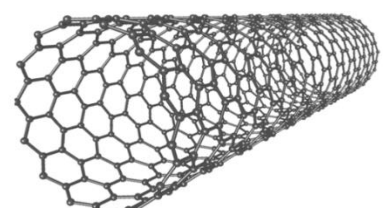
3D

Graphite

3D

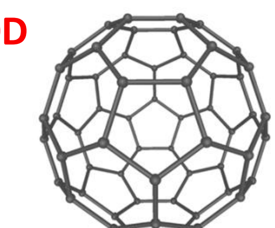
Carbon nanotube

1D



Fulleren

0D



Fabrication methods of graphene

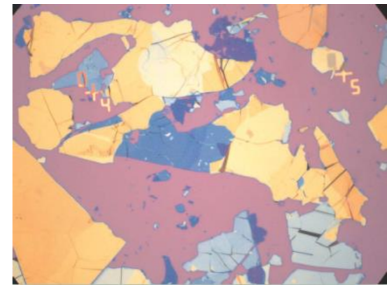
(1) Exfoliation ("Scotch tape" method):

K. Novoselov et al., Science 306, 666 (2004)

A. Geim and K. Novoselov in 2004 (Manchester University)

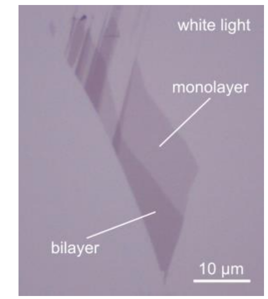
Graphite

⇒



Graphite's debris on a substrate after exfoliation

⇒

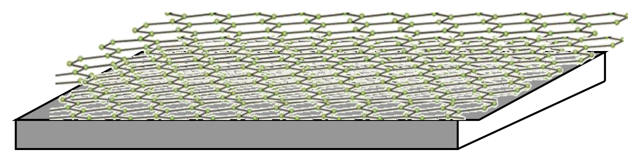


Identification in optical microscope

(2) Thermal decomposition of SiC:

Mono- or multilayer graphene appears on the surface of SiC at high temperatures (GeorgiaTech, Atlanta)

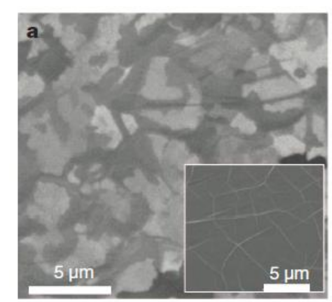
C. Berger et al., J. Phys. Chem. B 108, 19 912 (2004)



(3) Epitaxial growth of graphene on copper:

The very first large scale ("industrial") production of graphene on polycrystalline copper foil (KIAS, Seoul)

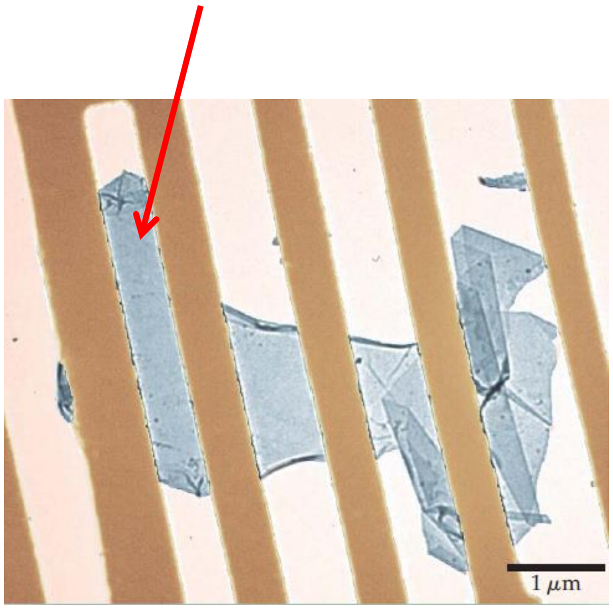
K. S. Kim et al., Nature 457, 706 (2009)



(4) Nowadays a number of other methods (epitaxy on various metals, on germanium etc.)

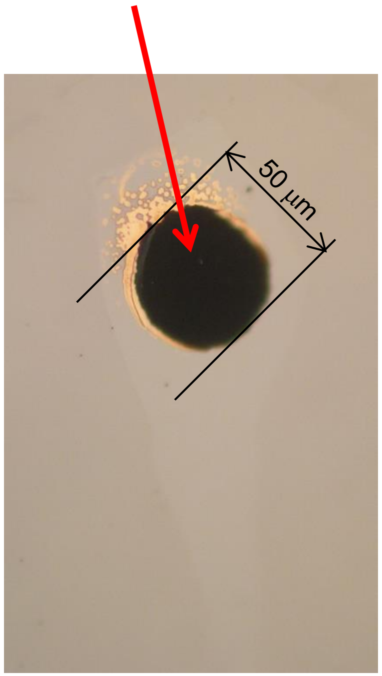
Mechanical stability of graphene

Self-standing graphene on metallic grid seen in electron microscope



J. C. Meyer et al.: Nature 446, 60 (2007)

Self-standing graphene membrane over large aperture



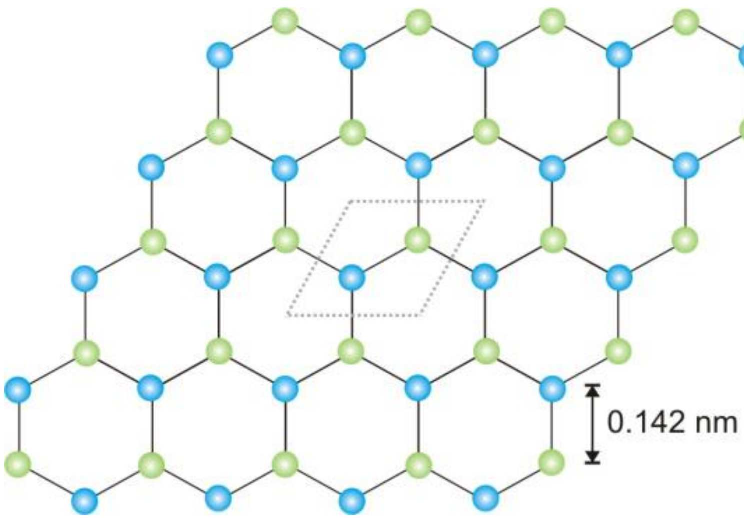
Graphene = the first 2D crystal (in reality 3D due to a weak rippling)

Existence of strictly 2D crystals in 3D excluded by thermodynamics

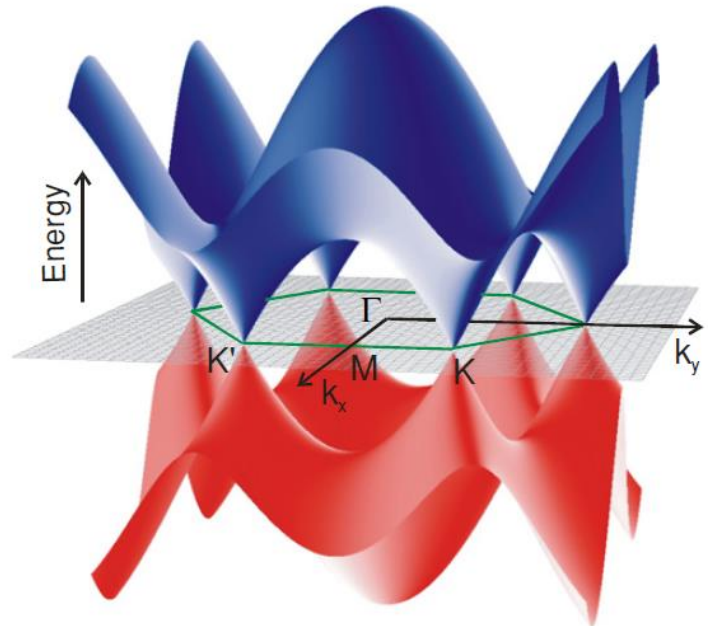
R. E. Peirels (1934) & L. D. Landau (1937)

Electronic band structure of graphene

Crystal lattice:



Electronic bands:



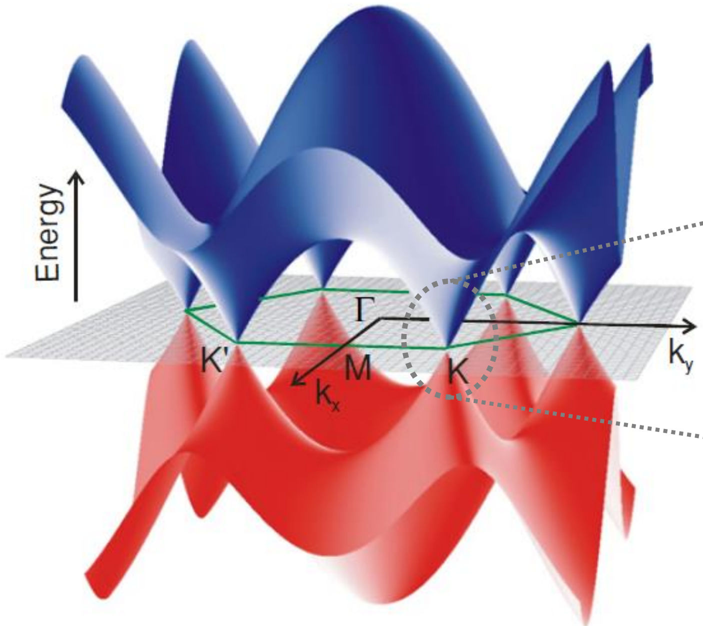
Linearity of bands around K points:

$$E(\mathbf{k}) \approx \pm\hbar v|\mathbf{k}| = \pm v|\mathbf{p}|$$

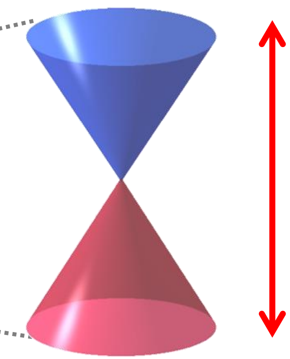
Electrons in graphene =
charged massless (relativistic) particles

$$E^2 = p^2c^2 + m_0^2c^4$$

Electronic band structure of graphene



Single cone approximation



ΔE~2 eV

Effective velocity of light ~10^6 m/s

Dirac (Weyl) equation for electrons in graphene:

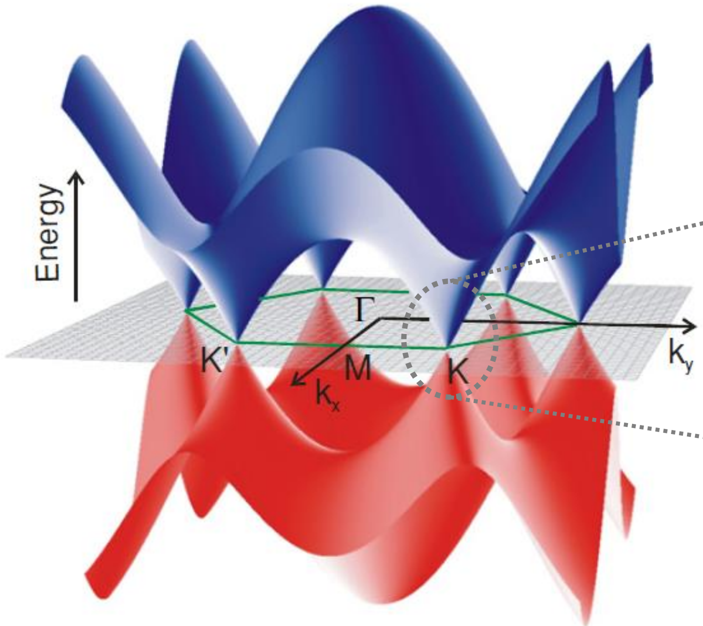
$$\hat{H} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_F \boldsymbol{\sigma} \cdot \mathbf{k}$$

K. Novoselov et al., Nature 438, 197 (2005)
Y. Zhang et al., Nature 438, 201 (2005)

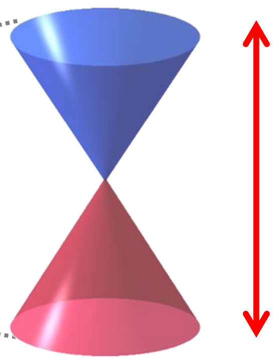
Analogy with quantum electrodynamics limited:

only in 2D and no real spin involved (pseudospin = K and K' valley degree of freedom)

Electronic band structure of graphene

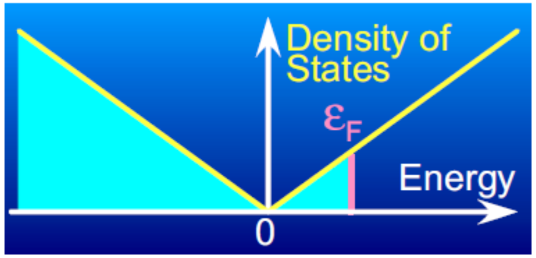


Single cone approximation



Electronic dispersion: $E(\mathbf{k}) \approx \pm \hbar v |\mathbf{k}|$

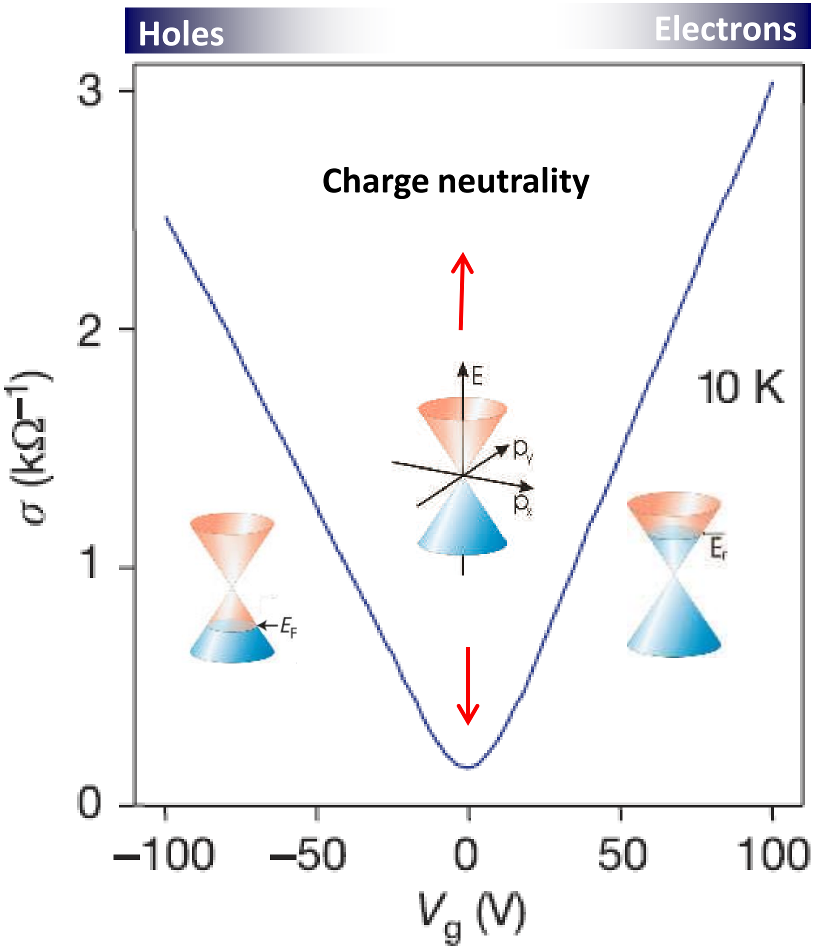
Density of states: $\mathcal{D}(E) = E/(\pi v^2 \hbar^2)$



btw. constant for 2D conventional
(=parabolic) bands: $\mathcal{D}(E) = m/(\pi \hbar^2)$

Effective mass? $m = 0, \infty \text{ or } E/v^2$

Basic transport properties of graphene



K. Novoselov et al., Nature 438, 197 (2005)
Y. Zhang et al., Nature 438, 201 (2005)

Electrical conductivity tunable by external gate via changing carrier density

$$\sigma_{dc} = e\mu n$$

Electron or hole conductivity (switched by the gate voltage)

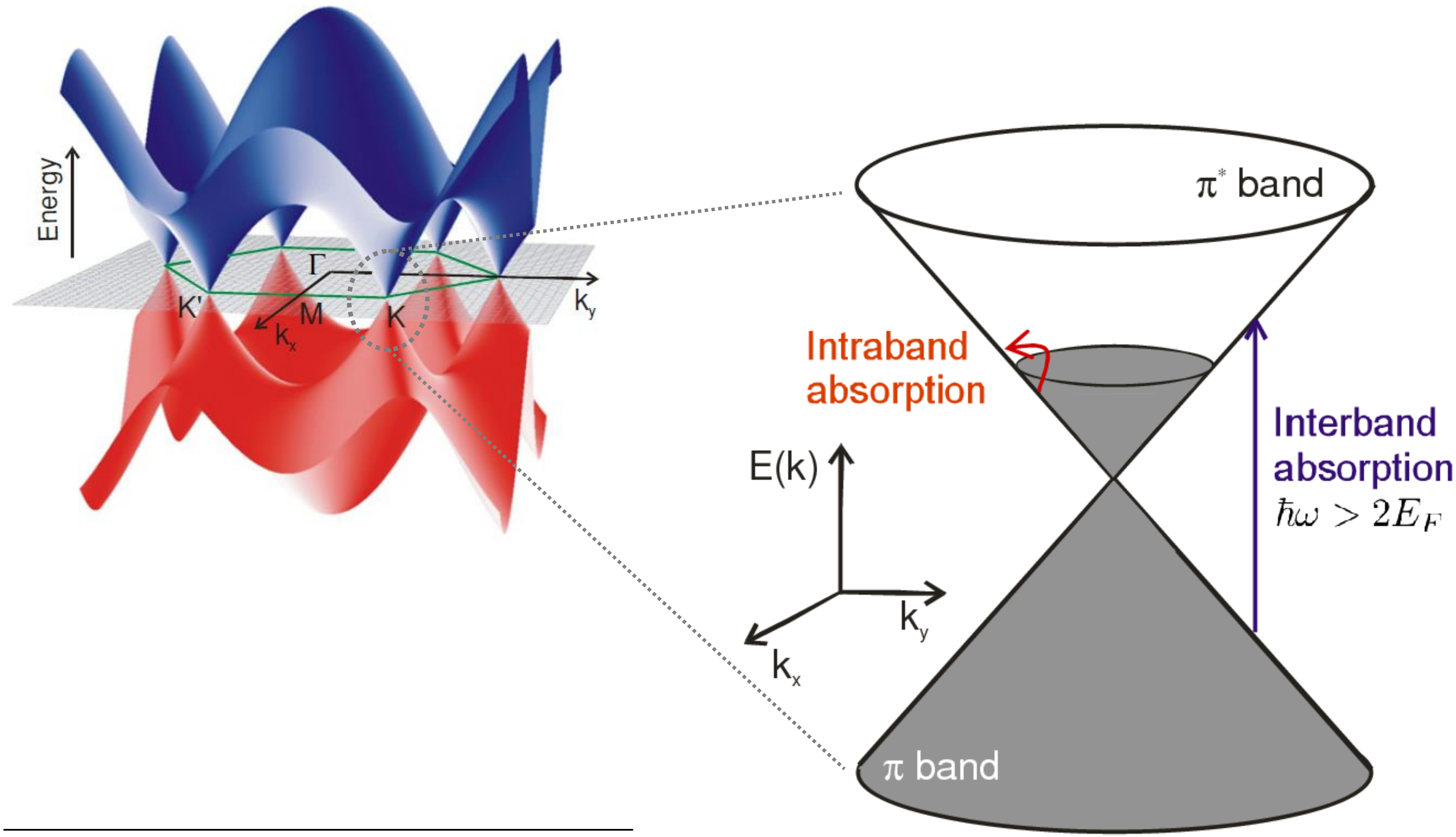
Further reading:

T. Ando, J. Phys. Soc. Jpn. 75, 074716 (2006)
E. H. Hwang et al., Phys. Rev. Lett. 98, 186806 (2007)
Z. H. Ni et al., Nano Letters 10, 3868 (2010)

No band gap = bad on/off ratio of potential transistors…

K. Novoselov, Nature Mat. 6, 721 (2007)

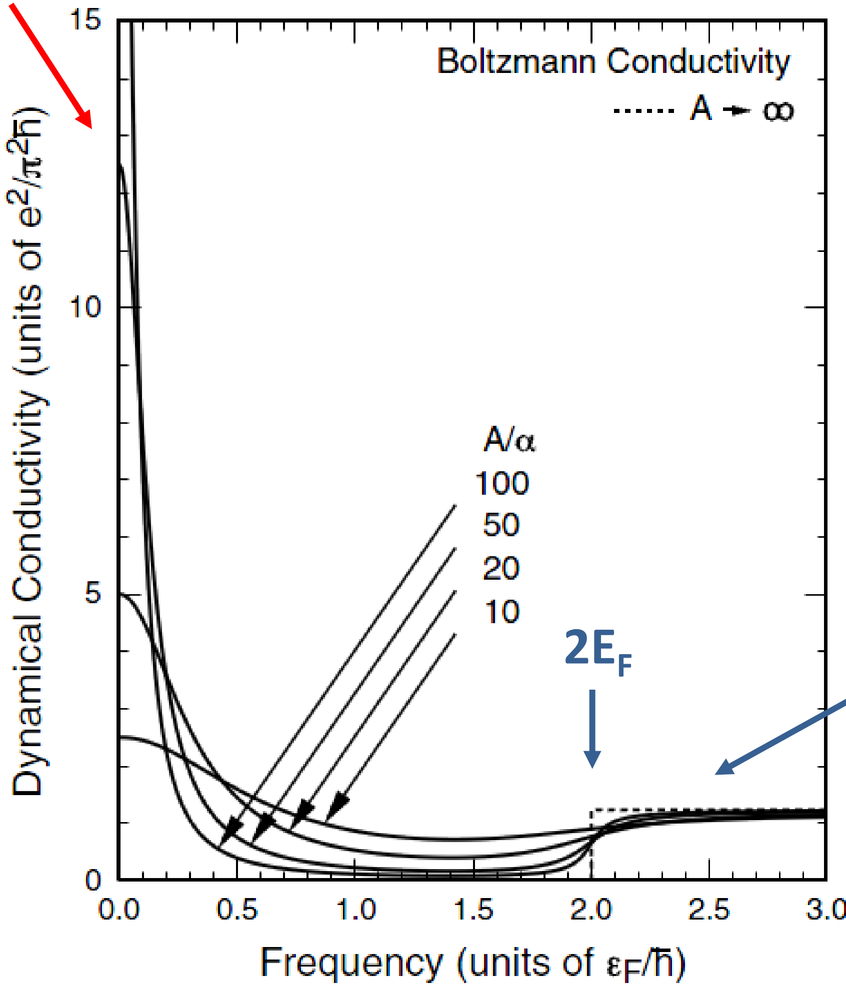
Optical response of graphene

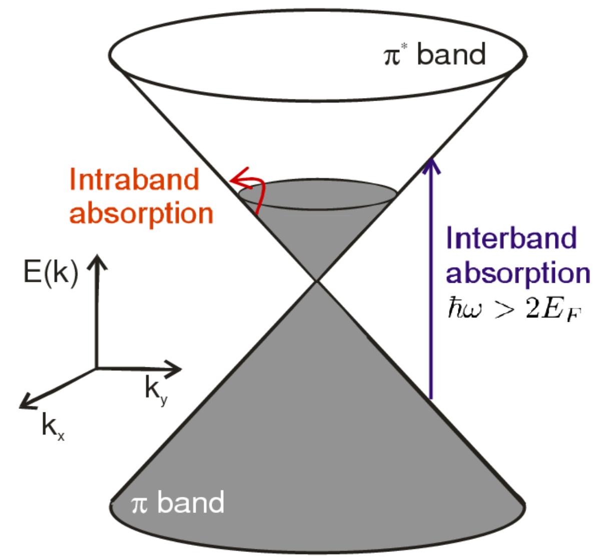


T. Ando, J. Phys. Soc. Jpn. 71, 1318 (2002)
Z. Q. Li et al., Nature Phys. 4, 532 (2008)
for review, see e.g., M. Orlita and M. Potemski, Semicond. Sci. Technol. 25, 063001 (2010)

Dynamical conductivity: Theory

Intraband (free-carrier, Drude-type) absorption





T. Ando, J. Phys. Soc. Jpn. 71, 1318 (2002)

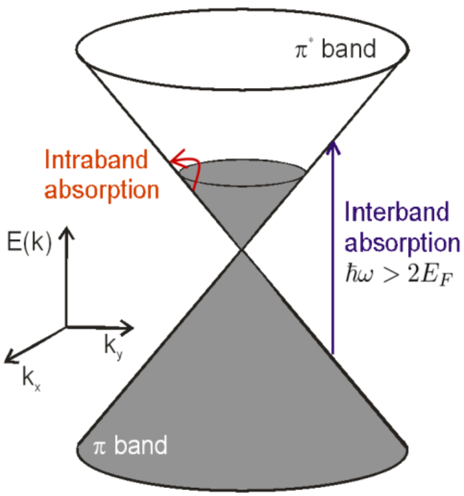
Interband absorption

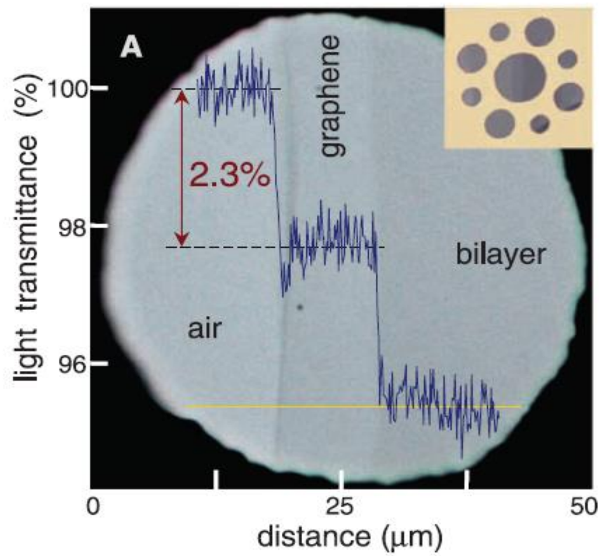
Absorption of light in solids (e.g., Fermi's golden rule):

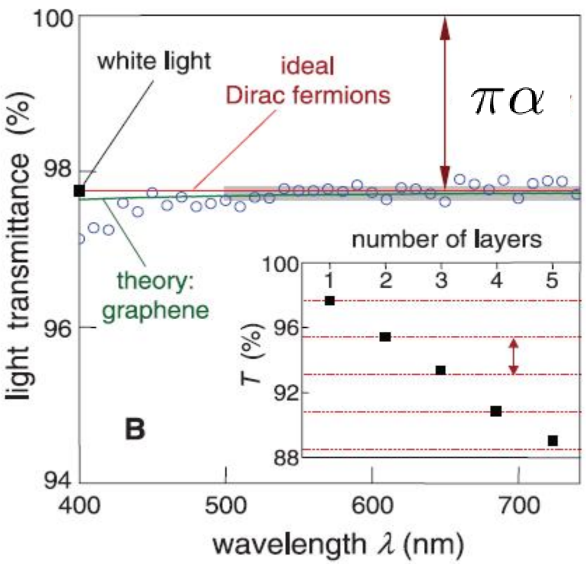
joint density of states

$$\lambda(\omega) \propto \frac{\mathcal{D}(\omega)}{\omega} = \text{const}$$

Universal dynamical conductivity







Absorption of light in solids (Fermi's golden rule):

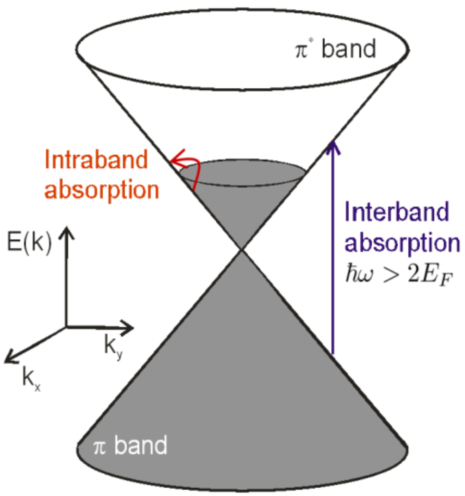
$$\lambda(\omega) \propto \frac{\mathcal{D}(\omega)}{\omega}$$

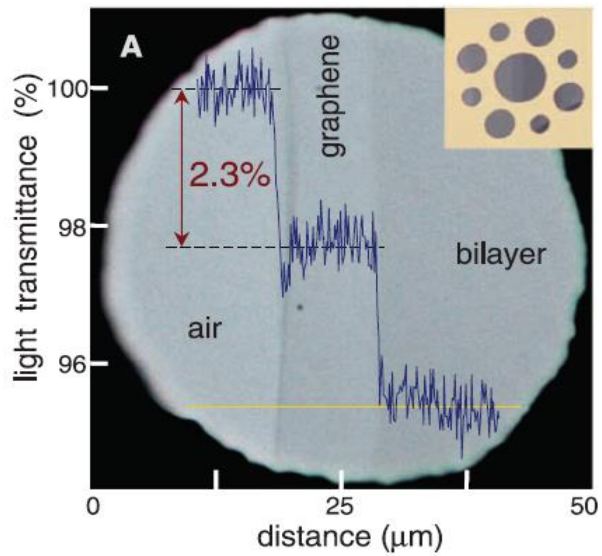
For conical bands in 2D:

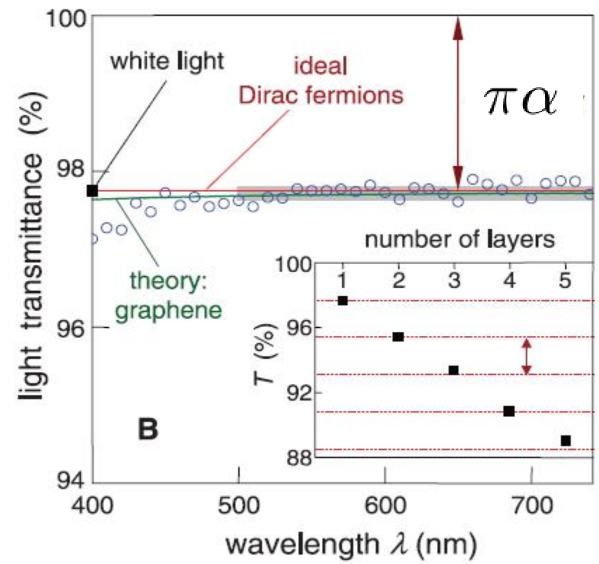
$$\mathcal{D}(\omega) \propto \omega$$

Dispersionless (interband) absorption of light…

Universal dynamical conductivity







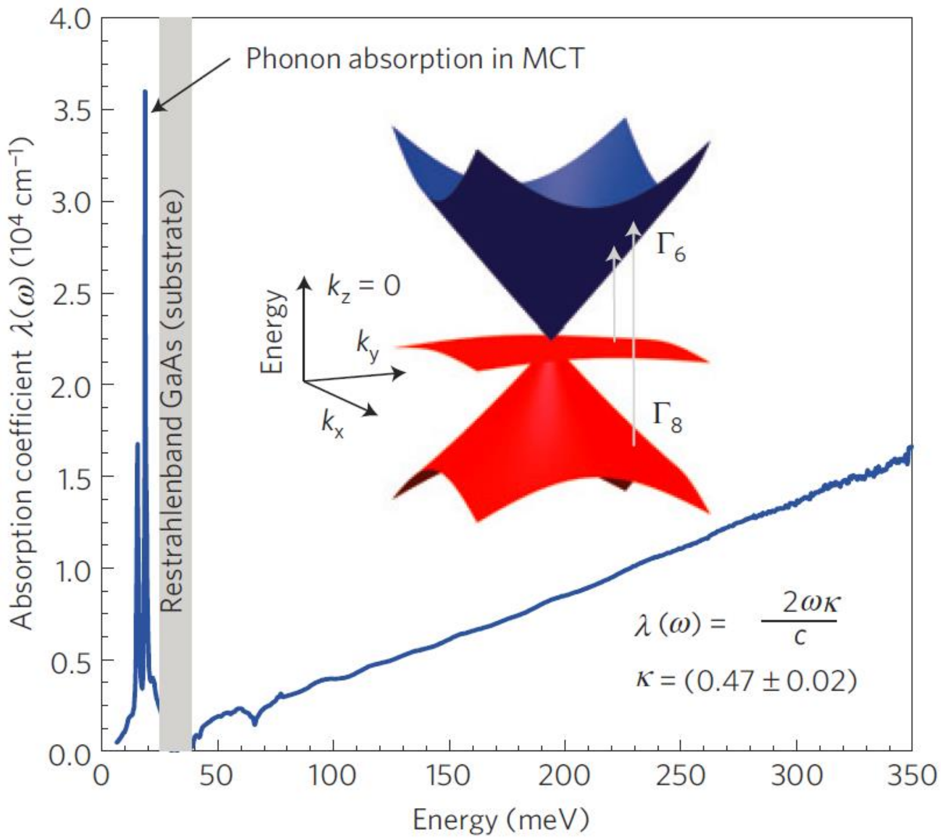
“Flat” absorption of light (2.3%) defined only by the fine structure constant:

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \doteq \frac{1}{137}$$

R. R. Nair et al., Science 320, 1308 (2008)
A. B. Kuzmenko et al., Phys. Rev. Lett. 100, 117401 (2008)

Btw. 2.3% = extremely strong absorption regarding only 1 atomic layer is involved!

Optical conductivity in systems with 3D conical bands



M. Orlita et al., Nature Physics 10, 233 (2014)

Absorption of light in solids (e.g., Fermi's golden rule):

joint density of states

$$\lambda(\omega) \propto \frac{\mathcal{D}(\omega)}{\omega}$$

For conical bands in 3D:

$$\mathcal{D}(\omega) \propto \omega^2$$

Absorption coefficient linear in photon frequency!

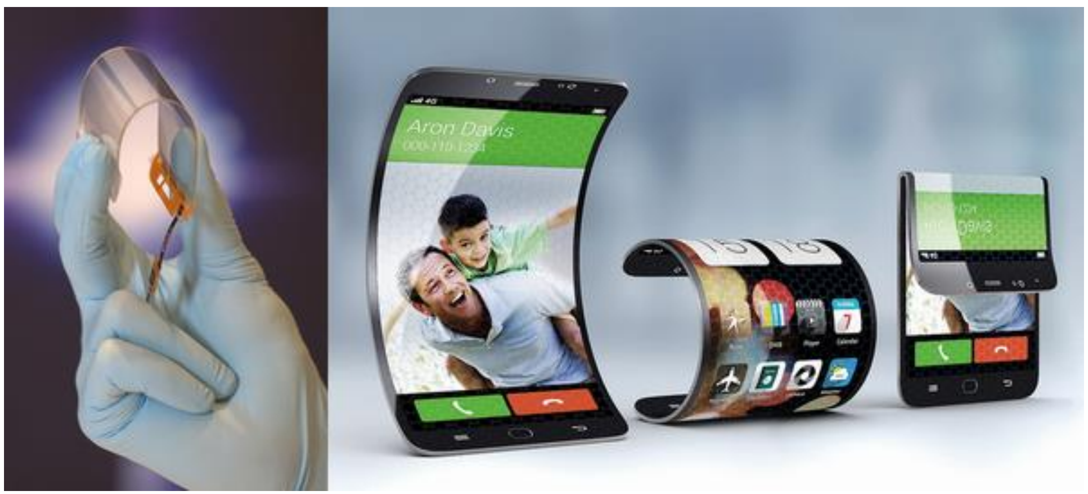
see also T. Timusk et al., Phys. Rev. B 87, 235121 (2013)

Applications of graphene in optoelectronics?

High transparency + good electrical conductivity + high flexibility =

new generation of touch screens?

cheap replacement of ITO?



J.-H. Ahn and B. H. Hong, Nature Nanotechnology 9, 737 (2014)

Massive and massless electrons in magnetic field - Landau levels (LLs)

Conventional massive carriers:

$$E = \frac{p^2}{2m}$$

Massless Dirac fermions:

$$E(\vec{p}) = \pm v_F |\vec{p}|$$

LL spectrum:

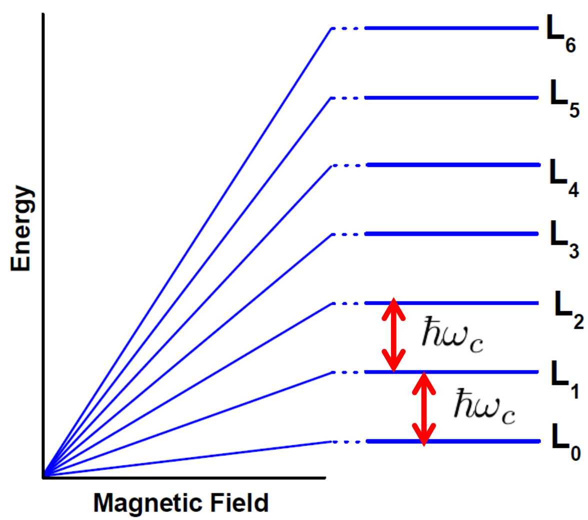
$$E_n = \hbar\omega_c(n + 1/2)$$

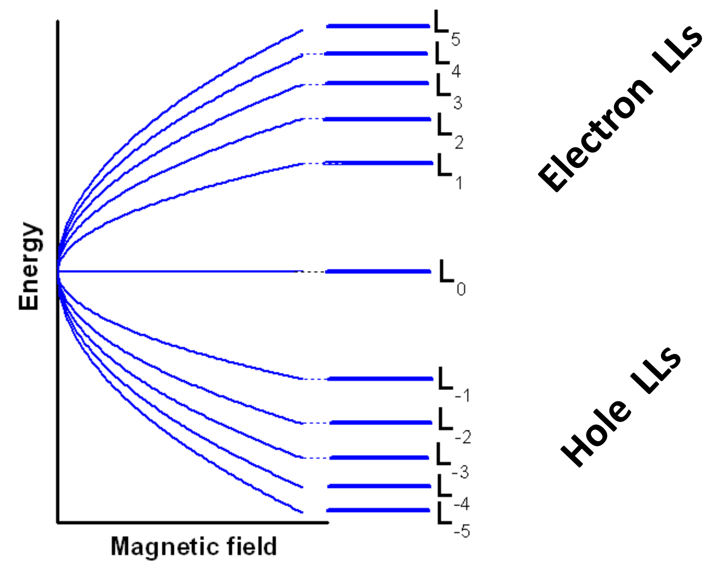
$$E_n = \pm v_F \sqrt{2e\hbar|Bn|}$$

Cyclotron frequency:

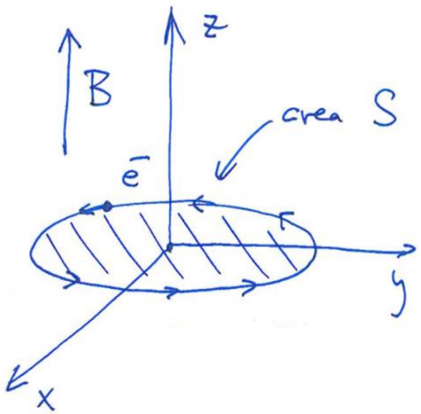
$$\omega_c = eB/m$$

$$\omega_c = v_F \sqrt{eB/(2\hbar)}$$





Charged particle in magnetic field: semi-classical approach



Semiclassical quantization (Bohr-Sommerfeld)

$$\Phi = B \cdot S = (n+\gamma)\cdot \Phi_0$$

- Φ: total magnetic flux
- n: orbital index (Landau level)
- Φ_0: flux quantum $= \frac{h}{e}$

Only "certain" orbits are allowed

$$r_n = \sqrt{2\,\frac{n+\gamma}{eB}\cdot\hbar} \qquad p_n = \sqrt{2eB\hbar\,(n+\gamma)}$$

$(p = \hbar k)$

Conventional parabolic band $\quad E = \frac{p^2}{2m} \xrightarrow{B\neq 0} E = \frac{\hbar e B}{m}(n+\gamma)$

$\gamma = \frac{1}{2}$

"Relativistic" particles $\quad E = v_F|\vec{p}| \xrightarrow{B\neq 0} E = v_F\sqrt{2e\hbar B(n+\gamma)}$

Quantum Hall effect (QHE) in conventional semiconductors

VOLUME 45, NUMBER 6 PHYSICAL REVIEW LETTERS 11 AUGUST 1980

New Method for High-Accuracy Determination of the Fine-Structure Constant Based on Quantized Hall Resistance

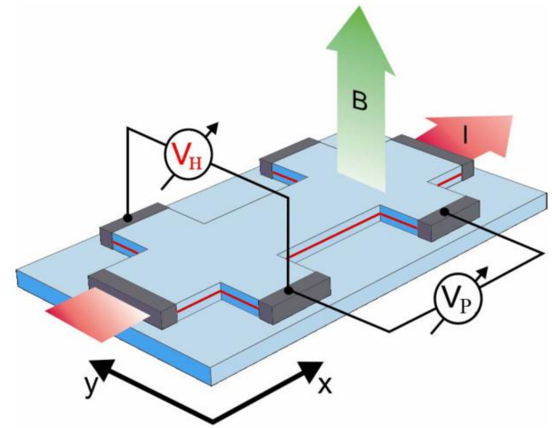
K. v. Klitzing
Physikalisches Institut der Universität Würzburg, D-8700 Würzburg, Federal Republic of Germany, and Hochfeld-Magnetlabor des Max-Planck-Instituts für Festkörperforschung, F-38042 Grenoble, France

and

G. Dorda
Forschungslaboratorien der Siemens AG, D-8000 München, Federal Republic of Germany

and

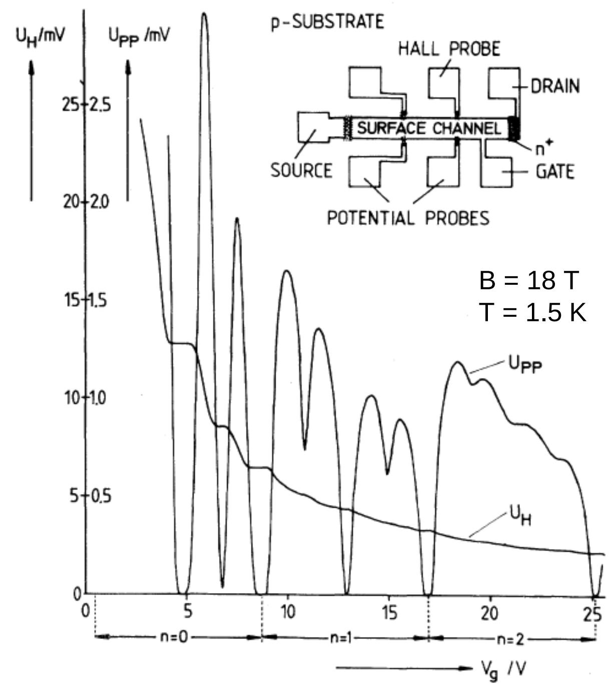
M. Pepper
Cavendish Laboratory, Cambridge CB3 0HE, United Kingdom
(Received 30 May 1980)



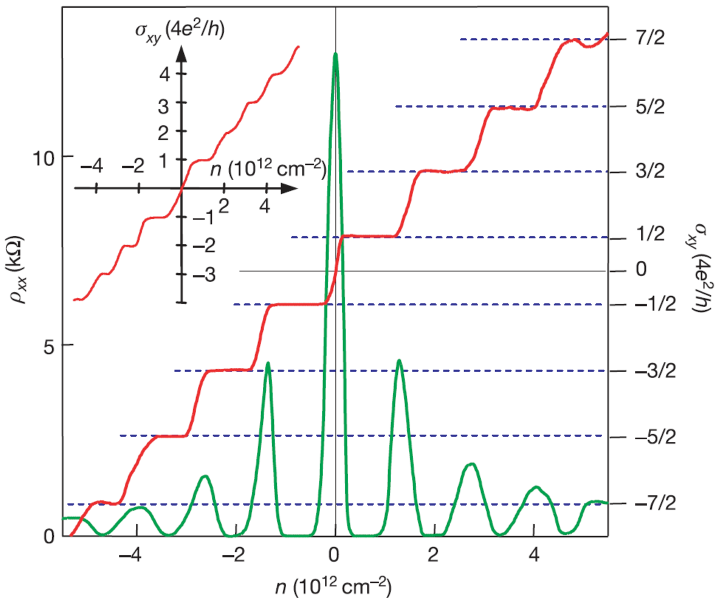
Quantization of Hall resistance
(given just by elementary charge and Planck constant)

$$R_H = \frac{U_H}{I} = \frac{h}{e^2}\frac{1}{n}$$

Fundamental effect discovered by Klaus von Klitzing in 1980 in magneto-transport experiments on 2D semiconductor structures (Nobel prize 1985)



Quantum Hall effect in graphene



"Half-integer" QHE :

Analogous to integer QHE in conventional semiconductors

Resistance quantization modified due to particular zero-mode Landau level typical of graphene:

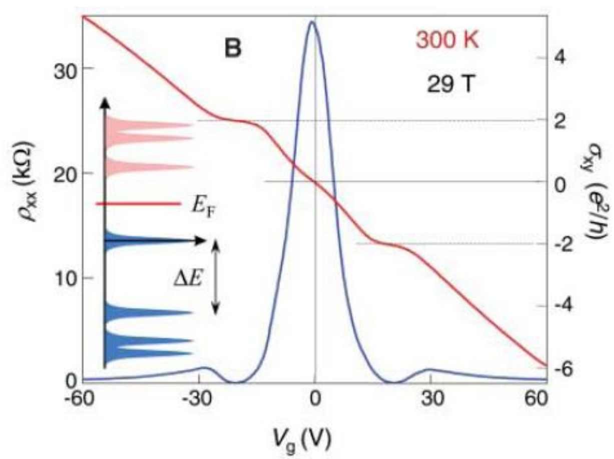
$$R_H = \frac{U_H}{I} = \frac{h}{e^2}\frac{1}{n+1/2}$$

K. Novoselov et al., Nature 438, 197 (2005)
Y. Zhang et al., Nature 438, 201 (2005)

QHE @ room temperature:

First QHE at room temperature ever observed, promising for applications in metrology (resistance standards)

K. Novoselov et al., Science 315, 1379 (2007)



Graphene – a new material for resistance standard

Quantum Hall effect device based on epitaxial graphene on SiC substrates

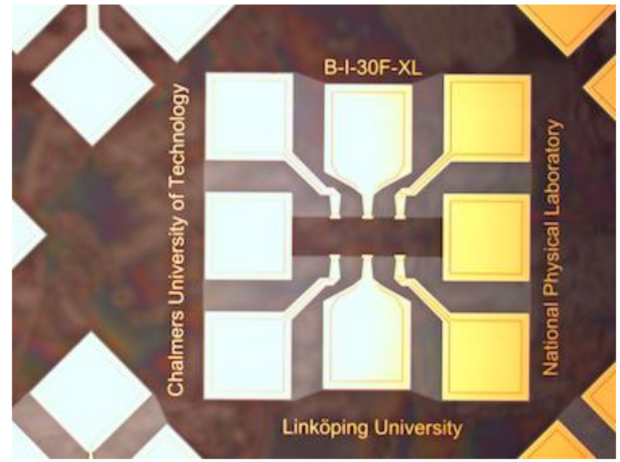


Table-top quantum Hall effect standard, cryogen free (T~4K, B< 5T), significantly simpler as compared to the previously setups based on GaAs heterostructure…

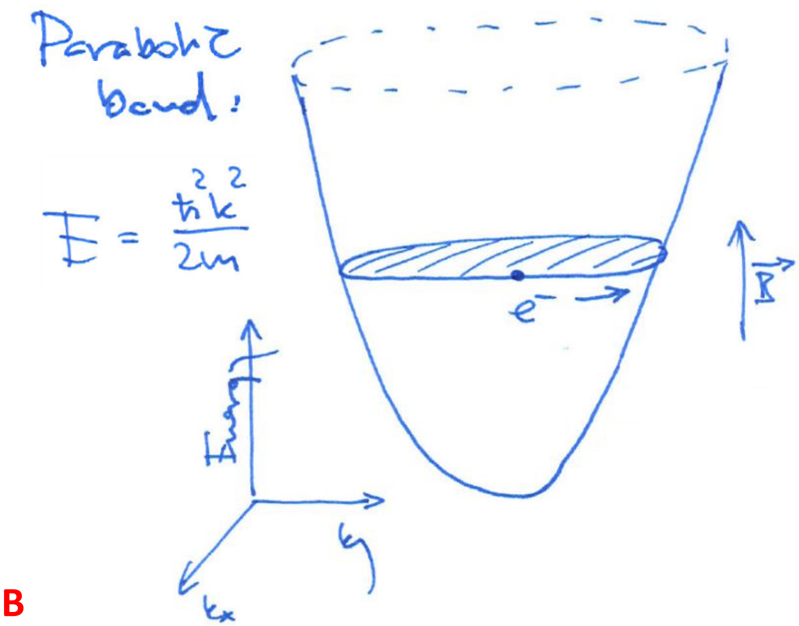
One of very first applications of graphene!

T. Janssen et al., 2D Mater. 2, 035015 (2015)

Optical response of massive particles (classical regime)

Charged particle in magnetic field:

$$\frac{d\mathbf{p}}{dt} = e[\mathbf{v} \times \mathbf{B}]$$



Cyclotron motion at frequency:

$$\omega_c = \frac{eB}{m}$$

← Linear in B

← Cyclotron mass

Cyclotron resonance in (semi)conductor physics ⇨ **Single-particle effective mass**

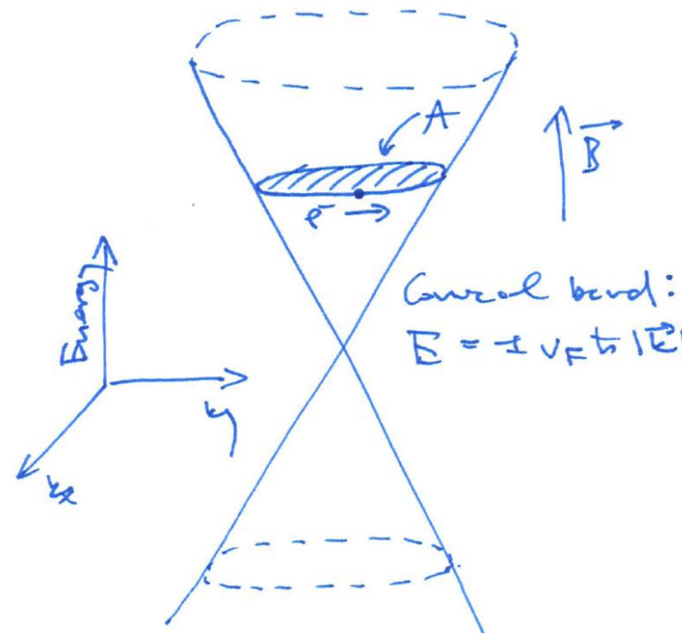
Single-particle mass, no many-body effects, cyclotron resonance always dominated by classically defined frequency

W. Kohn, Phys. Rev. 123, 1242 (1961)

Optical response of massless particles (classical regime)

Charged particle in magnetic field:

$$\frac{d\mathbf{p}}{dt} = e[\mathbf{v} \times \mathbf{B}]$$



Cyclotron motion at frequency:

$$\omega_c = \frac{eB}{\underbrace{E/v^2}}$$

Linear in B

Cyclotron mass (energy dependent)

"Effective" effective mass of massless particles, i.e., Einstein relation

$$E = mv^2$$

Bwt. definition of cyclotron mass:

$$m = \frac{\hbar^2}{2\pi}\frac{\partial A}{\partial \varepsilon}$$

see, e.g., Ashcroft & Mermin

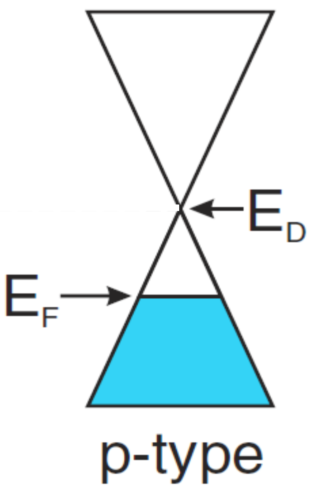
Cyclotron resonance in doped epitaxial graphene

Classical regime

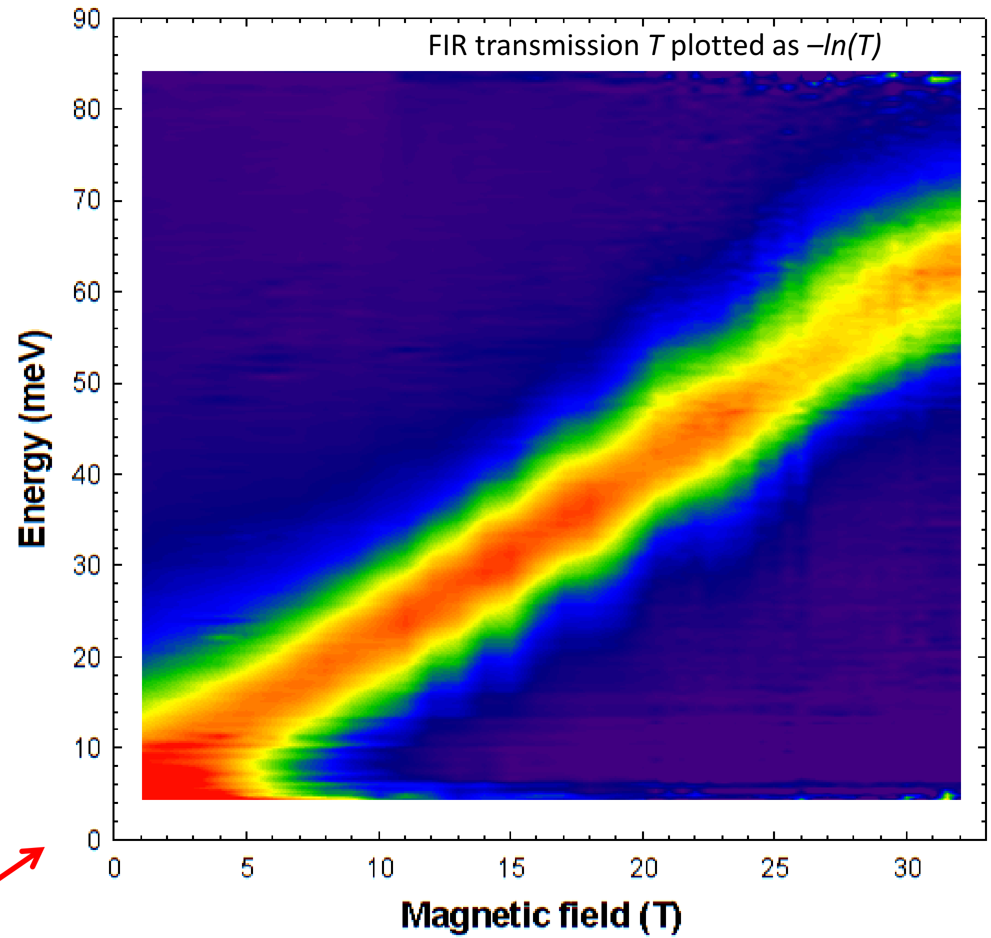
$$\omega_c \tau = \mu . B \sim 1$$

$$\mu \approx 3 \times 10^3 \ \mathrm{cm}^2/(\mathrm{V.s})$$

$$E_F \approx -300 \ \mathrm{meV}$$



$$\omega_c = \frac{eB}{m} = v^2 \frac{eB}{E_F}$$



A. M. Witowski et al, PRB B 82, 165305 (2010)
M. Orlita et al., NJP 14, 095008 (2012)

Magneto-optical response of graphene (quantum regime)

$$\omega_c \tau = \mu . B \gg 1$$

Landau level spectrum:

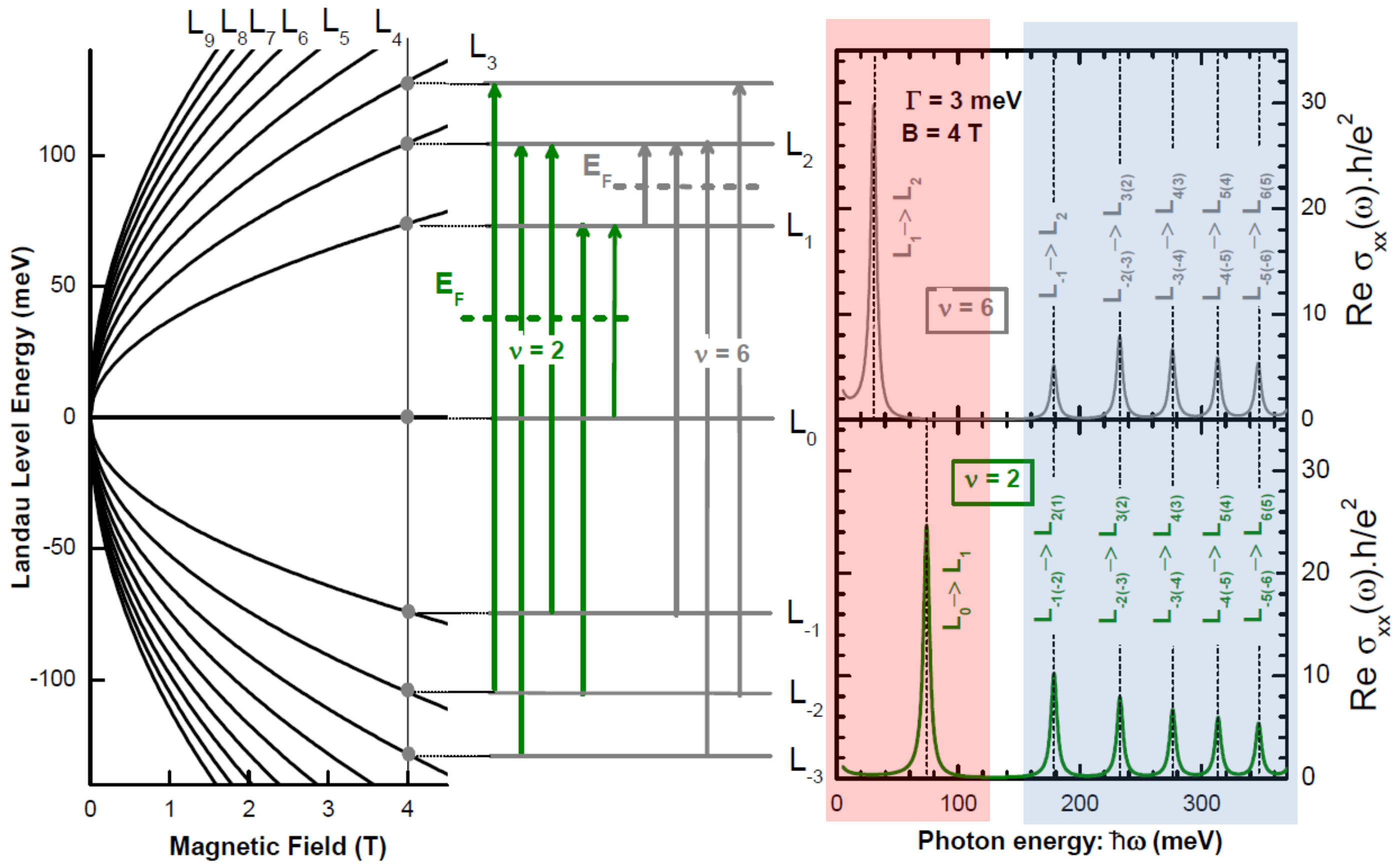
$$E_n = \pm v_F \sqrt{2e\hbar |Bn|}$$

Selection rules:

$$|n| \rightarrow |n| \pm 1$$

Cyclotron resonance

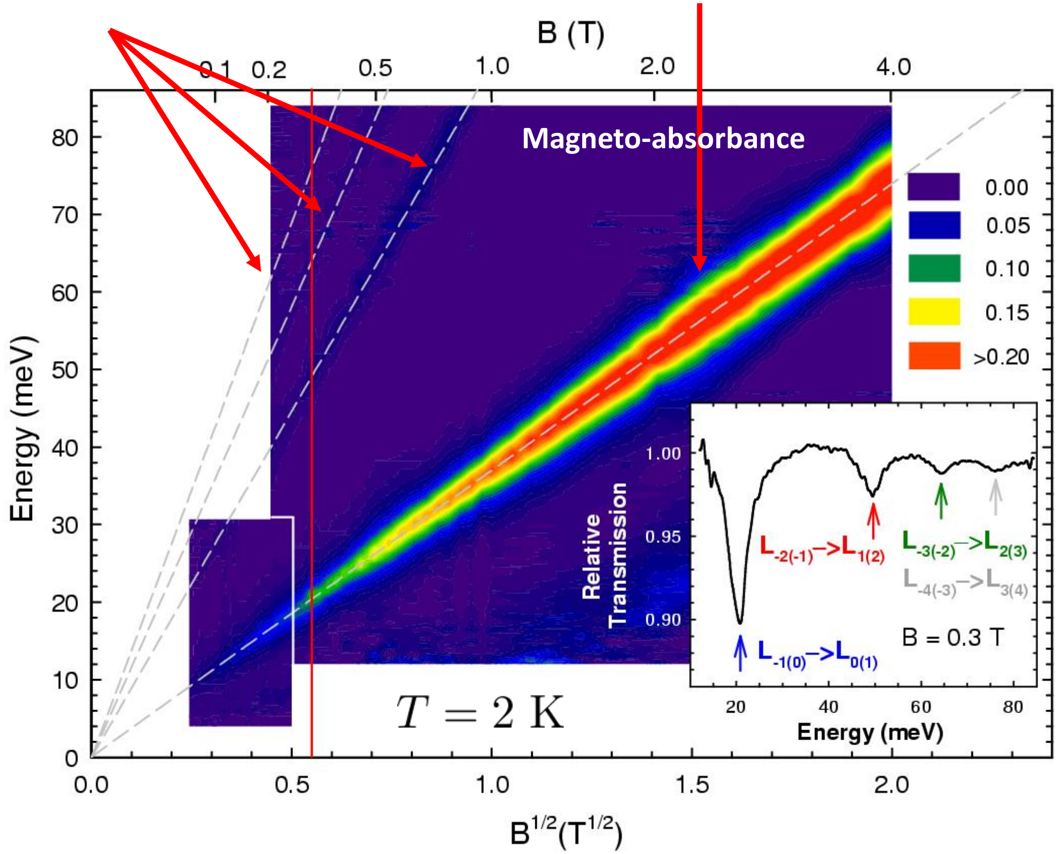
Interband inter-LL transitions



Magneto-transmission of (multilayer epitaxial) graphene

Interband inter-Landau level transitions

Cyclotron resonance



Energy spectrum:

$$E_n = \pm v_F \sqrt{2e\hbar|Bn|}$$

Selection rules:

$$|n| \rightarrow |n| \pm 1$$

Characteristic $\sqrt{B}$ response in the quantum regime !

M. Orlita et al., Phys. Rev. Lett. 101, 267601 (2008)

ZOO - Electronic band structure of graphene stacks

Basic characteristics and further reading…

AA stacking: always preserving linear (graphene-like) dispersion

C. J. Tabert and E. J. Nicol, Phys. Rev. B 86, 075439 (2012)
Z. Liu et al., Phys. Rev. Lett. 102, 015501 (2009)
Y.-H. Ho et al., Appl. Phys. Lett. 97, 101905 (2010)

AB stacking: most often and most stable, often denoted as Bernal stacking, resulting in the combination of parabolic and linear bands

B. Partoens and F. M. Peeters, Phys. Rev. B 74, 075404 (2006)
M. Koshino and T. Ando, Phys. Rev. B 76, 085425 (2007)
S. Berciaud et al., Nano Letters 14, 4549 (2014)

ABC (rhombohedral): relatively complex band structure with possible topologically protected surface states

W. Bao, et al., Nature Phys. 7, 948 (2011)
C. H. Lui et al., Nature Physics 7, 944 (2011)
Y. Henni et al., Nano Lett. 16 , 3710 (2016)

Rotational stacking: nearly isolated graphene sheets, but with a Moire structure (angle dependent) and van Hove singularities in the density of states

J. Hass et al., Phys. Rev. Lett. 100, 125504 (2008)
M. Orlita et al., Phys. Rev. Lett. 101, 267601 (2008)
I. Brihuega et al. Phys. Rev. Lett. 109, 196802 (2012)
L. A. Ponomarenko et al., Nature 497, 594 (2013)

Optical response of Bernal-stacked bilayer graphene

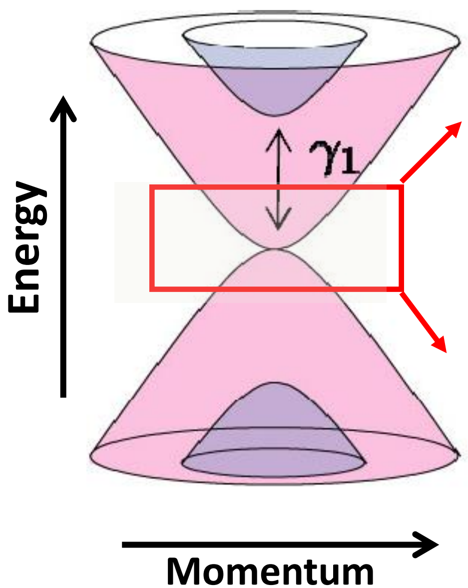
Landau level spectrum:

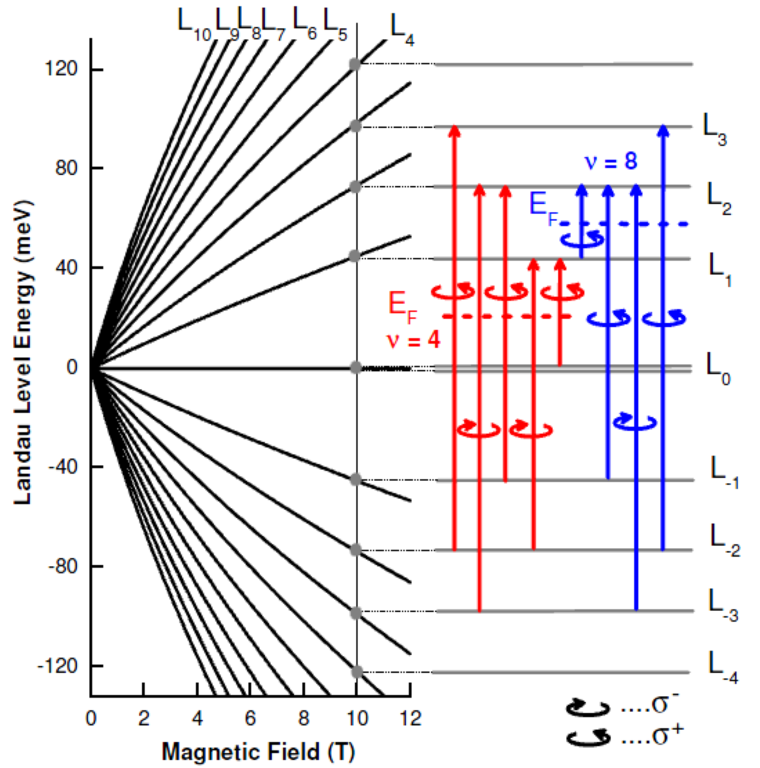
$$E_n = \text{sign}(n)\hbar\omega_c\sqrt{|n|(|n|+1)}$$

$$\omega_c = eB/m$$
$$m = \gamma_1/v_F^2$$
$$m \approx 0.03m_0$$

Selection rules:

$$|n| \to |n| \pm 1$$





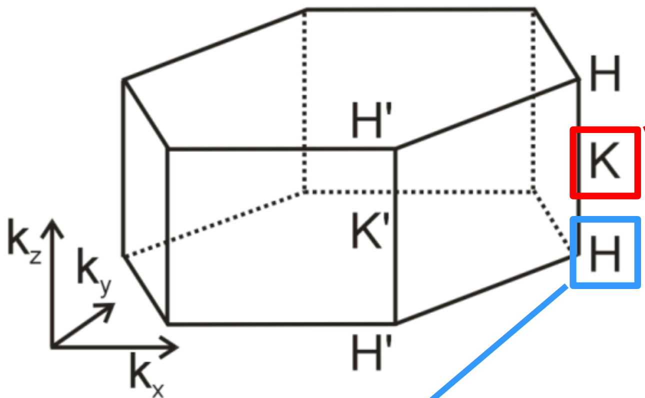
Experiments:

E. A. Henriksenet al., Phys. Rev. Lett. 100, 087403 (2008)
M. Orlita et al., Phys. Rev. B 83, 125302 (2011)

Linear in B response!

Electronic band structure in graphite

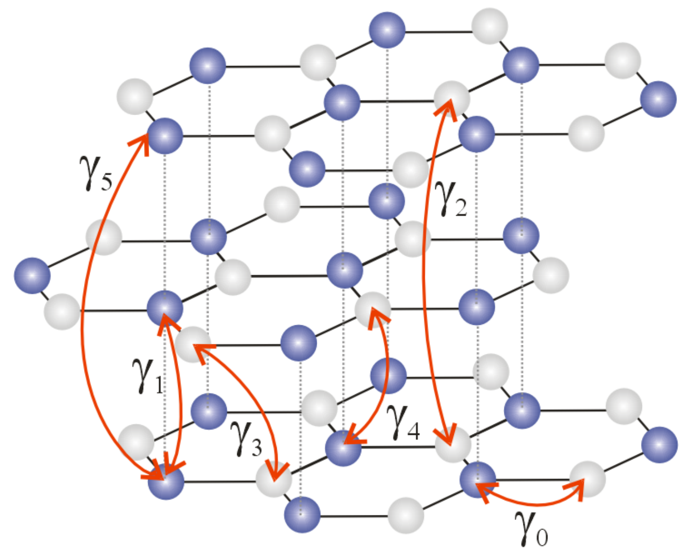
Brillouin zone of bulk graphite:



Electron pocket

Hole pocket

Bernal stacking of graphene layers:



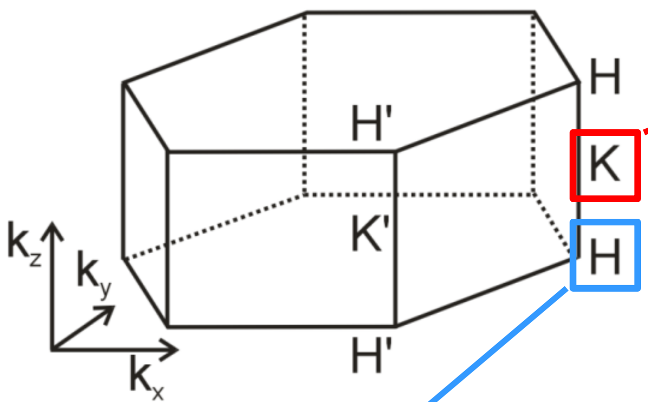
Widely explored in the past

P. R. Wallace, Phys. Rev. 71, 622 (1947)
J. C. Slonczewski and P. R. Weiss, Phys. Rev. 109, 272 (1958)
J. W. McClure, Phys. Rev. 119, 606 (1960)

Highly anisotropic material, compensated semimetal with hole and electron densities about ~10^{11} cm^{-2}, strongly diamagnetic, high mobility material (at low T)

Magneto-optical response of graphite

Brillouin zone of bulk graphite:



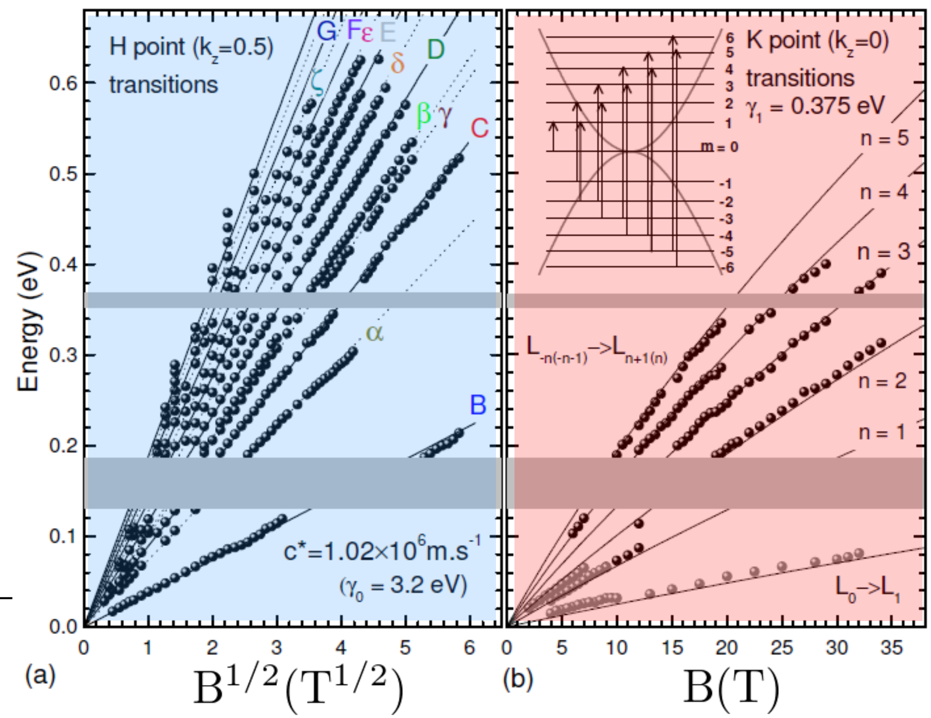
Effective bilayer graphene (massive particles)

response linear in B

Effective graphene monolayer (massless Dirac fermions)

response linear in $\sqrt{B}$

Magneto-transmission (fan chart):



M. Koshino and T. Ando, Phys. Rev. B 76, 085425 (2007)
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Further reading

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A. K. Geim and A. H. MacDonald, Phys. Today 60, 35 (2007)

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Electronic properties:

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M. O. Goerbig, Rev. Mod. Phys. 83, 1193 (2011)

Optical properties:

F. Bonaccorso, Z. Sun, T. Hasan and A. C. Ferrari Nature Photonics 4, 611 (2010)

M. Orlita and M. Potemski, Semicond. Sci. Technol. 25, 063001 (2010)

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