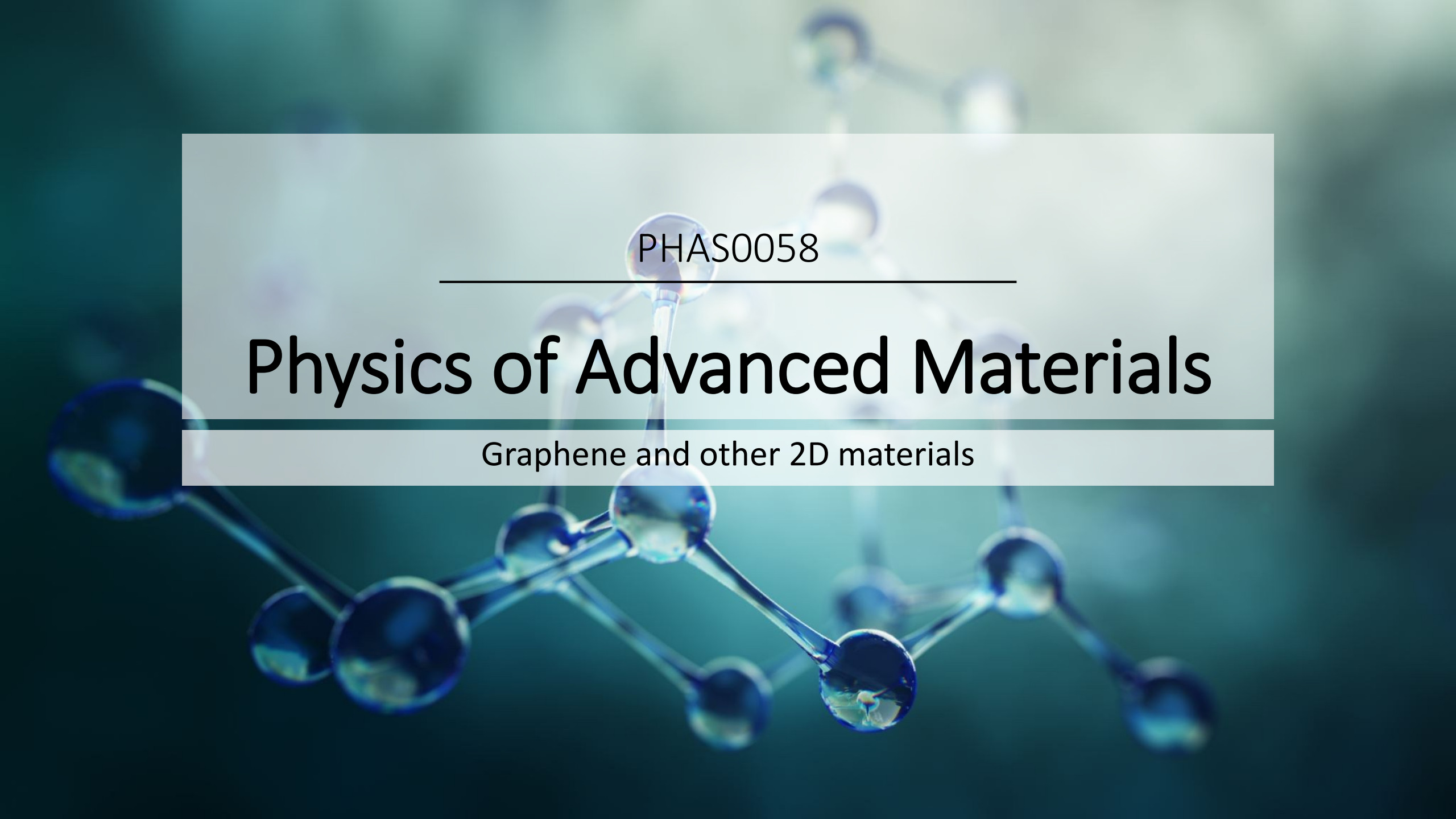


PHAS0058

Physics of Advanced Materials

Graphene and other 2D materials

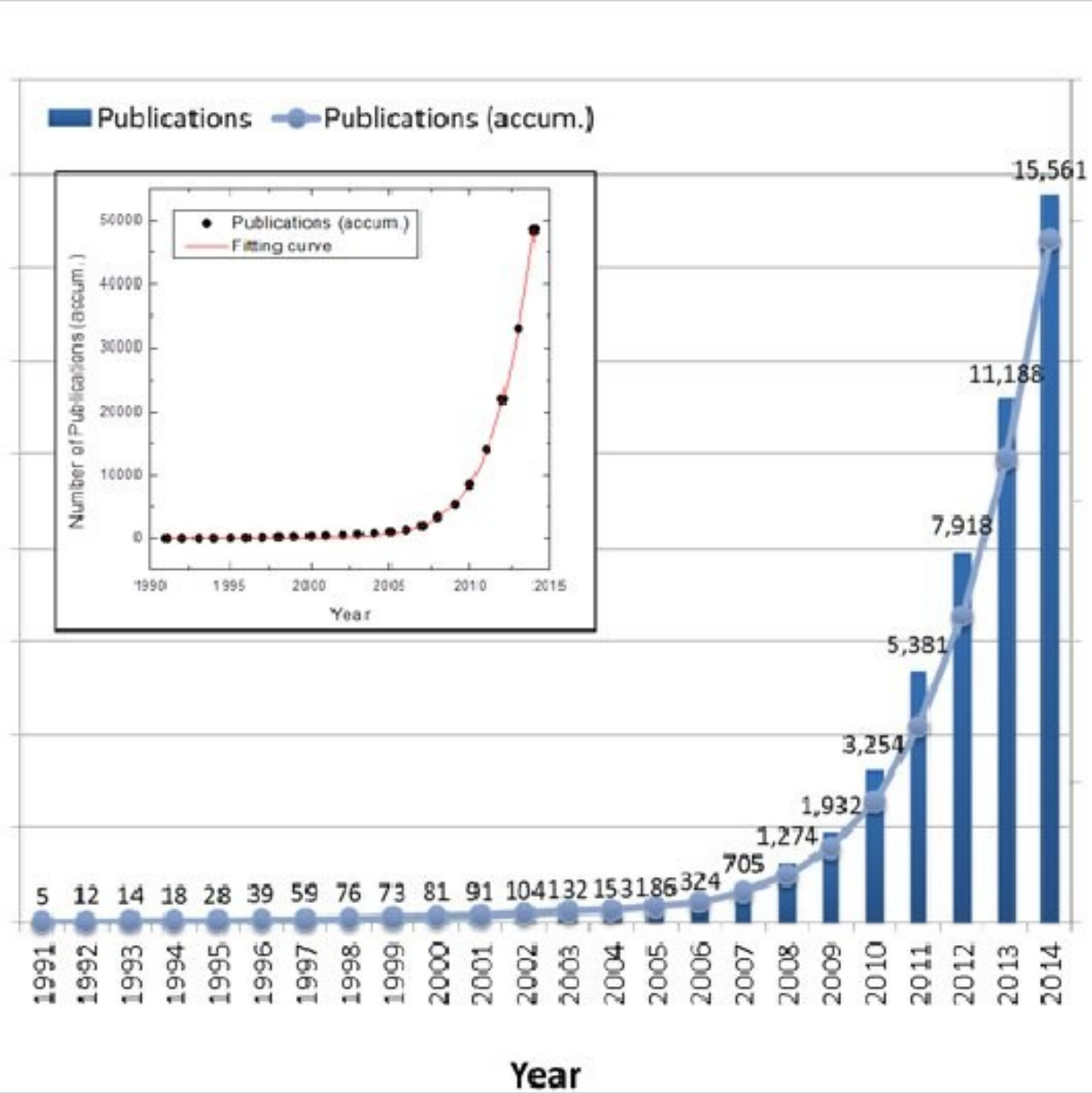
In this and next lecture…

- Context
- Energy structure
- Relativistic effects and doping
- Optical properties
- Quantum Hall Effect
- Other 2D materials
- Manufacturing and applications

* Self-study:
  - 2D Bravais lattices
  - Miller indices
  - hexagonal and rhombohedral systems
  - Casimir force
  - Fermi energy/level

Context

“The wonder material”



Numbers of publications on graphene:

- from 5 in 1991 to >29k in 2017

- Nobel Prize in 2010

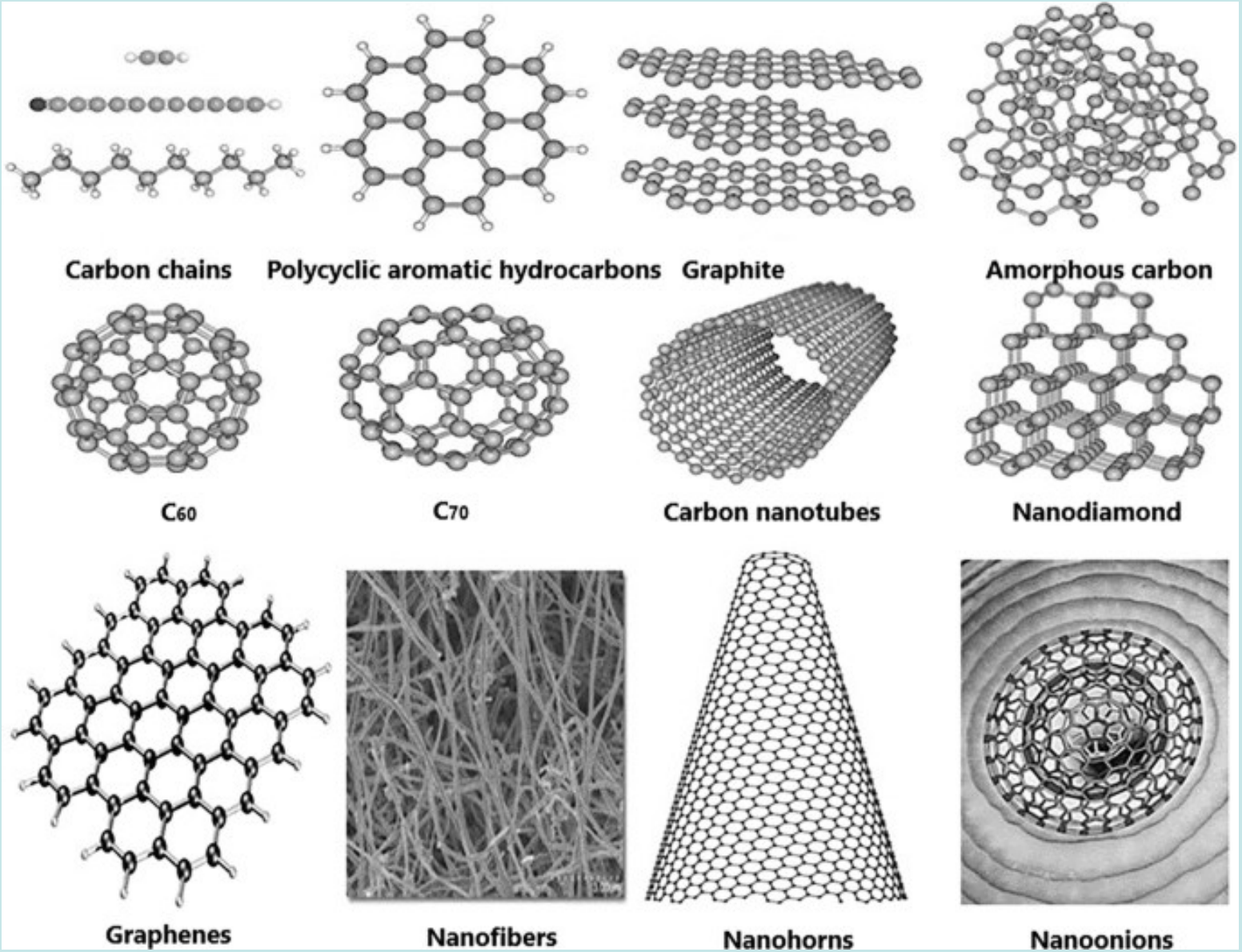
Allotropes

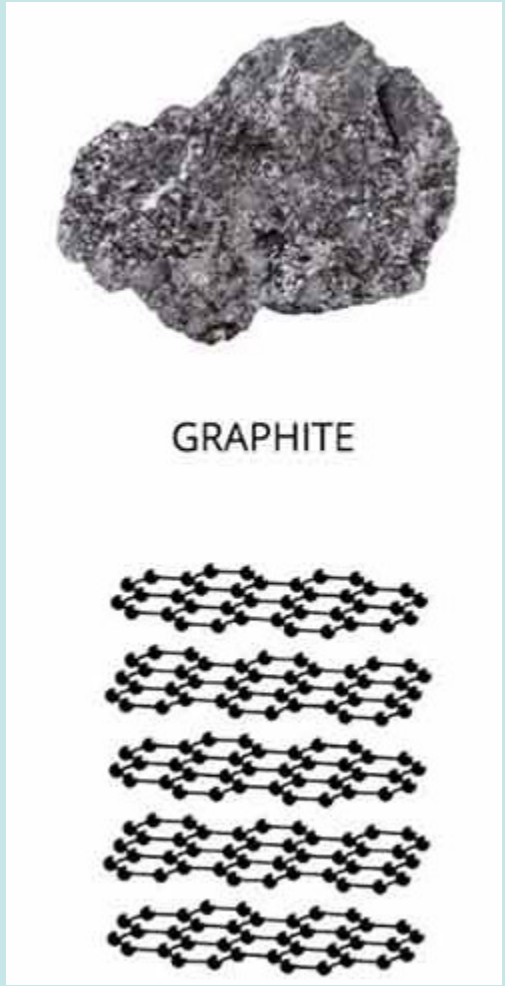
Allotropes: (gr. ἄλλος *(allos)*, meaning 'other', and τρόπος *(tropos)*, meaning form')
different physical forms in which an element can exist

Examples:

- Carbon: *graphite, diamond, coal, nanotubes…*
- Sulfur: *α-sulphur, β-sulphur, …*
- Silicon: *amorphous, crystalline, silicene*
- Antimony: *blue-white, yellow, black, explosive*
- …

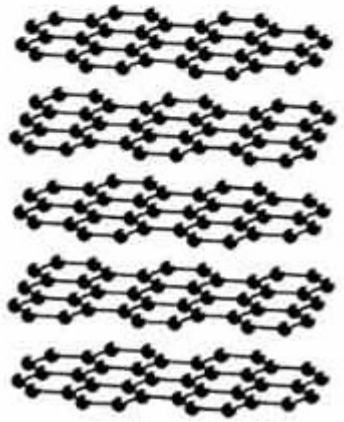
Carbon allotropes





Graphite

GRAPHITE

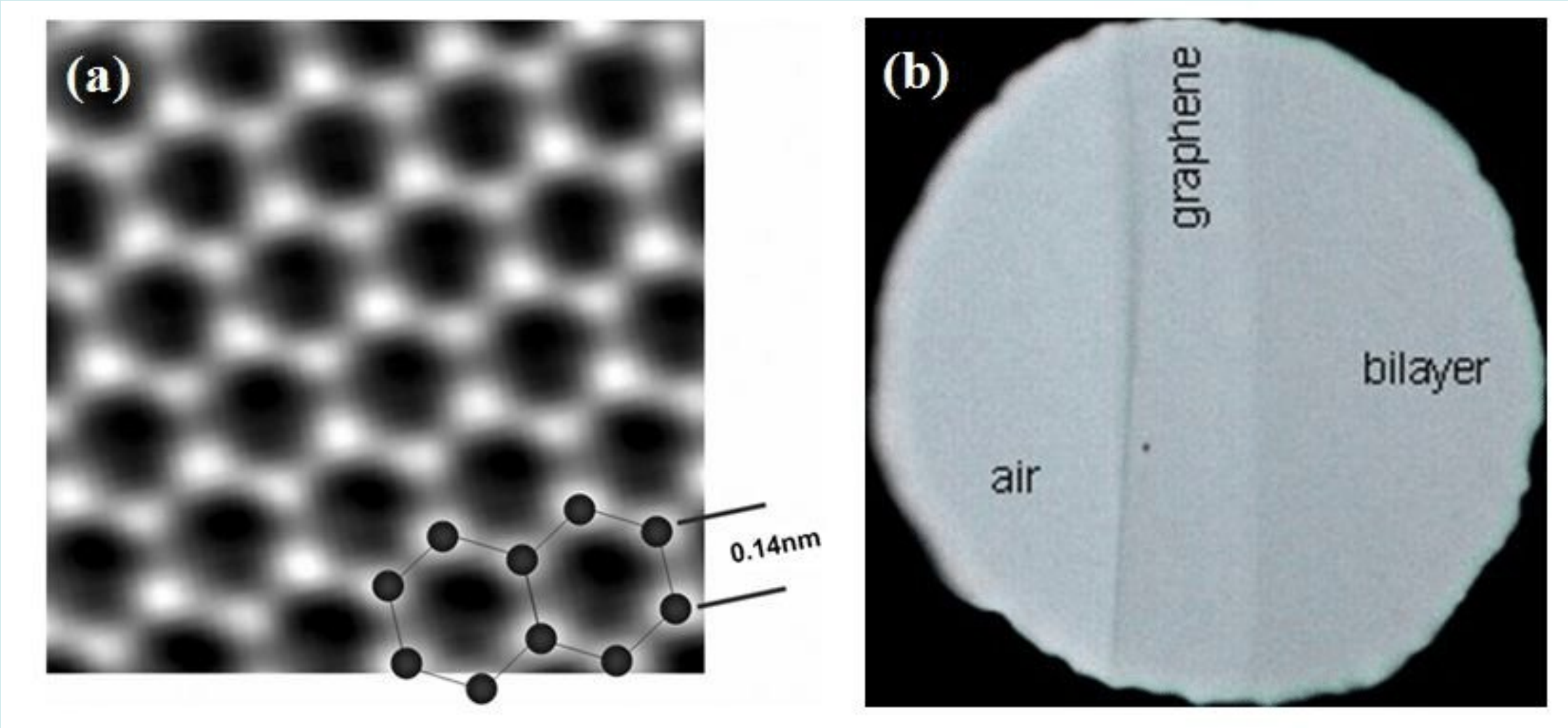


Intra-sheet bonding:
- covalent (strong)
- conjugated
- good conductivity in plane

Inter-sheet bonding:
- weak (mixture of Van der Walls, Casimir, delocalosation, …)
- gives lubricant properties
- enables shearing of sheets (wiritng)
- bad conductivity across the planes

2 forms:
- α (hexagonal) – flat or buckled
- β (rhombohedral) – only at temperatures below 1300^{o}C

Graphene



a) TEM image of a graphene sheet illustrating the crystalline lattice (bond length ~ 0.14 nm) (Dato et al. 2009),

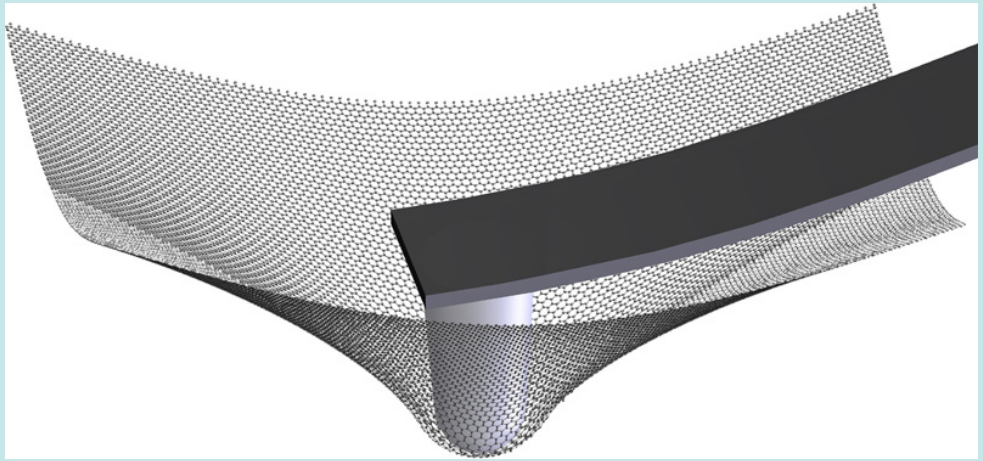
b) b) A single sheet graphene can be visualized by eye due to its capacity to absorb 2.3% of white light (Kuzmenko, van Heumen et al. 2008).

Graphene - highlights

Features:

- strong: 200x more resistant than steel
- lightweight: 5x lighter than aluminium
- high thermal and electrical conductivity
- transparent
- flexible
- virtually limitless derivatives

Lee, C. et al., Science, 321 (5887), pp. 385-388, 2008



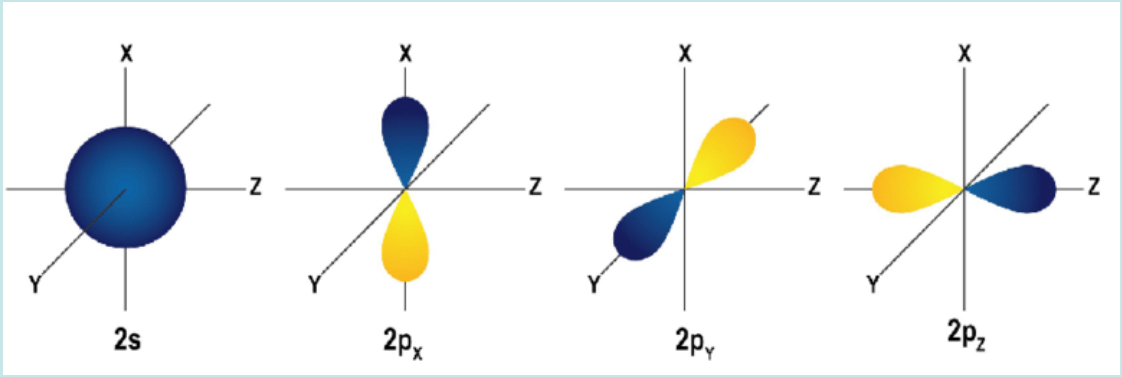
Challenges:

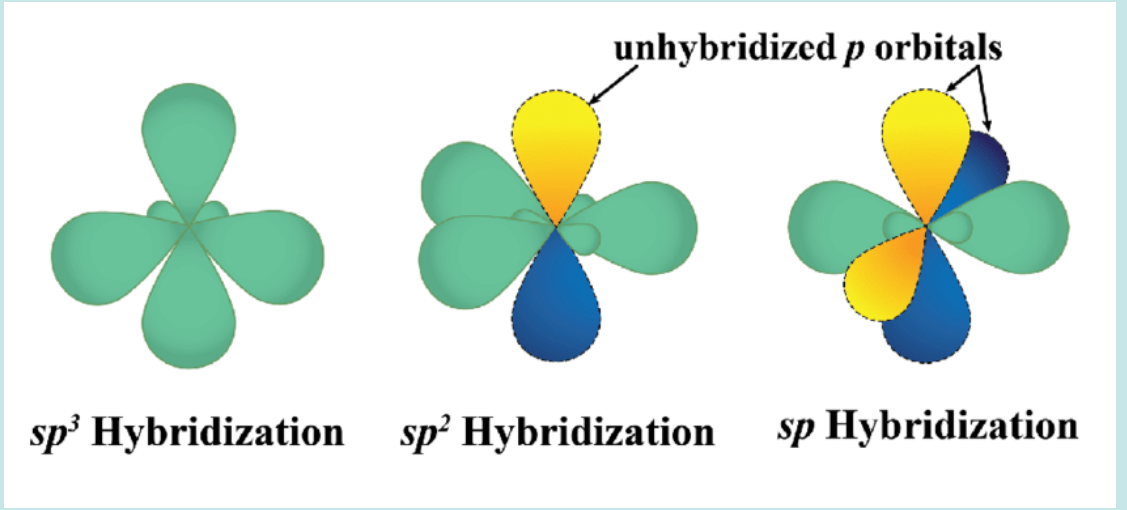
- large scale fabrication
  - peeling – not feasible
  - CVD – mechanical defects during peeling or oxidation by acids
- cost
- toxicitiy of reagents

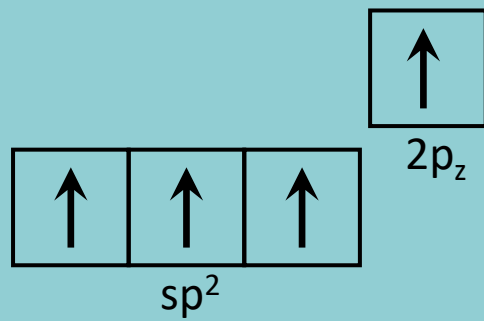
The opportunities and challenges of Graphene | Coffee & Conversation: Prof. Konstantin Novoselov
https://youtu.be/7dSPrW7aci0

Energy structure of graphene

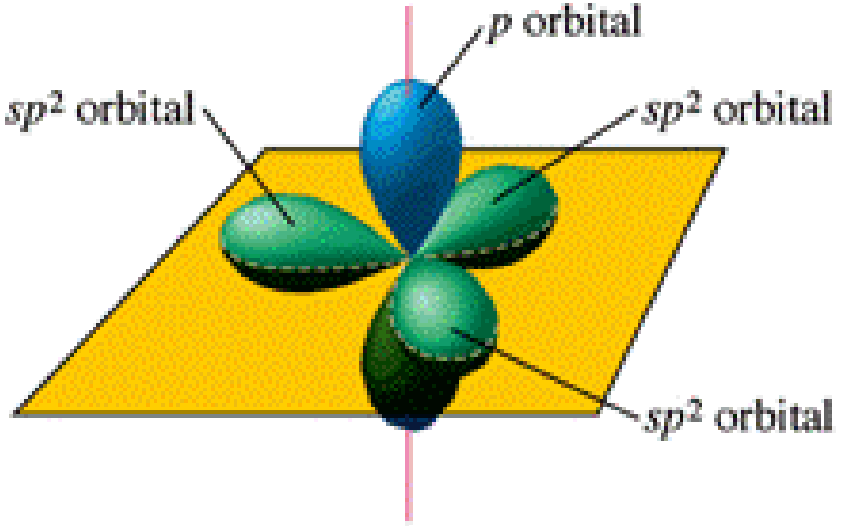
sp_2 hybridisation



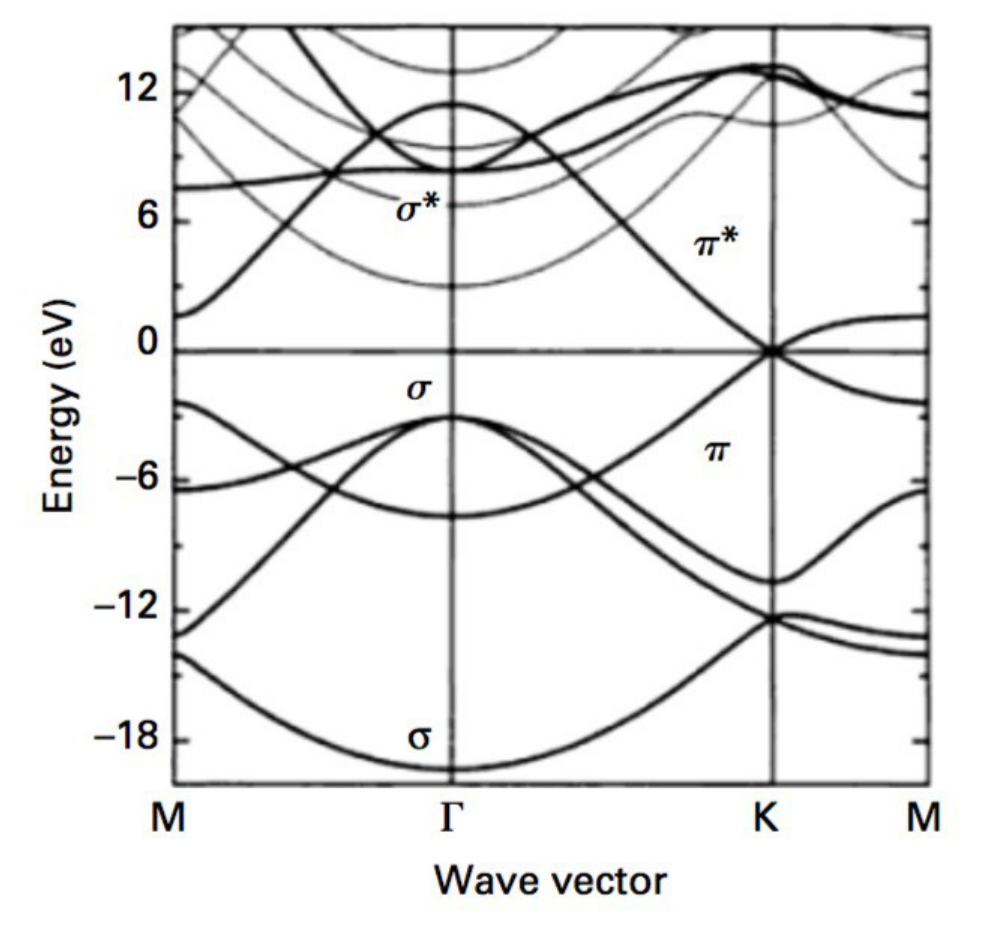




sp2 hybridisation



A quick look at the band structure



- sp^2 hybridisation results in σ- and π-orbitals formation
- high crystallinity leads to new phenomena
- band structure depends on position in the reciprocal lattice

Bravais lattice

Bravais lattice: infinite array of discrete points generated by a set of discrete translations operations described analytically as:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

where R is the vector of the (generic) lattice point, n_i are any integers and a_i are the so-called *primitive vectors*

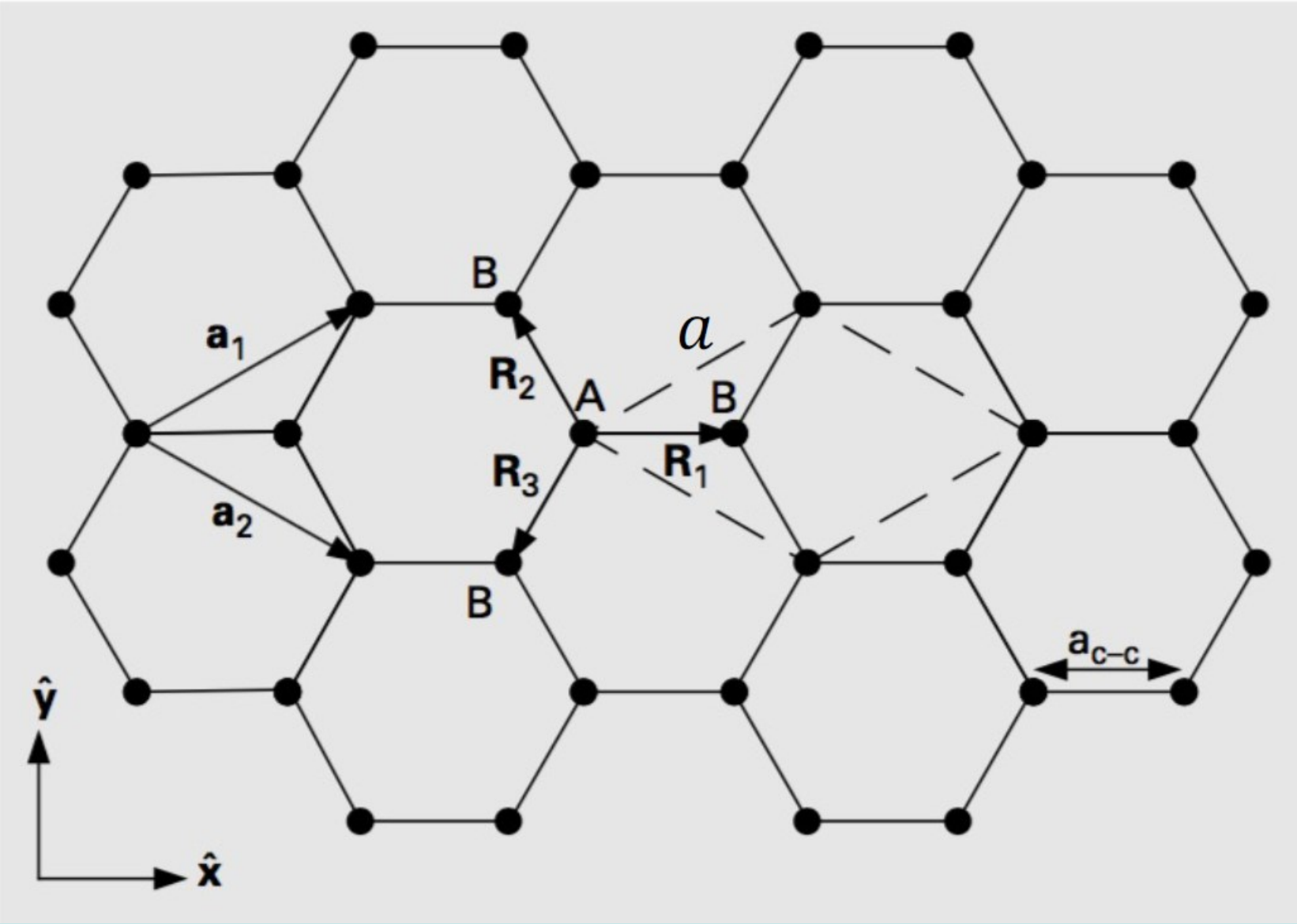
CRYSTAL = **lattice** + **basis**

a periodic arrangement of one or more atoms (the basis, or motif) repeated at each lattice point

set of vectors

one or more atoms to which lattice vectors are applied

Graphene lattice



honeycomb:

- A and B atoms not equivalent
- lattice looks different from different points

hexagonal:

- 2 atom basis
- two vectors
- $a = \sqrt{3}a_{c-c} = \sim 2.46\text{Å}$

$$a_1 = \left(\frac{\sqrt{3}a}{2}, \frac{a}{2}\right)$$

$$a_2 = \left(\frac{\sqrt{3}a}{2}, \frac{a}{-2}\right)$$

Reciprocal lattice (in 2D)

Reciprocal lattice: lattice defined by a vector fulfilling a condition:

$$G_m \cdot R_n = 2\pi N \quad \text{where } N \in \mathbb{Z}$$

For a 2D lattice, this is also a Bravais lattice with basis:

$$\boldsymbol{b}_1 = 2\pi \frac{\boldsymbol{R a_2}}{a_1 \cdot \boldsymbol{R a_2}}$$

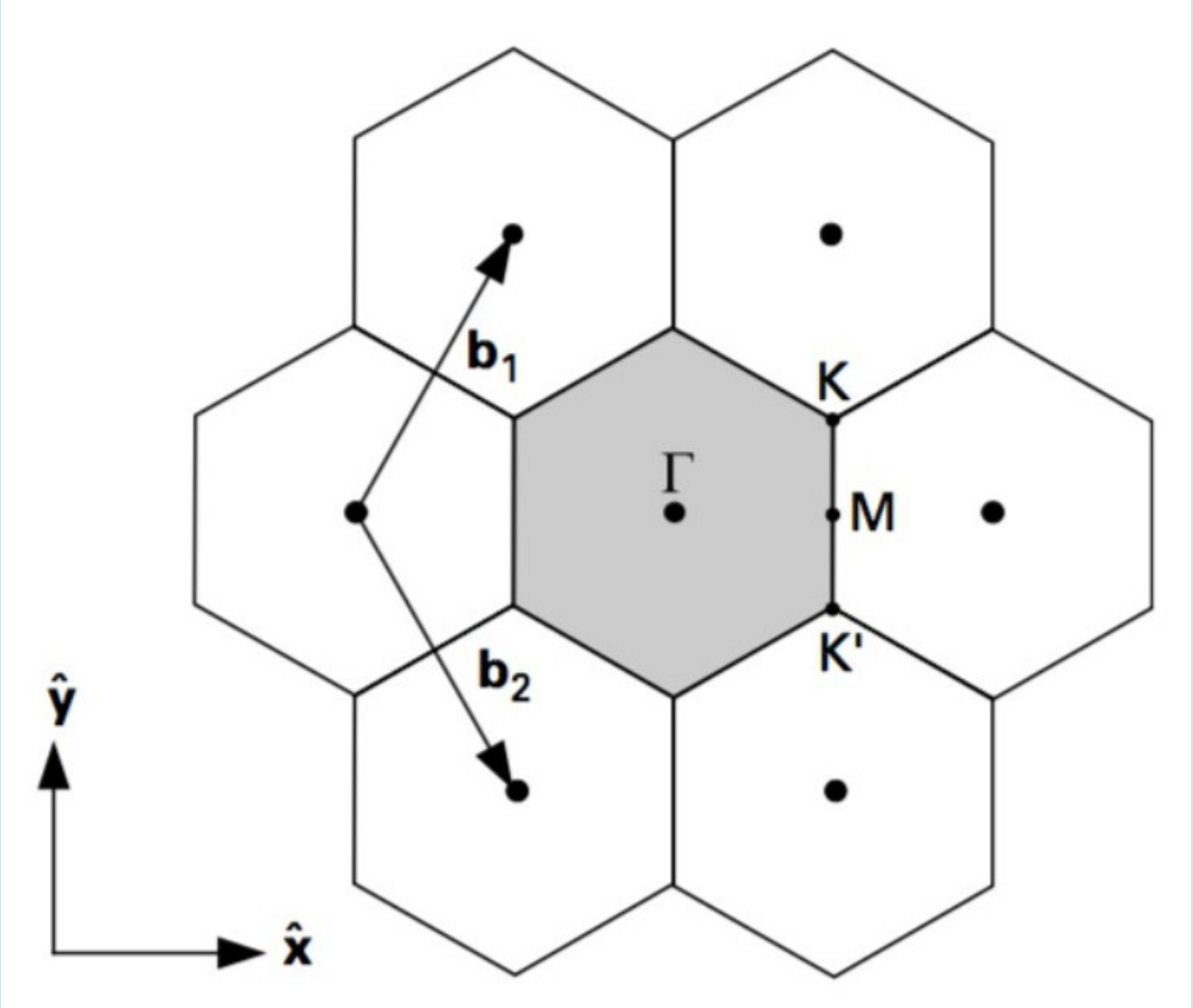
$$\boldsymbol{b}_2 = 2\pi \frac{\boldsymbol{R a_1}}{a_2 \cdot \boldsymbol{R a_1}}$$

where R is the rotation matrix:

$$R = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

Reciprocal lattice in graphene

- first Brillouin zone shaded
- high symmetry points: Γ, K, M and K’
- 6 K-points – each shared with 3 hexagons
- 6 M-points – each shared with two hexagons



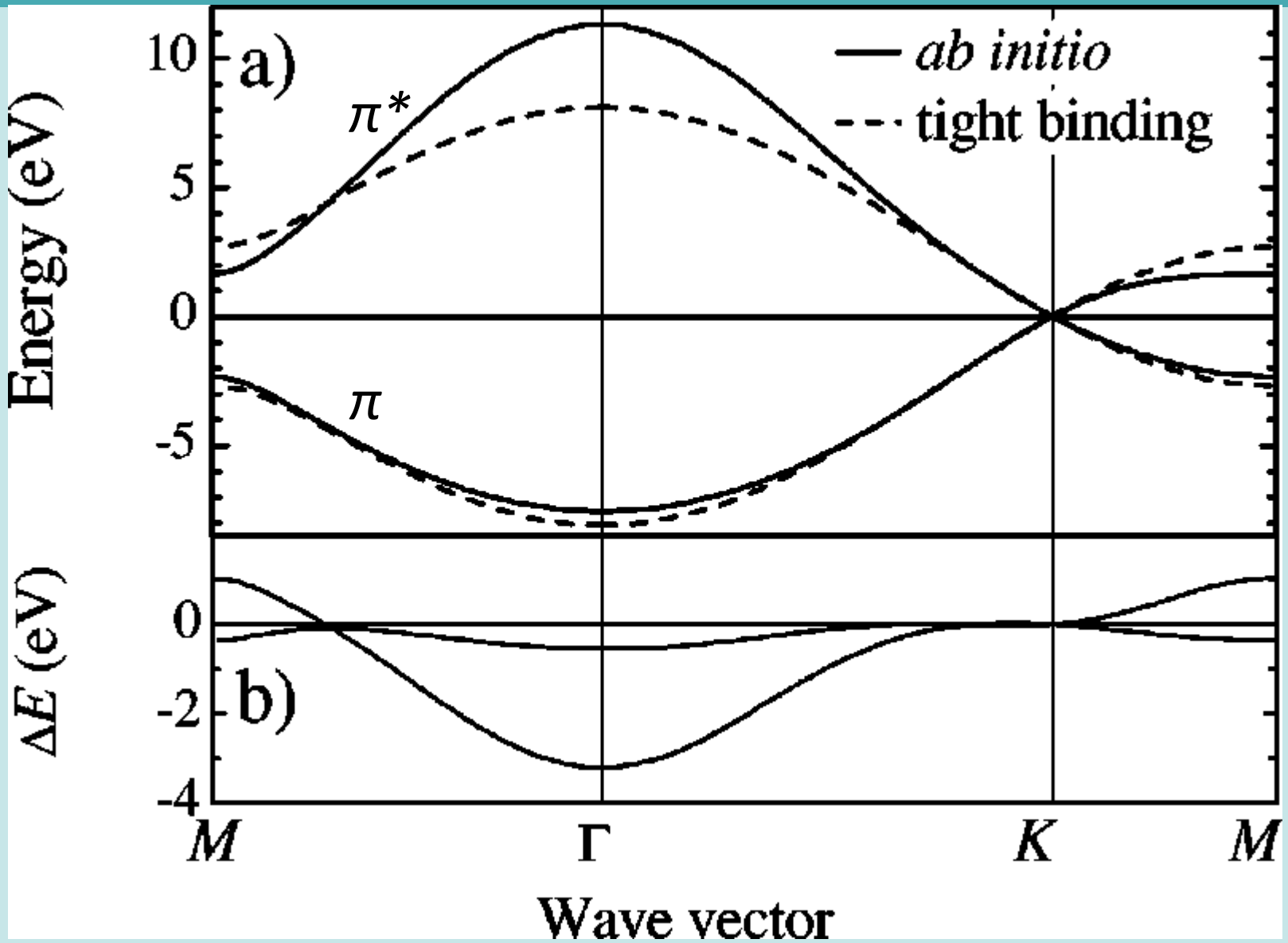
Bloch theorem

$$\psi(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u(\boldsymbol{r}) \xrightarrow{+\,Schroedinger} \Psi(\boldsymbol{r}+\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\Psi(\boldsymbol{r})$$

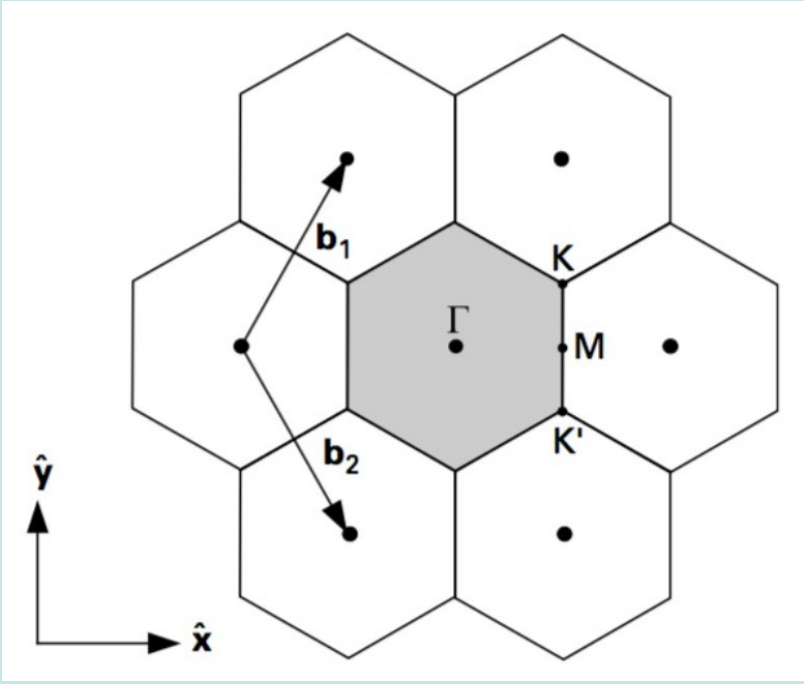
- u – periodic function with lattice periodicity
- unique solutions for energy bands found within the Brillouin zone
- energy graphed along the high-symmetry directions
- k-space - reciprocal lattice
- wavevector k - vector that locates any point within the Brillouin zone

Solution found with assistance of the Tight-binding approximation (Nearest Neighbour tight-binding model)…

Theoretical solution for energy structure of graphene

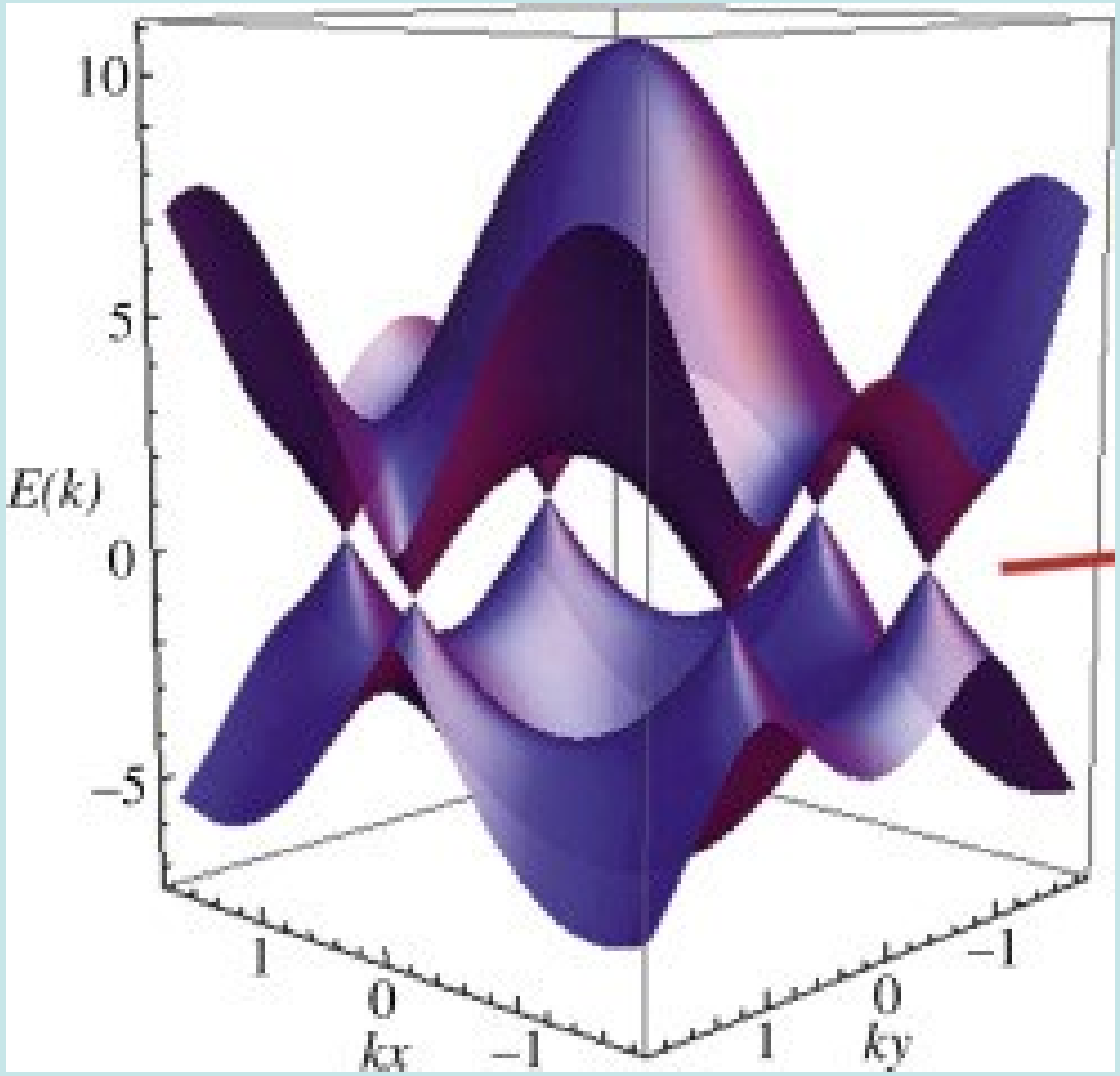


- band gap depends on wavevector
- Fermi energy: E=0 at K-point



Reich, S. et al. (2002). Phys. Rev. B. 66. 10.1103/PhysRevB.66.035412.

3D band gap structure



semi-metal

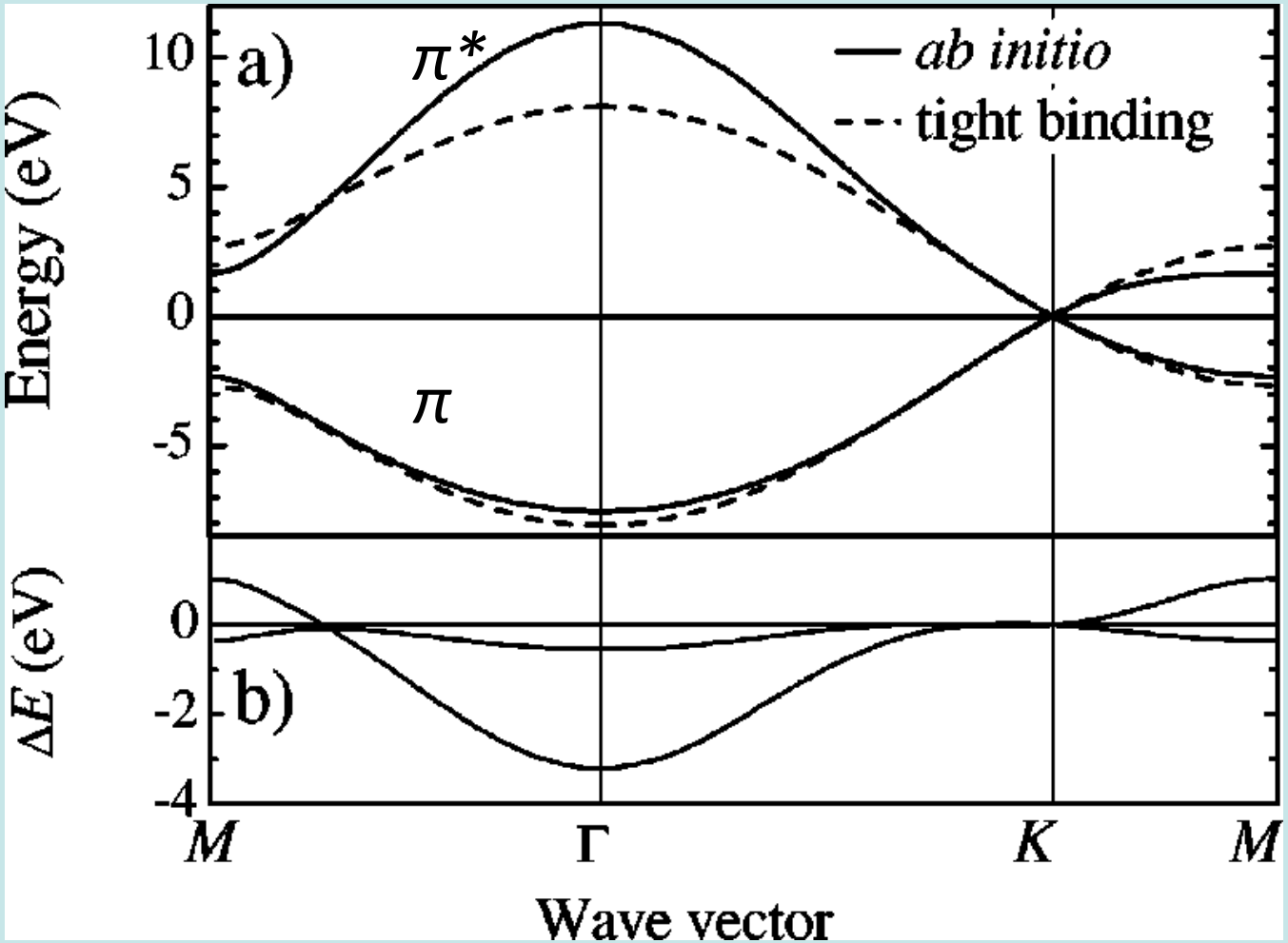
or

zero-bandgap semiconductor:

- no bandgap at E_F
- conduction bands touch at E_F

Yotsarayuth Seekaew, et al.,Carbon-Based Nanofillers and Their Rubber Nanocomposites, 2019

Electron-hole symmetry



- π* and π branches have similar structure
- within restricted range (around E_F): mirror images of each other
- valid approximation for most practical considerations

Reich, S. et al. (2002). Phys. Rev. B. 66. 10.1103/PhysRevB.66.035412.

Low energy approximation

e-h symmetry leads to emergence of identical equilibrium properties:

- density of states
- group velocity
- carrier density

$$g(E) = \frac{2}{\pi}\left|k\frac{dk}{dE}\right| = \frac{2}{\pi}\left|k\left(\frac{dE}{dk}\right)^{-1}\right|$$

$$E(k)^{\pm} = \pm\gamma\sqrt{1 + 4\cos\frac{\sqrt{3}a}{2}k_x\cos\frac{a}{2}k_y + 4\cos^2\frac{a}{2}k_y}$$

- γ – transfer integral corresponding to e hopping between neighbouring atoms
- difficult to determine analytically
- γ often used as a fitting parameter for ab-initio computations and experiments
- proportional to Fermi (group) velocity ($v_F \approx \frac{10^6 m}{s} = \frac{c}{300}$)
- commonly used values: $\gamma \sim 2.7 - 3.3\ eV$

Relativistic effects

Switching the origin to K

- all interesting phenomena occur near E_F – at K points
- charging coordinates origin to K we get:

$$E(\boldsymbol{k})^{\pm}_{linear} = \pm\hbar v_F|\boldsymbol{k}| = \pm\hbar v_F\sqrt{k_x^2 k_y^2} = \pm\hbar v_F k$$

- giving a linear dispersion relationship with v_F as the gradient

Consequences:

- linear dispersion = **massless particles** (zero effective rest mass)
- need to work with Dirac's relativistic QM wave equation
- the 6 K points are called **Dirac points**

Einstein energy-momentum relation

$$E^2 = (pc)^2 + (m_0c^2)^2$$

Einstein energy-momentum relation:
E – energy
p – momentum
c – speed of light
m_0 – rest mass of the particle

for $E \propto \boldsymbol{p}$ (or $\boldsymbol{k}$):

- particle behaves as if it was massless
- charge carriers become ‘massless Dirac electrons’ for k near K
- mobility reaches 100 000 cm^2/Vs

Dirac cones

- all interesting phenomena occur near E_F – at K points
- charging coordinates origin to K we get:

$$E(\boldsymbol{k})^{\pm}_{linear} = \pm\hbar v_F|\boldsymbol{k}| = \pm\hbar v_F\sqrt{k_x^2 k_y^2} = \pm\hbar v_F k$$

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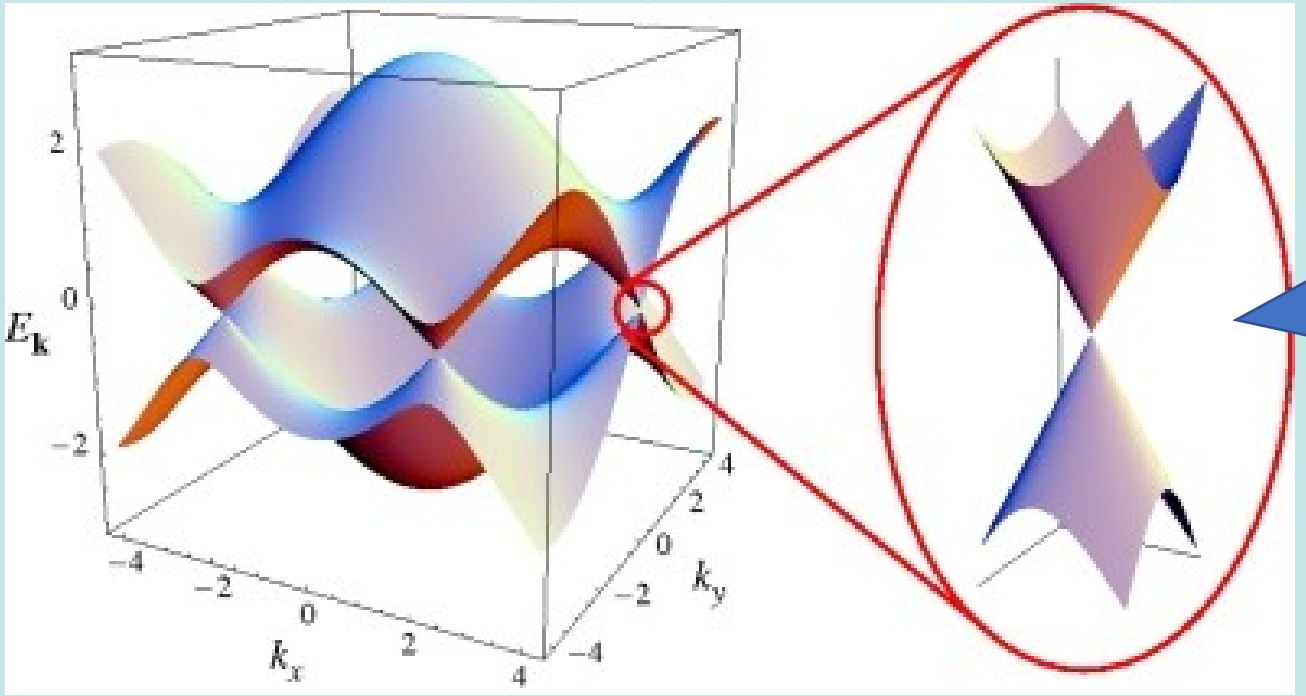


Dirac cone:

- 'hollow' – states inside not allowed
- experimentally confirmed up to $\pm$ 0.6 eV

Density of states

From NNTB solution:

$$g(E) = \frac{2}{\pi}\left|k\frac{dk}{dE}\right| = \frac{2}{\pi}\left|k\left(\frac{dE}{dk}\right)^{-1}\right|$$

where g(E) is normalised to the area of the lattice

Substituting simplified E(k) we obtain:

$$g(E) = \frac{2}{\pi(\hbar v_F)^2}|E| = \beta_g|E|$$

where:

- $\beta_g \approx 1.5 \times 10^{14} eV^{-2} cm^{-2}$ (material constant)
- |E| necessary to account for =ve and –ve energy (e or holes)

$g(E_F)=0$!

Carrier densities

Carrier density: no. of states that are occupied per unit area at a given temperature:

$$n = \int_0^{E_{max}} g(E) f(E_F) dE = \frac{2}{\pi \hbar^2 v_F^2} \int_0^{E_{max}} \frac{E}{1 + e^{(E - E_F)/k_B T}} dE$$

Fermi-Dirac distribution

$$\boldsymbol{n = \frac{2}{\pi} \left(\frac{k_B T}{\hbar v_F} \right)^2 F_1(E_F / k_B T)}$$

E_{max} - the maximum energy in the energy band
$f(E_F)$ – Fermi-Dirac distribution
F_1 – Fermi-Dirac integral of order one

Intrinsic carrier densities

when no doping present:

- E_F is at 0 eV and
- E_F is independent of temperature
- $\rightarrow F_1 = \frac{\pi^2}{12}$

$$\boldsymbol{n_i = p_i = \frac{\pi}{6}\left(\frac{k_B T}{\hbar v_F}\right)^2 \approx 9 \times 10^5 T^2 \text{ cm}^{-2}}$$

at room temperature: $n \approx 8 \times 10^{10} cm^{-2}$

- alteration of carrier concentration leads to change of v_F (deviations from linearity for large shifts in E_F)
- best way to engineer v_F (only small changes, e.g. by changing dielectric constant of the substrate)

Extrinsic carrier densities

when graphene is doped with impurities:

- in the limit $\frac{E_F}{k_B T} \to \infty$

$$\boldsymbol{n \cong \frac{\lambda}{\pi}\left(\frac{E_F}{\hbar v_F}\right)^2}$$

where λ – fitting parameter:

- λ=1.1 gives less than 10% error for $\frac{E_F}{k_B T}$>4
- λ=1 gives less than 5% error for $\frac{E_F}{k_B T}$>8

for holes:

- equivalent structure to n

$$\boldsymbol{p = \frac{2}{\pi}\left(\frac{k_B T}{\hbar v_F}\right)^2 F_1(-E_F)/k_B T}$$

Doping methods

1. Oxidative doping
   - by a nearby species
   - easiest to control

2. Substitutional doping
   - by replacing carbon with another element
   - requires controlled breaking of covalent bonds
   - difficult to control potential side reactions (e.g. with substrate or residual gases)

3. Electrical doping
   - by application of an electric field (‘electrostatic gating’)
   - shifts E_F away from the Dirac point

Optical properties of graphene

Interband absorption

optical sheet conductivity (from NNTB model):

$$\boldsymbol{\sigma(\omega) = \frac{\pi e^2}{2h}}$$

corresponds to absorption:

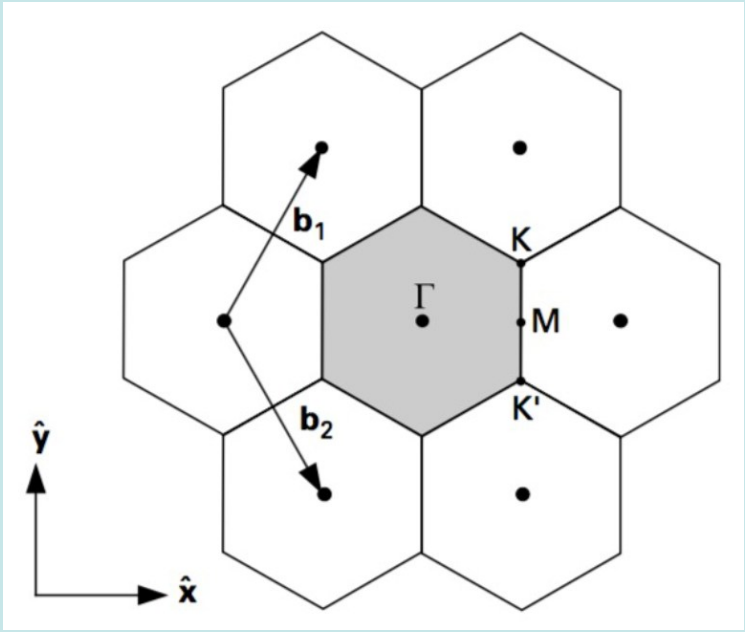
$$\mathbf{A(\omega) = \frac{4\pi}{c}\sigma(\omega) = \pi\alpha \approx 2.29\%}$$

with Fine structure constant: $\alpha = \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c}$

-> absorption independent of frequency!

-> no. of layers can be calculated from the measured transmission/absorption!

Recap of lecture 5

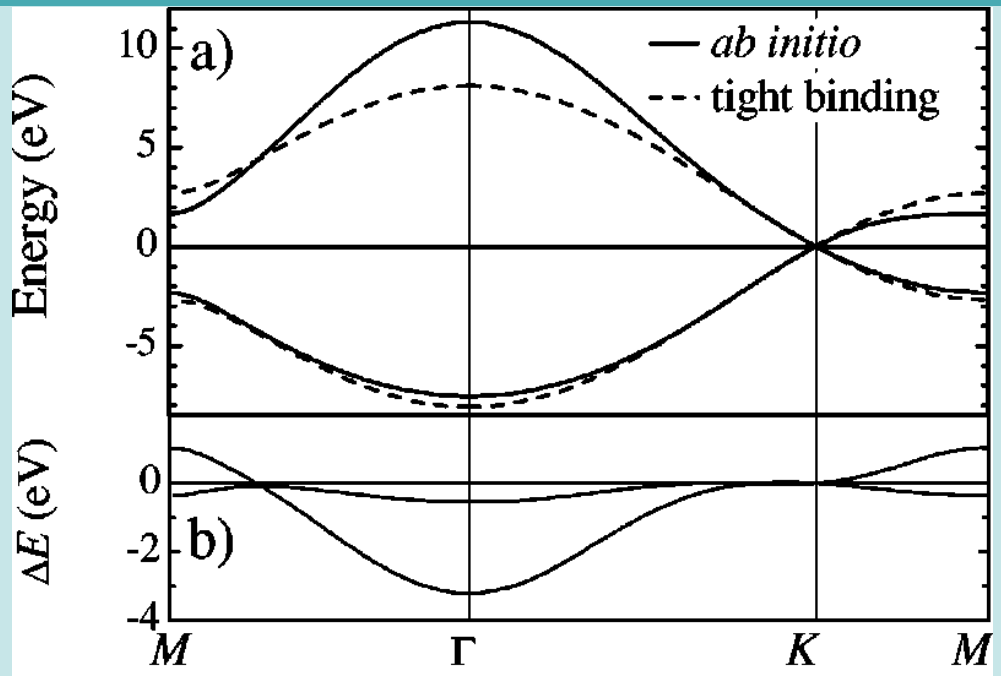


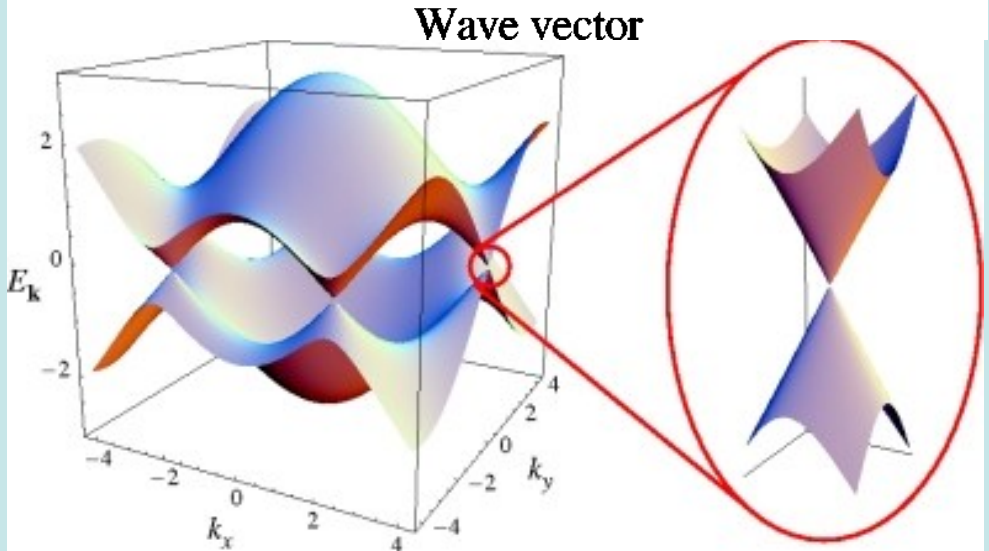
$$\boldsymbol{b_1 = 2\pi \frac{Ra_2}{a_1 \cdot Ra_2}}$$

$$\boldsymbol{b_2 = 2\pi \frac{Ra_1}{a_2 \cdot Ra_1}}$$

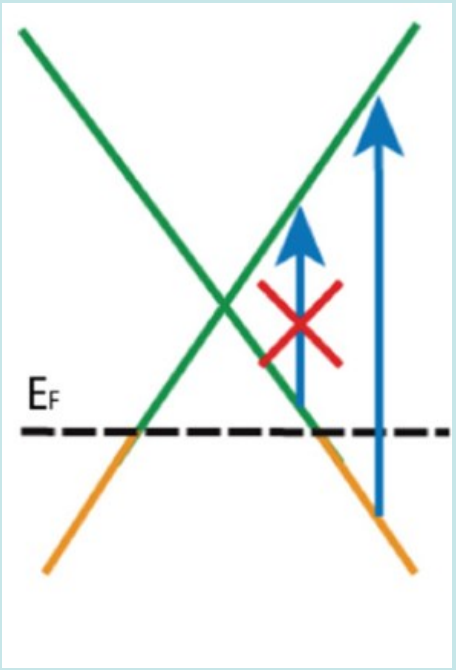
$$\boldsymbol{n_i = p_i = \frac{\pi}{6}\left(\frac{k_B T}{\hbar v_F}\right)^2 \approx 9 \times 10^5 T^2 \text{ cm}^{-2}}$$

$$\boldsymbol{n \cong \frac{\lambda}{\pi}\left(\frac{E_F}{\hbar v_F}\right)^2}$$





$$\boldsymbol{\sigma(\omega) = \frac{\pi e^2}{2h}}$$

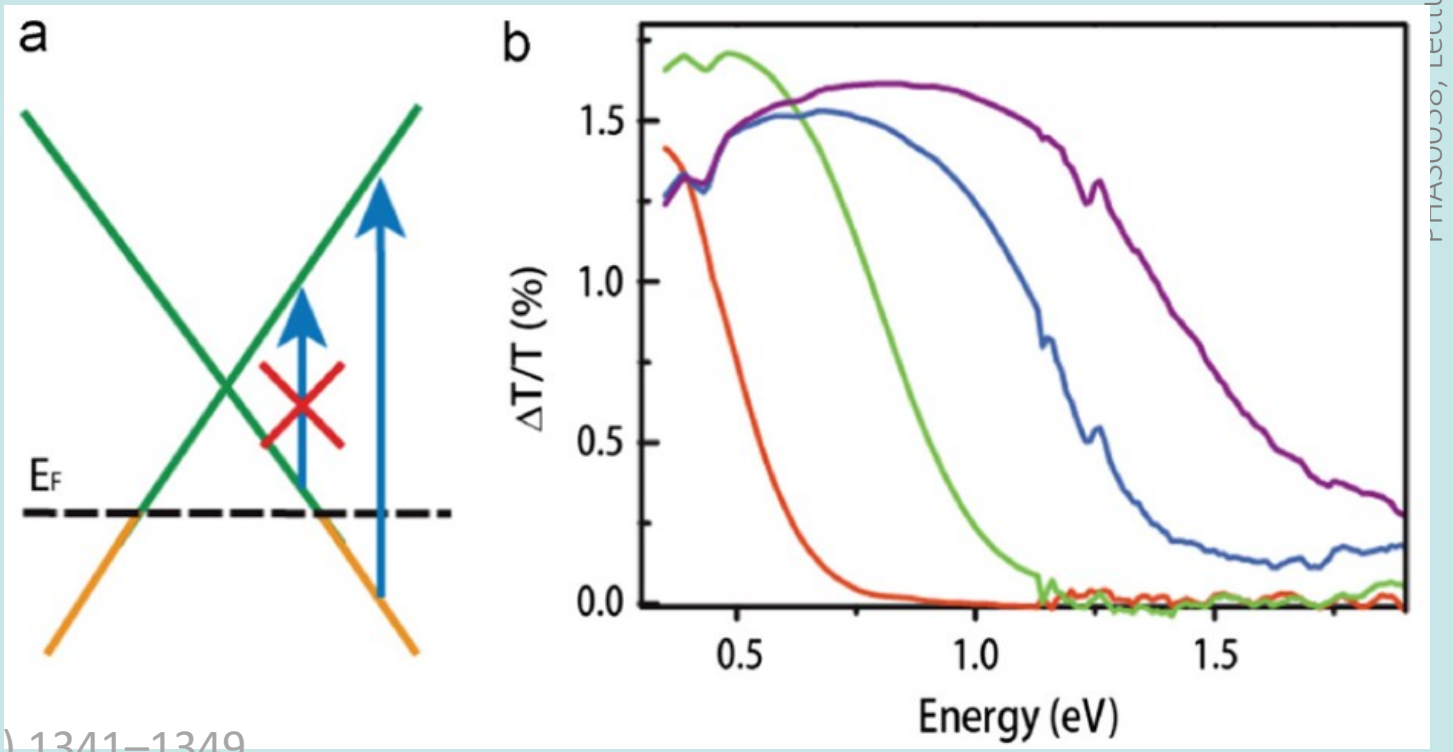


Pauli blocking

Pauli blocking: strong change in the interband absorption due to shift of E_F (**electrical doping or hole-doping)**

$$\sigma(\omega) = \frac{\pi e^2}{4h}\left[\tanh\frac{\hbar\omega + 2E_F}{4k_BT} + \tanh\frac{\hbar\omega - 2E_F}{4k_BT}\right]$$

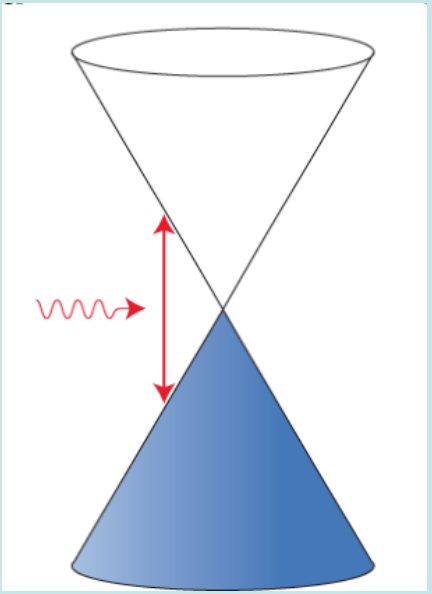
- interband transitions for photon energies below $2|E_F|$ are suppressed
- energies above $2|E_F|$ unaffected
- allows easy measurement of E_F



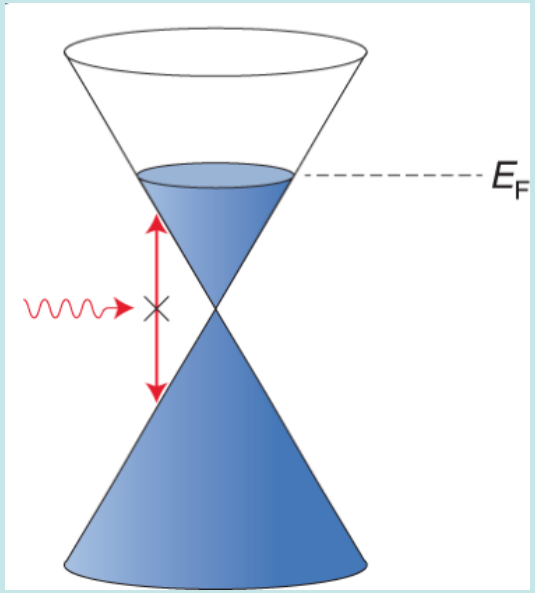
K.F. Mak et al. / Solid State Communications 152 (2012) 1341–1349

Recap on Fermi level

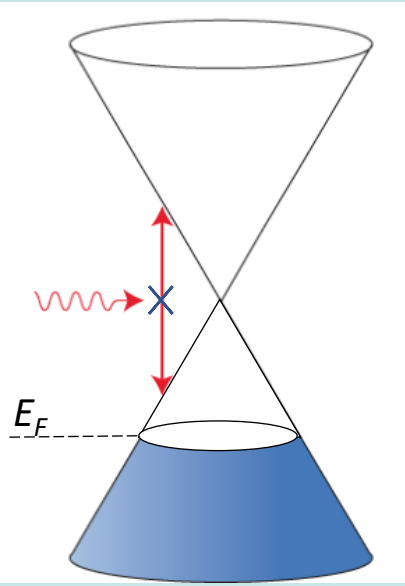
Fermi level: energy below which the one-electron levels are occupied and above which they are unoccupied (in semiconductors a synonym of chemical potential)



no doping

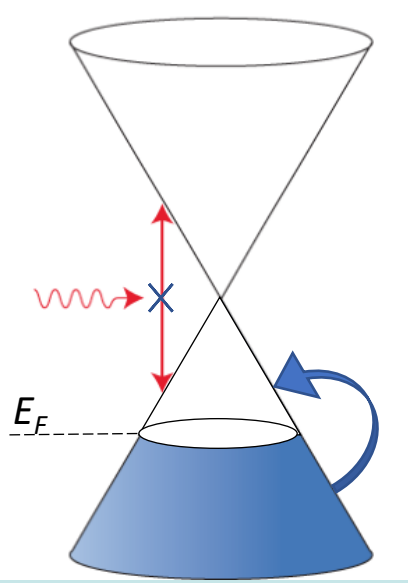


electrons doping



holes doping

Intraband transitions



- direct absorption not allowed (momentum not conserved)
- extra scattering with phonons or defects necessary
- Drude model:

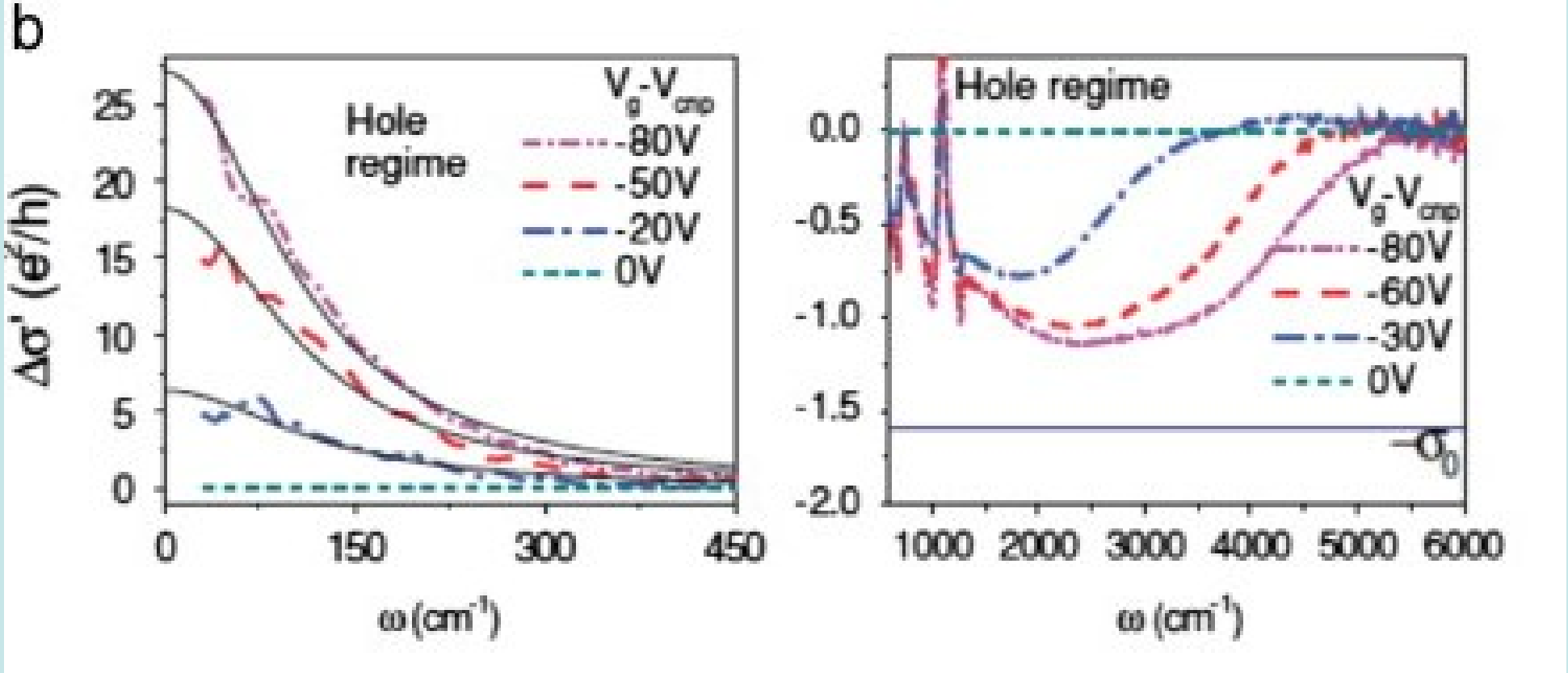
$$\sigma(\omega) = \frac{\sigma_0}{1 + i\omega\tau}$$

$$A(\omega) = \frac{4\pi}{c} Re\,[\sigma(\omega)]$$

- σ_0 - DC conductivity
- τ – electron scattering time
- ω – frequency of light
- A – optical absorbance at normal incidence

F. Wang and S. Shi, " OpGcal ProperGes of Graphene“, doi.org/10.1017/9781316681619.04

Intraband transitions – experimental proof

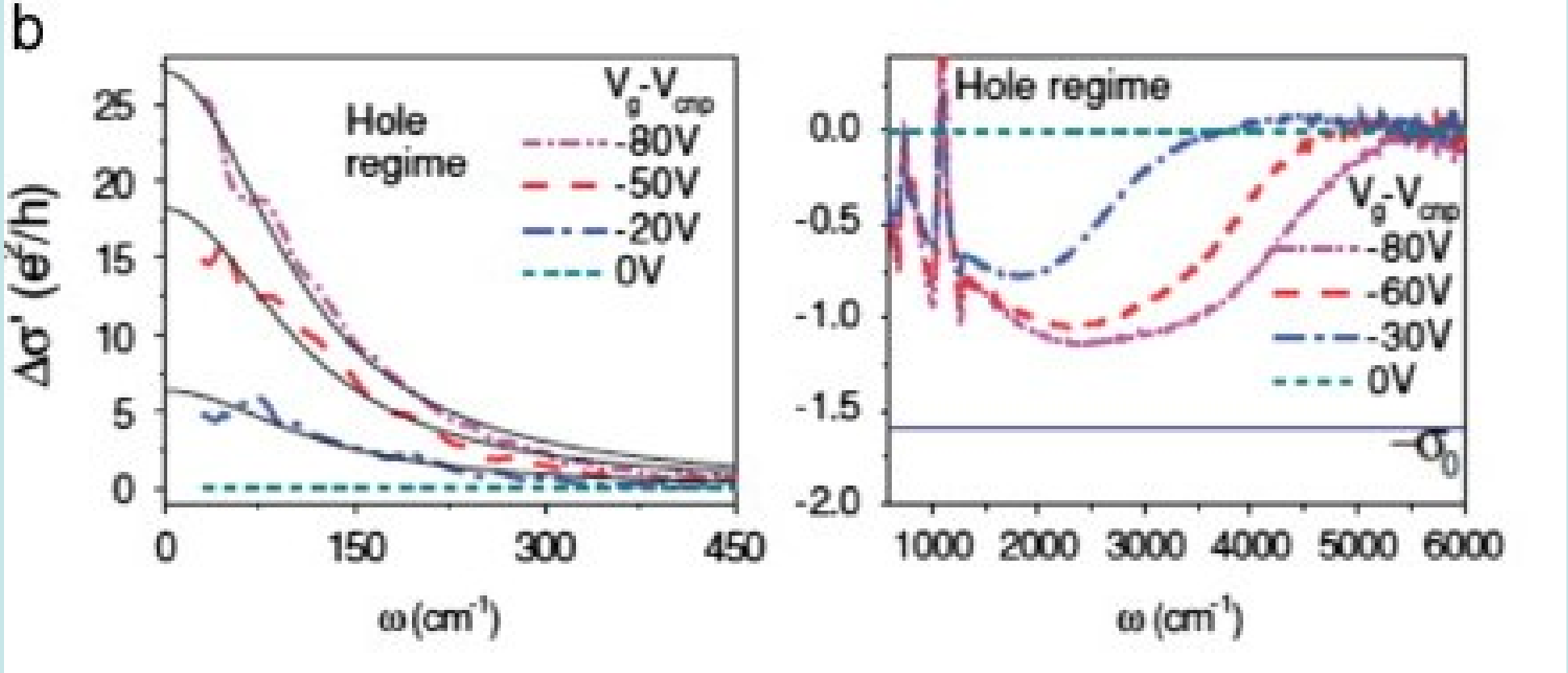


- electrostatic doping induces changes in IR conductivity
- CVD sample

$$\sigma(\omega) = \frac{\sigma_0}{1 + i\omega\tau}$$

F. K.F. Mak et al. / Solid State Communications 152 (2012) 1341–1349

Determining E_F from a spectrum



- electrostatic doping induces changes in IR conductivity
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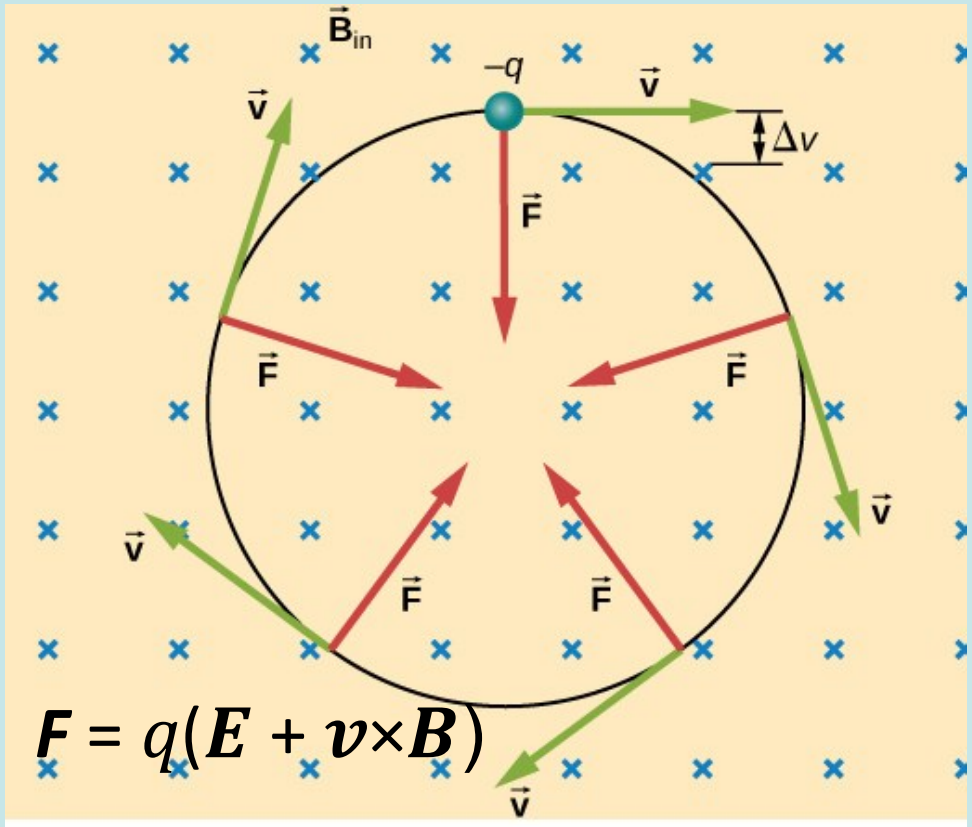
$$\sigma(\omega) = \frac{\sigma_0}{1 + i\omega\tau}$$

F. K.F. Mak et al. / Solid State Communications 152 (2012) 1341–1349

Quantum Hall effect in graphene

Landau quantisation

Landau quantisation: quantisation of cyclotron orbits of charged particles in magnetic fields



Lorentz force + 2D confinement

⬇

Landau quantisation

⬇

Landau levels

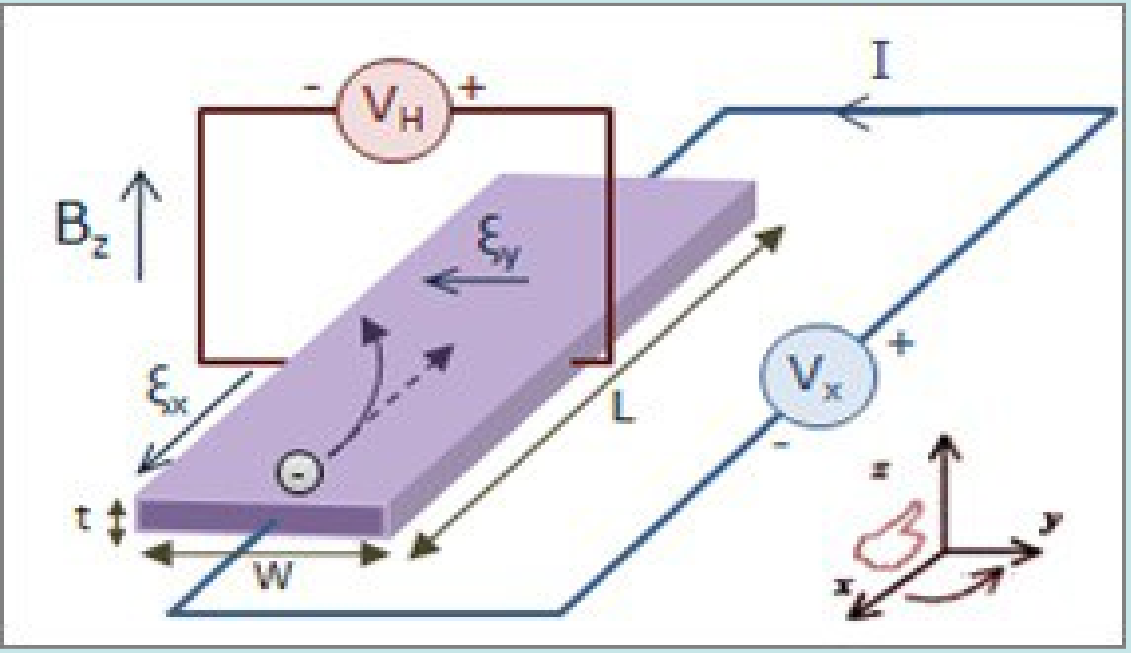
Landau levels

Landau levels: discrete energy values of allowed cyclotron orbits; each set of wave functions with the same *n*

$$\Psi(x,y) = e^{ik_y y}\phi_n(x - x_0)$$

- energy levels of harmonic oscillator
- observable at low T and strong B ($kT \ll \hbar\omega_c$)
- degenerate due to cyclic boundaries, i.e. $k_y = \frac{2\pi N}{L_y}$ where $0 \leq \mathrm{N} \leq \frac{\mathrm{m}\omega_c L_x L_y}{2\pi\hbar}$
- subject to boundary conditions for small size (L)

Hall effect in 3D and 2D materials



- production of voltage difference across electrical conductor, perpendicular to an electric current in the conductor and to the applied magnetic field (perpendicular to the current)
- due to Lorentz force
- now “ordinary Hall effect”

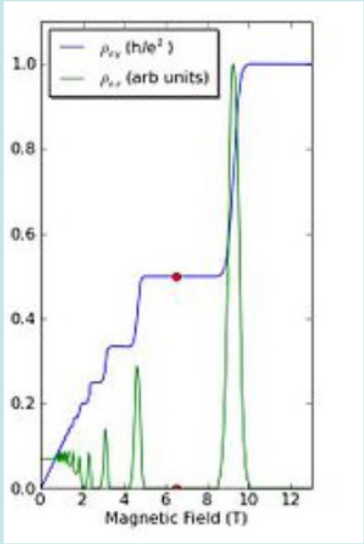
$$V_{H3D} = \frac{I_x B_z}{etn_V}$$

for 2D t->0

$$V_{H2D} = \frac{I_x B_z}{en_A}$$

Quantum Hall Effect (QHE)

$$\sigma = \frac{I_{channel}}{V_{Hall}} = \nu \frac{e^2}{h}$$



- quantisation of conductance
- at low T and strong B
- integer or fractional QHE, depending on the filling factor ν
- each quanta = filling of a Landau level (i.e. once a level is filled resistivity cannot increase)
- energetical 'cost' of occupying next state: ωB
- subtle manifestation of the principle of gauge invariance
- provides extremely precise way of measuring the fine structure constant

Quantum vs. ordinary Hall effect

Ordinary	Quantum
classical physics	quantum-mechanical version
in 3D or 2D (with modification)	observed in 2D electron systems at low T and strong magnetic fields
due to Lorentz force	due to the presence of Landau levels
measured via Hall VOLTAGE	measured via CONDUCTANCE

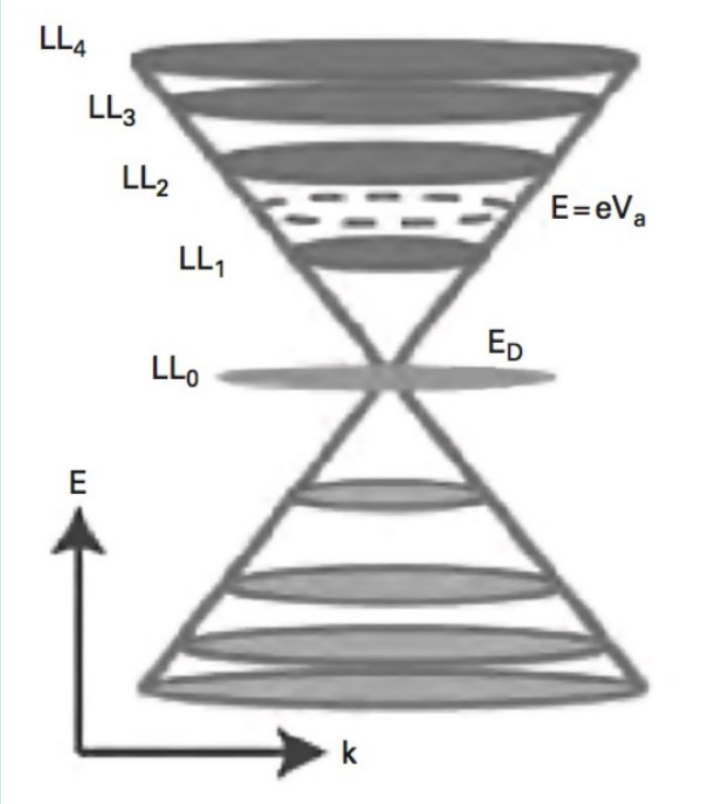
Landau levels in graphene

- Landau levels in traditional 2D materials

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_c = \frac{\left(n + \frac{1}{2}\right)\hbar eB}{m^*}$$

- Landau levels in graphene:

$$E_n = \mathrm{sgn}(n)\sqrt{2e\hbar v_F^2 B|n|}$$

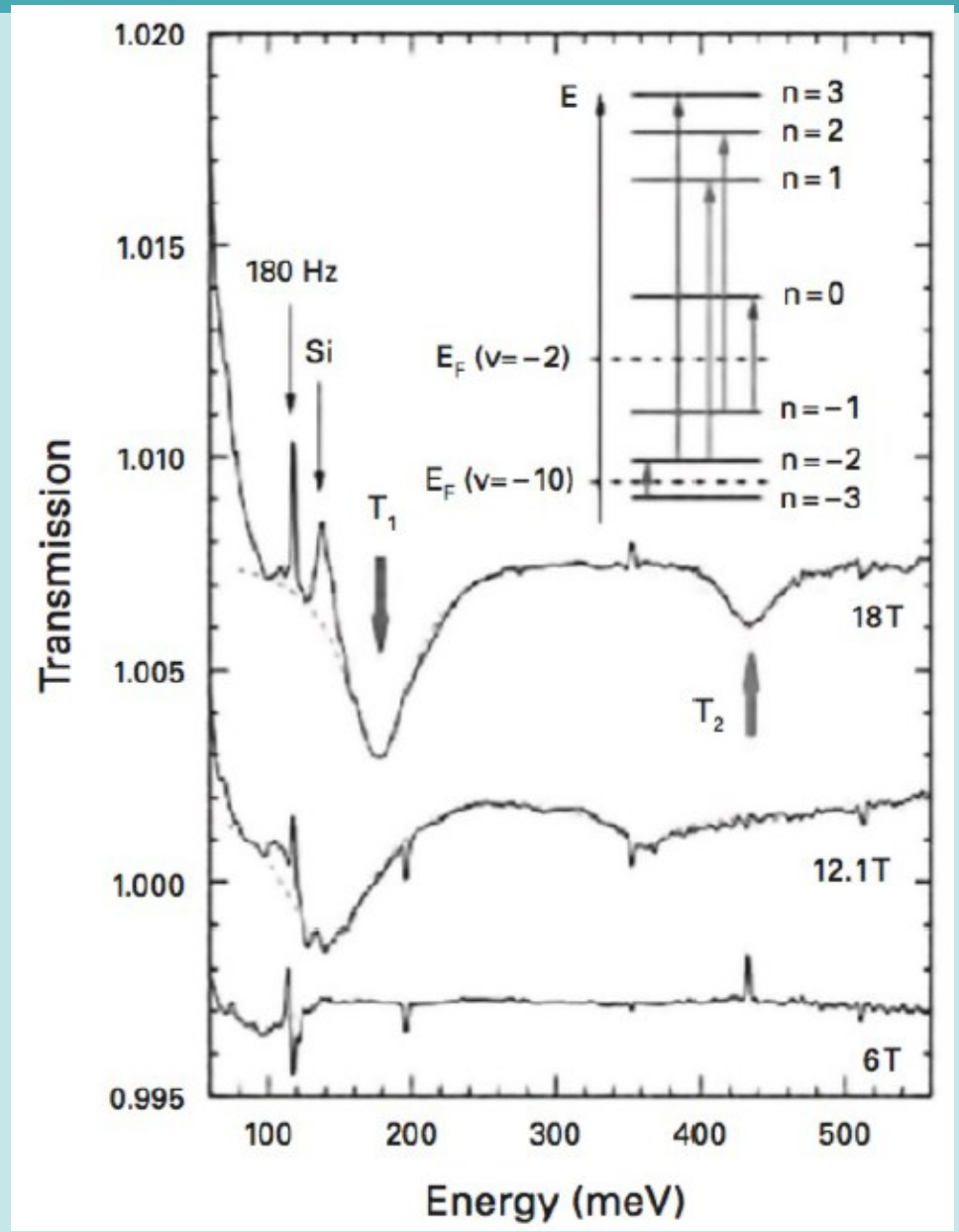


- massless Dirac electrons result in ‘half-integer’ QHE
- unequally spaced Landau levels
- each level 4-fold degenerate
- can be observed with IR spectroscopy

Landau level transitions in graphene

- normalised IR transmission spectra of holes in graphene
- two resonances: T_1 and T_2
- T1 corresponds to intraband Landau level transition n-1 -> n=0
- T2 is a degenerate interband transition:
    - n=-2 -> n=1
    - n=-1 -> n=2

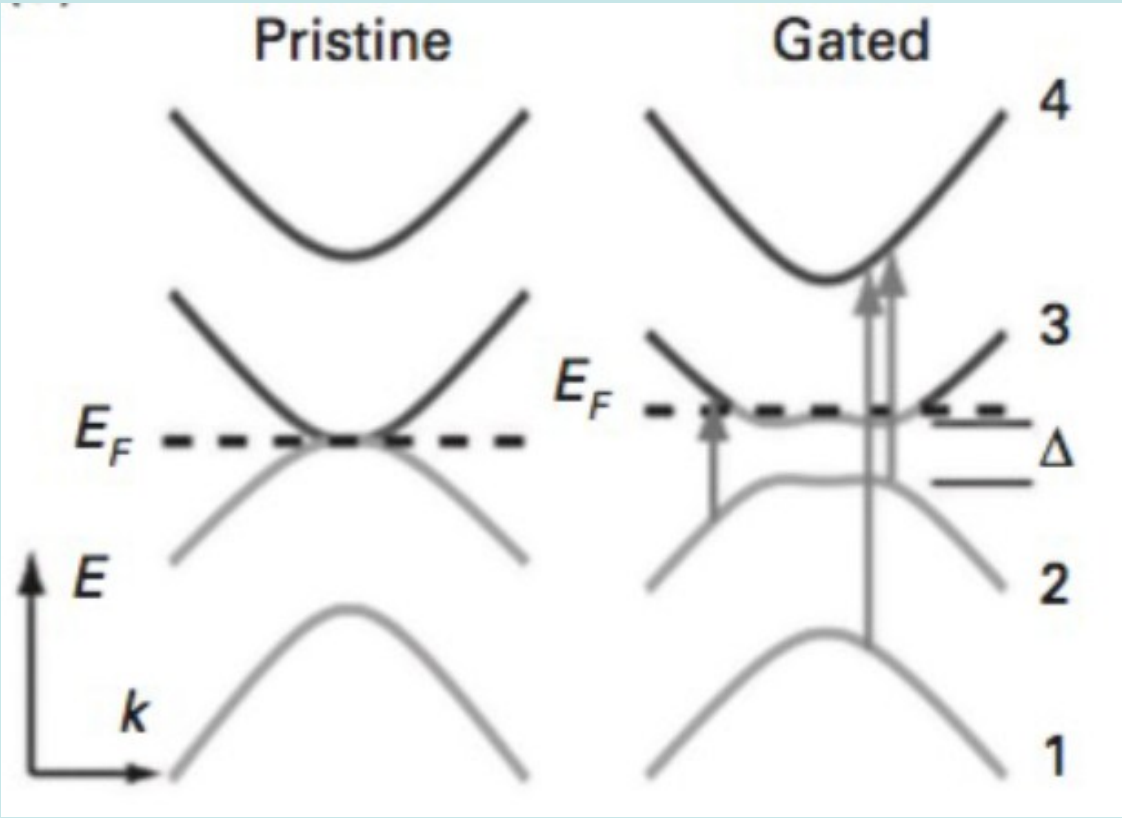
- allowed transitions in inset
- transition energy scales linearly with B (as expected)



Beyond graphene

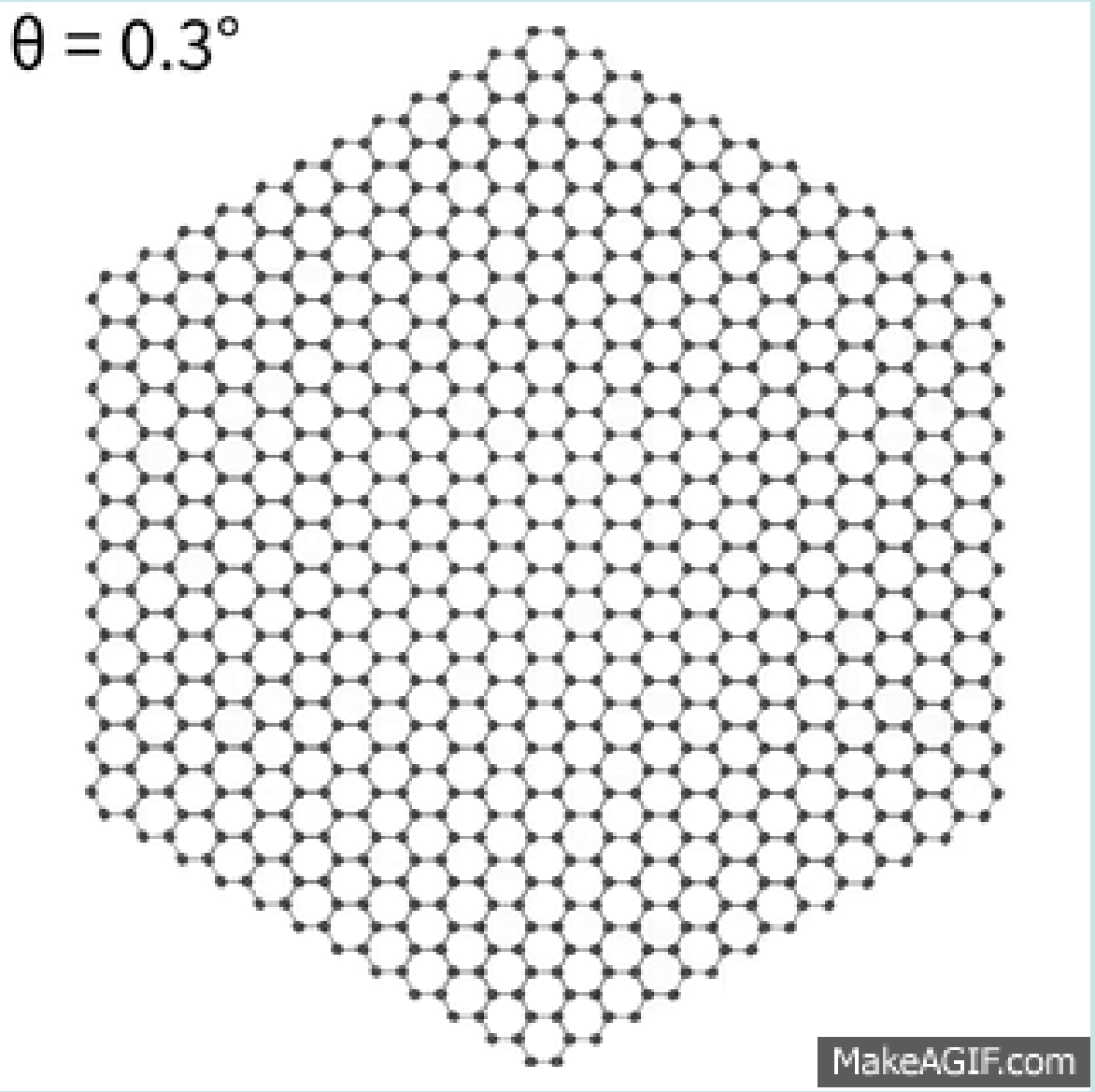
Other 2D materials

Bilayer graphene



- potential for controlling electronic states through interlayer coupling
- strong e-e interactions
- linear dispersion replaced or augmented by pairs of split hyperbolic bands
- new range of phenomena incl. widely tuneable electronic band gaps
- difficult to investigate theoretically
- extends to multi-layer graphene

Twisted heterostructures

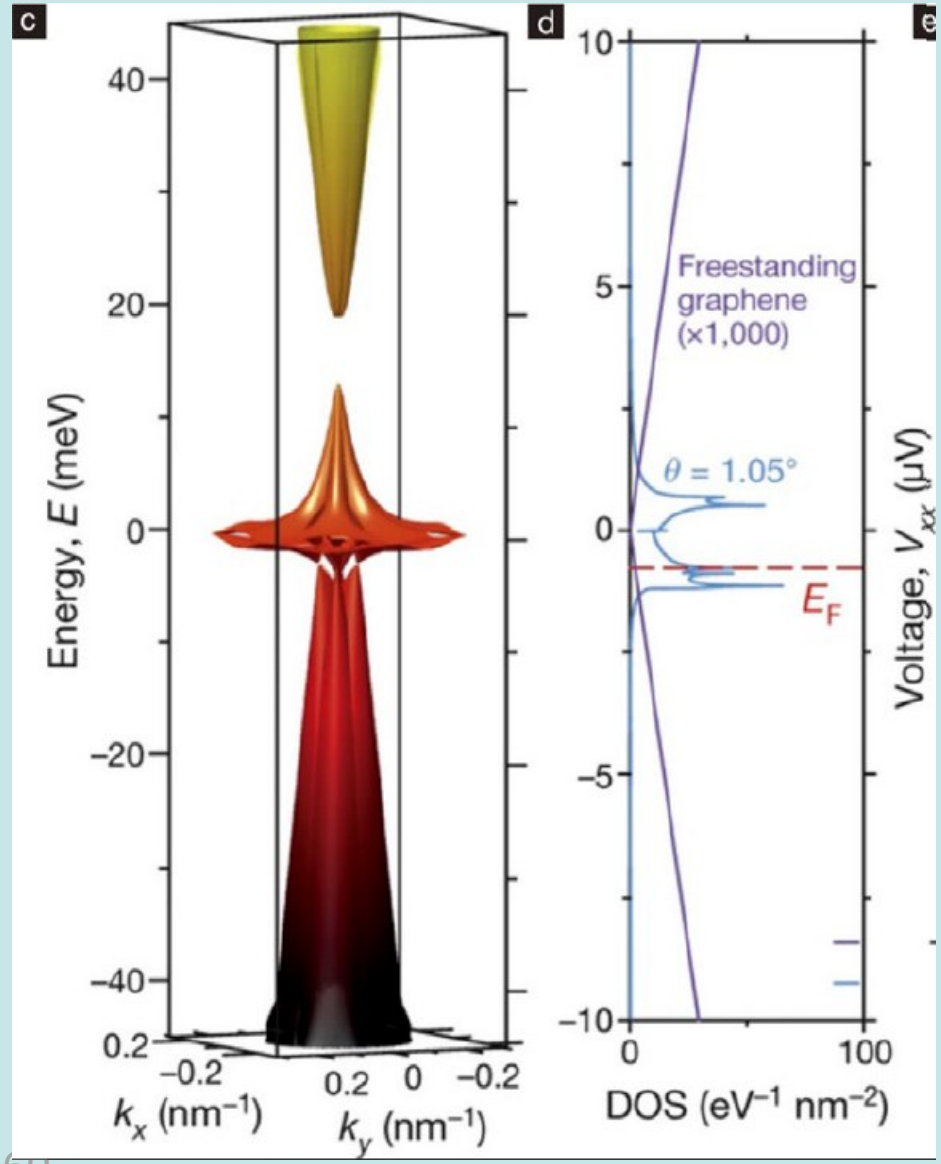


- different moiré patterns
- low-energy structure tunable with the twist angle
- strong coupling at small angles
- Dirac cones displaced in momentum space will hybridize
- van Hove singularity will appear between two Dirac cones

The Physics of Graphene, Mikhail I. Katsnelson, Cambridge University Press, (2020) https://doi-org.libproxy.ucl.ac.uk/10.1017/9781108617567

‘Magic angle’

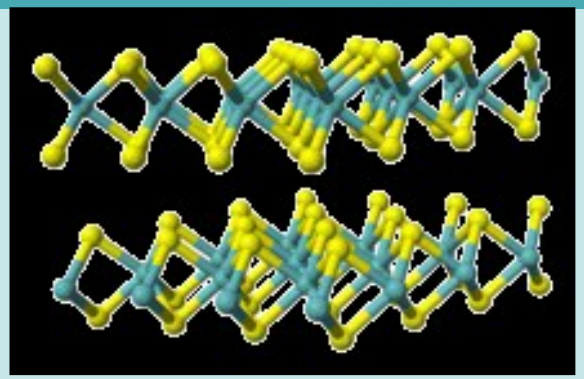
- two graphene layers twisted by 1.05°
- a nearly flat band structure
- superconductivity
- anomalous QHE
- ferromagnetism
- correlated insulating states
- more new physical phenomena being discovered



Y. Cao, et al., Nature 556 (2018) 43–50, https://doi.org/10.1038/nature26160.

Other 2D materials

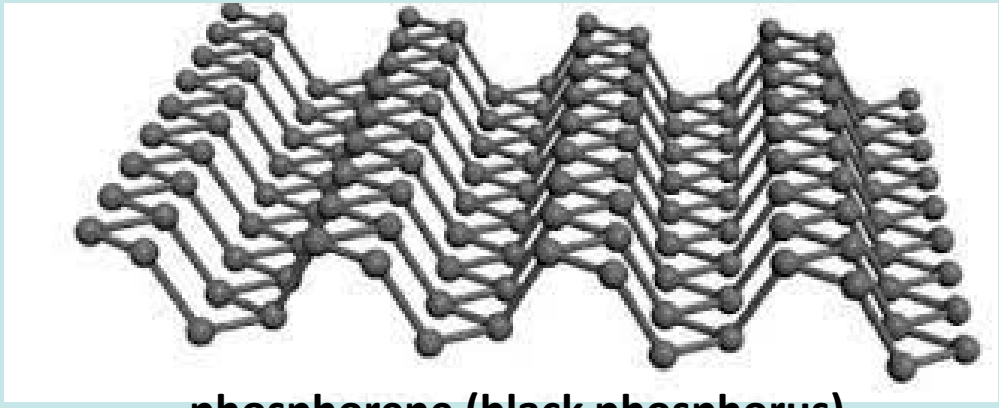
MoS_2



1st generation:
- graphene

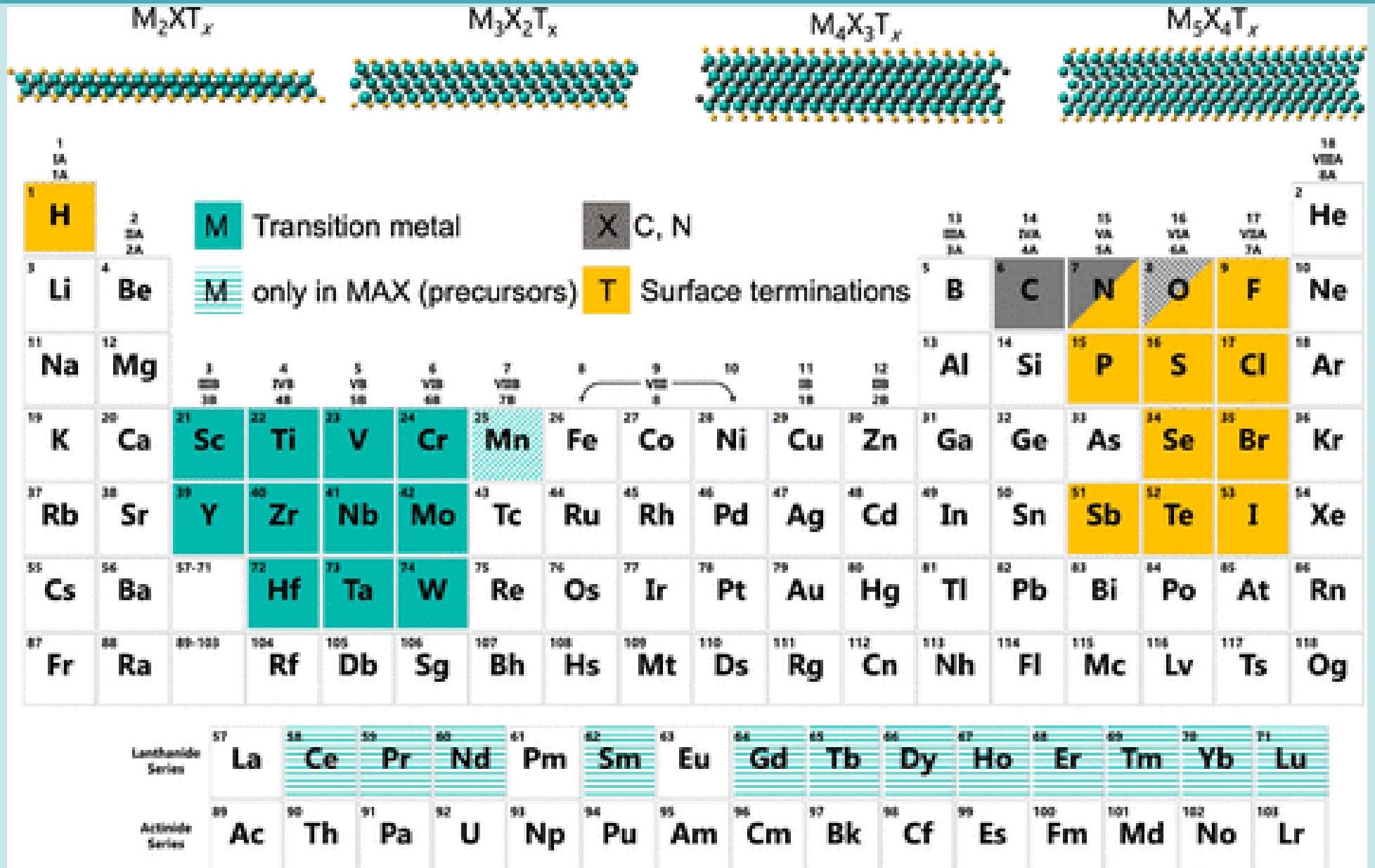
2nd generation:
- replace carbon atoms A with a group III (or II) element and carbon B with group V (or VI) element, e.g. hexagonal BN, BCN, functionalized graphene
- transition-metal chalcogenide materials, e.g. MoS_2, WS_2, $MoSe_2$, WSe_2 (MX2 in general)
  - not precisely in the same plane
  - strong bond in plane, weak between layers

3rd generation:
- silicene, phosphorene, arsenene, germanene, …
- similar conjugation to carbon
- other materials

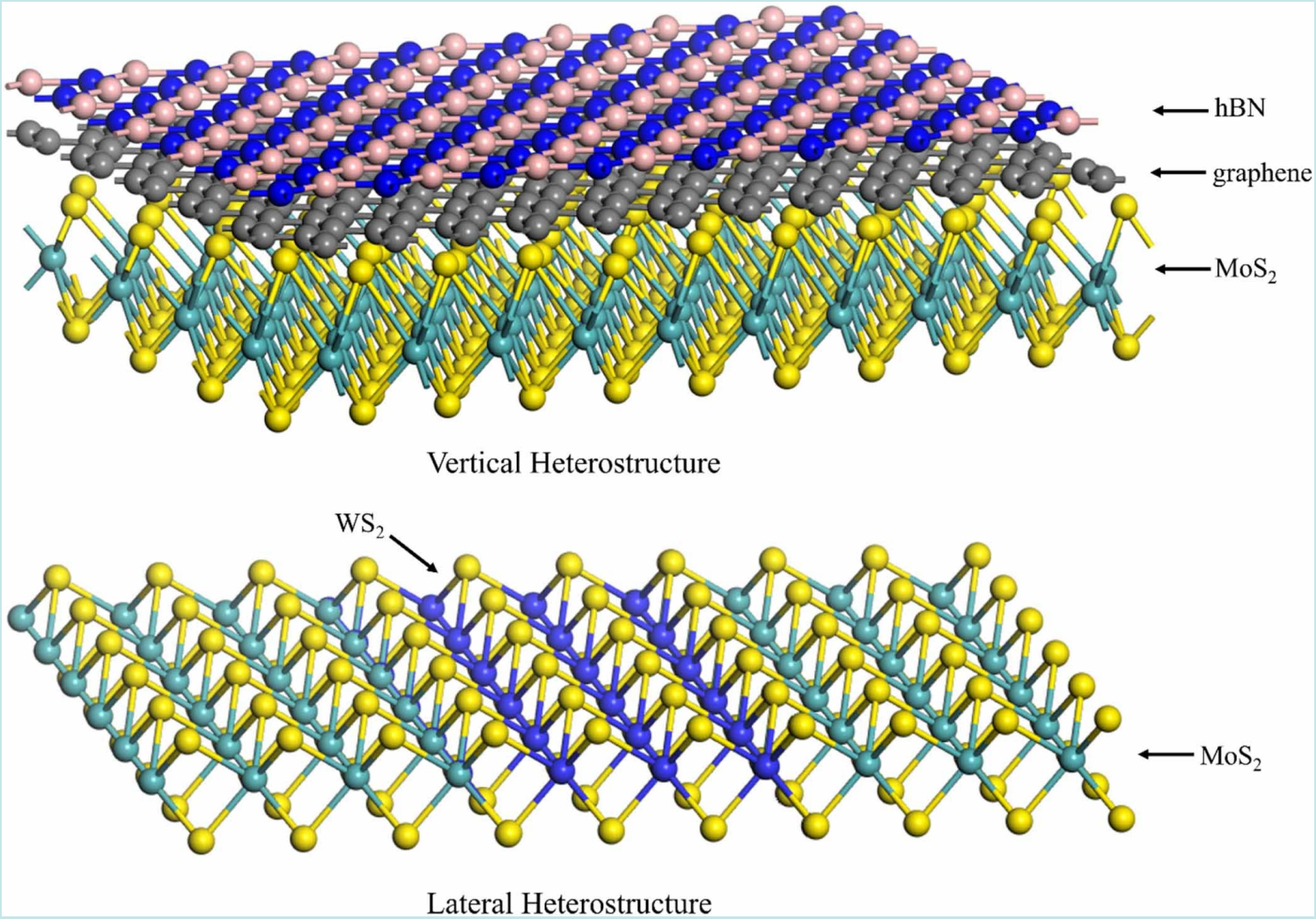


phosphorene (black phosphorus)

MXenes

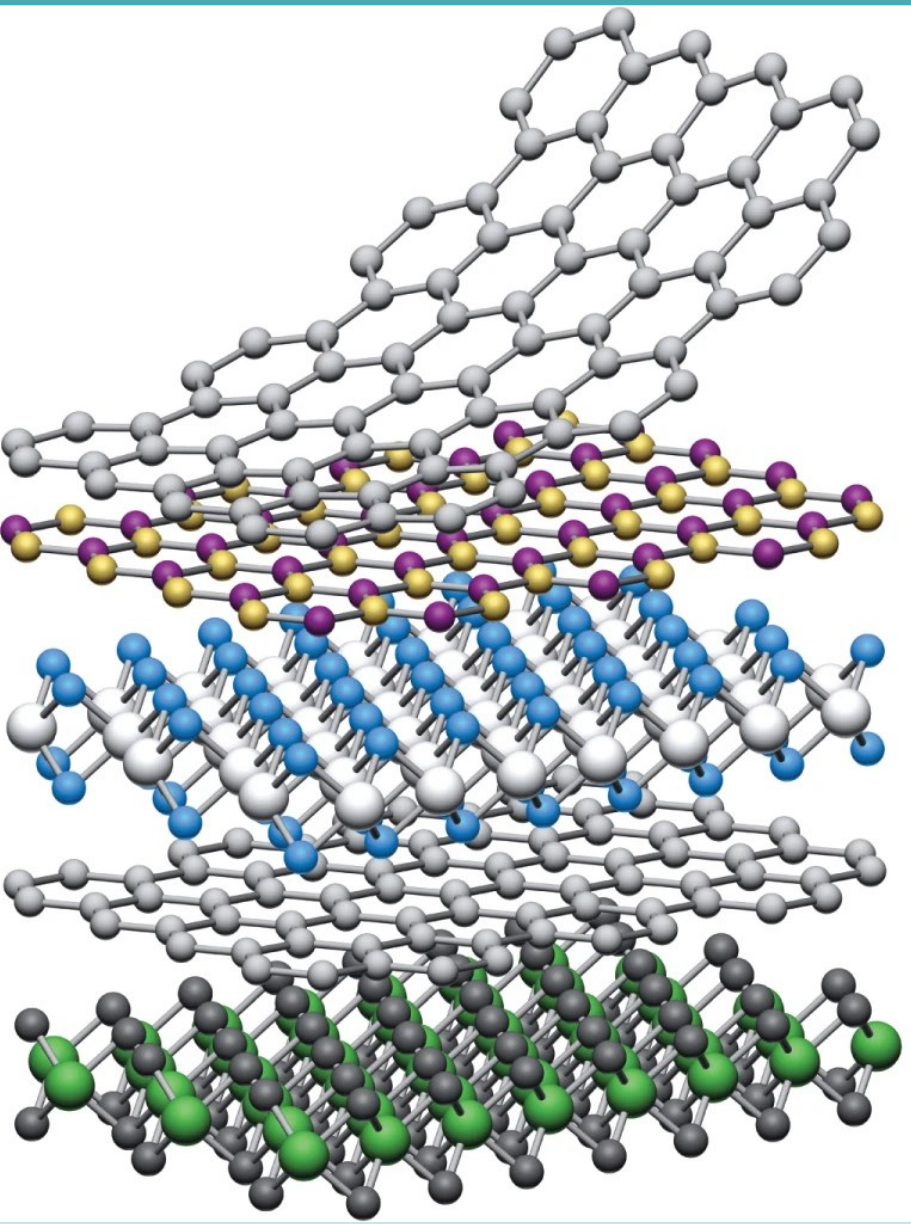

M_2XT_x
$M_3X_2T_x$
$M_4X_3T_x$
$M_5X_4T_x$
M Transition metal
M only in MAX (precursors)
X C, N
T Surface terminations
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Nb
Mo
Tc
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
57-71
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Po
At
Rn
Fr
Ra
89-103
Rf
Db
Sg
Bh
Hs
Mt
Ds
Rg
Cn
Nh
Fl
Mc
Lv
Ts
Og
Lanthanide Series
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Actinide Series
Ac
Th
Pa
U
Np
Pu
Am
Cm
Bk
Cf
Es
Fm
Md
No
Lr

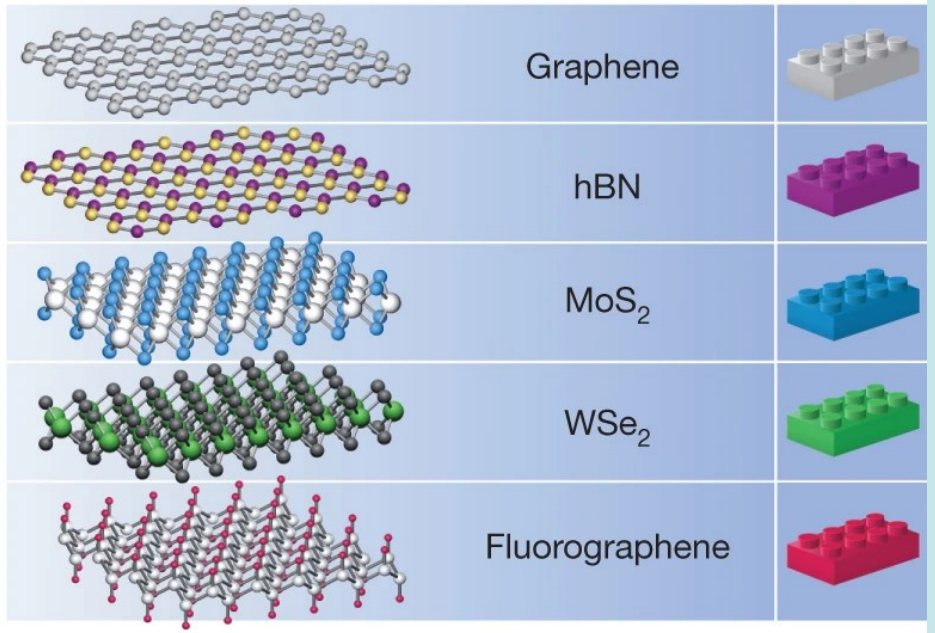
Stacking 2D layers

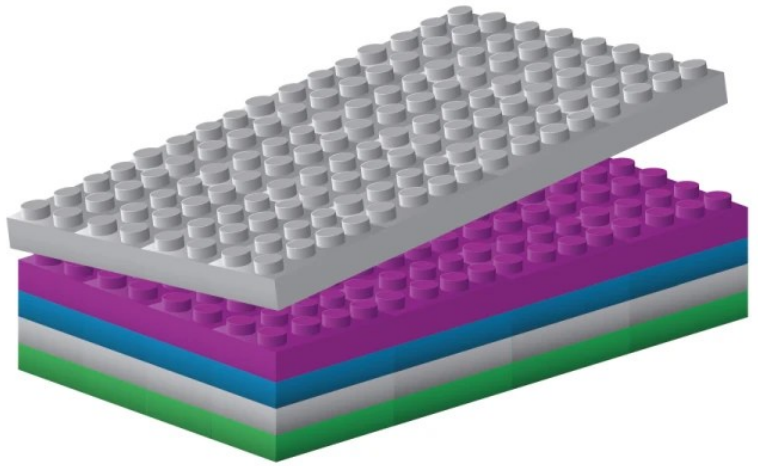


- aka Van der Walls heterostructures
- nowadays choose from >1000 2D materials

Stacking 2D layers





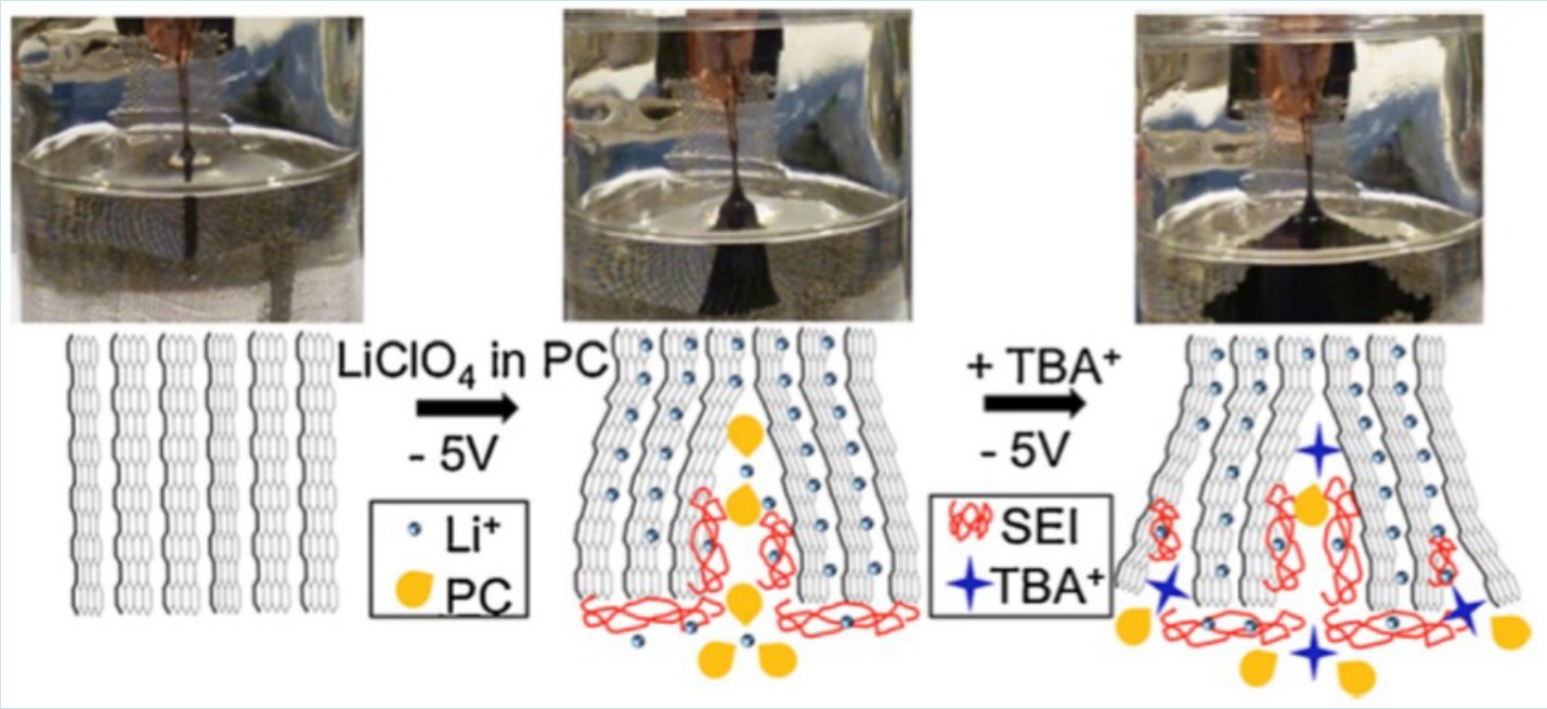


Geim, A., Grigorieva, I. Van der Waals heterostructures. *Nature* **499**, 419–425 (2013). https://doi.org/10.1038/nature12385

Fabrication and applications

Exfoliation

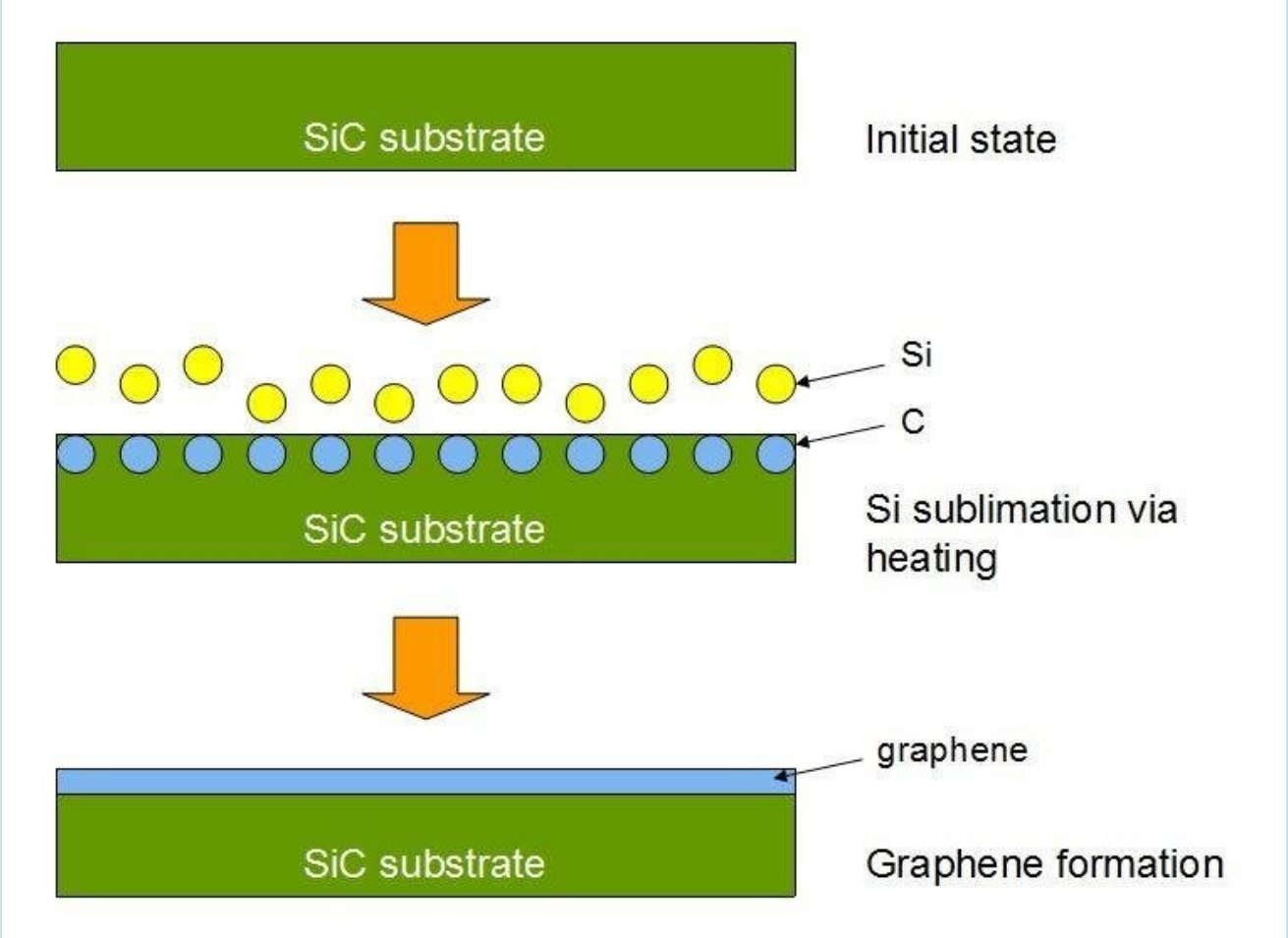
Exfoliation: a range of techniques relying on either chemical or electromechanical separation of graphene sheets using different intercalating species



K. Parvez et al. / Synthetic Metals 210 (2015) 123–132

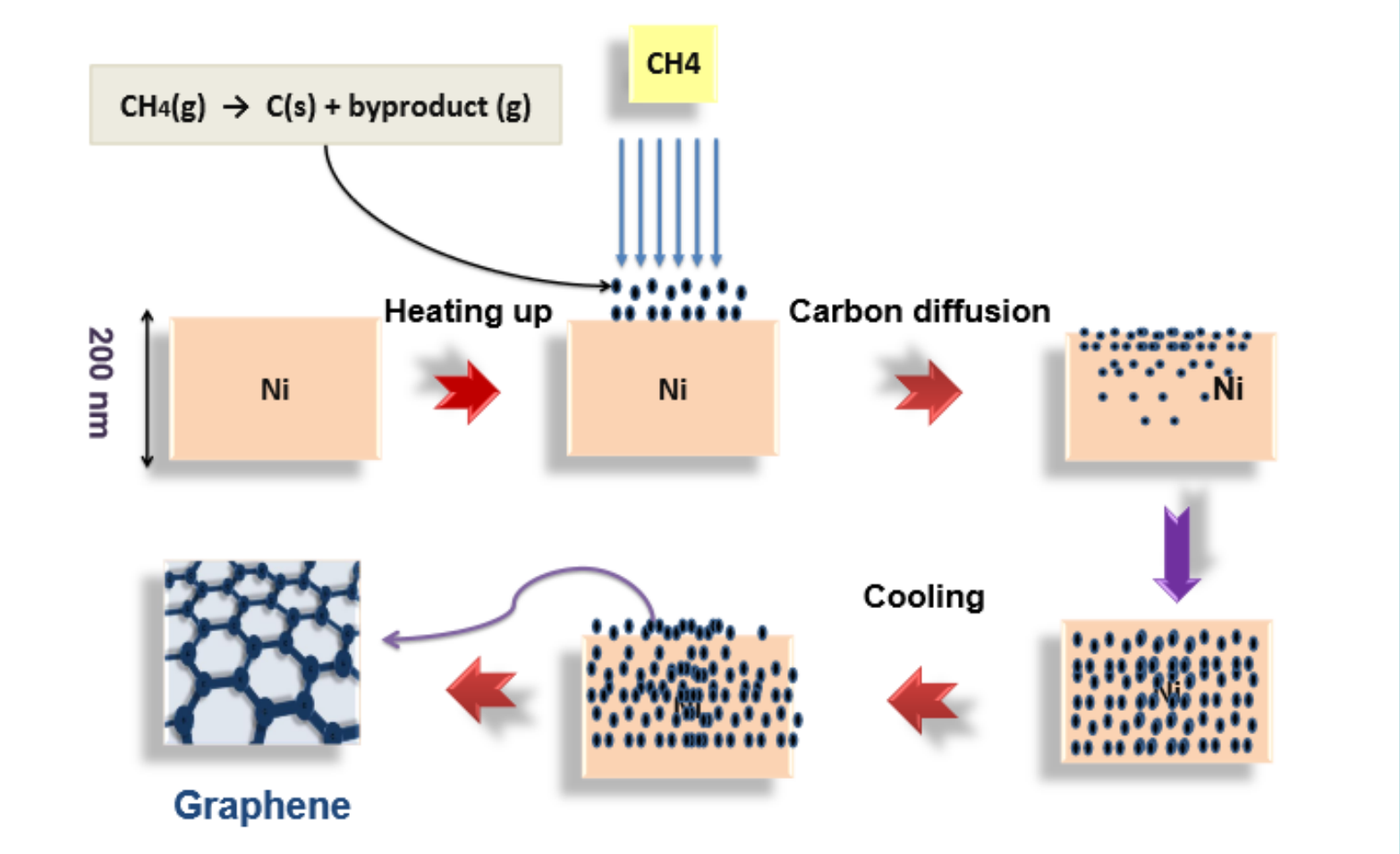
Epitaxial growth

Epitaxy: desorption of atoms from annealed surface (SiC) leading to a formation of graphene



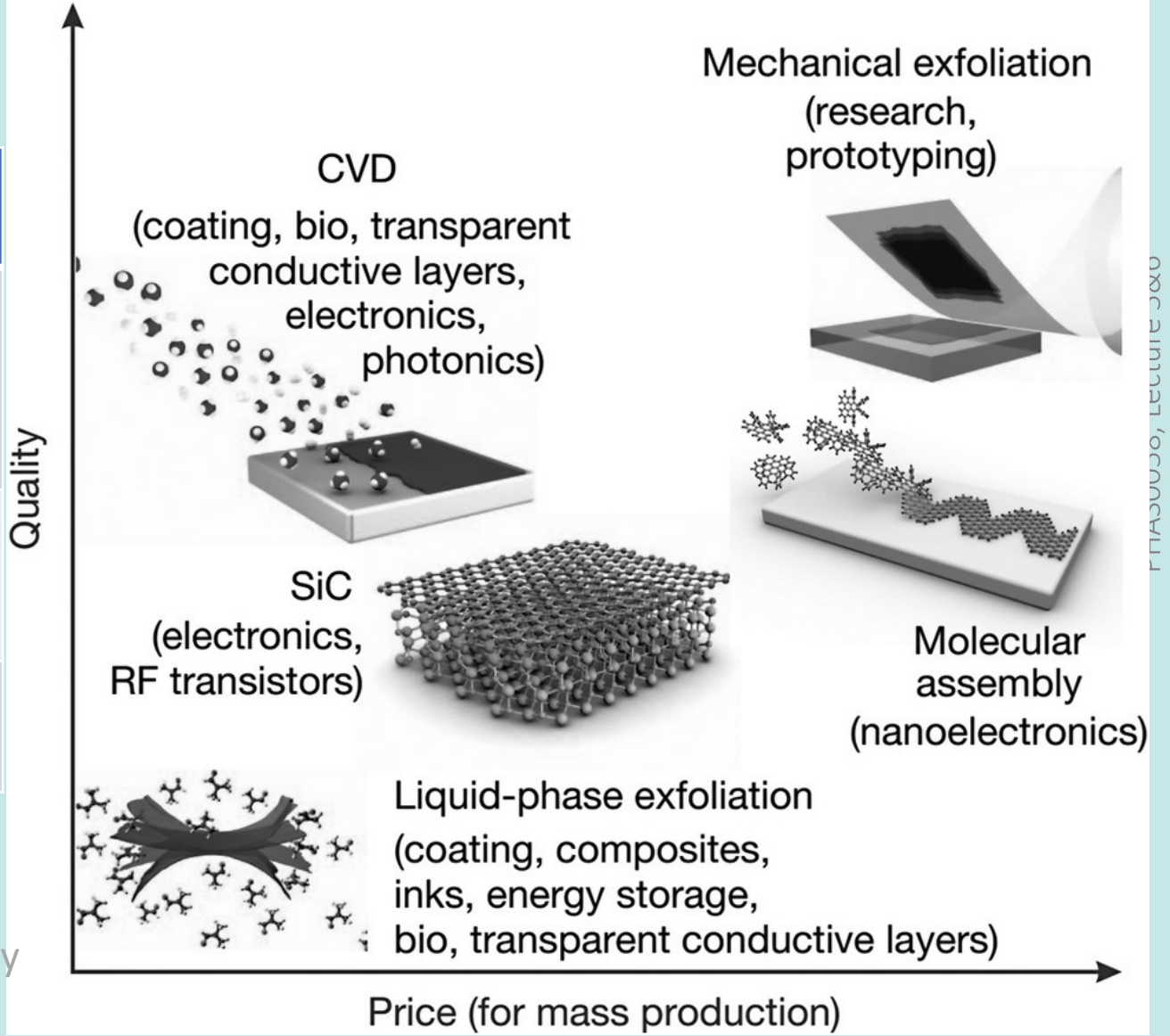
Chemical Vapour Deposition (CVD)

CVD: deposition of a thin film of carbon atoms onto a substrate (Co, Ni or SiO_2) using precursor gases (methane, etc.) and carrier gases (H_2 , Ar, etc.) at high temperatures



Fabrication

method	scale	purity	cost
exfoliation	small	oxides and intercalating species residue	reasonable
CVD	large	depends on growth conditions	relatively low
epitaxial	limited by substrate	high	expensive



Geng, D., & Loh, K. (2017). (pp. 238-256). Cambridge University Press. doi:10.1017/9781316681619.014

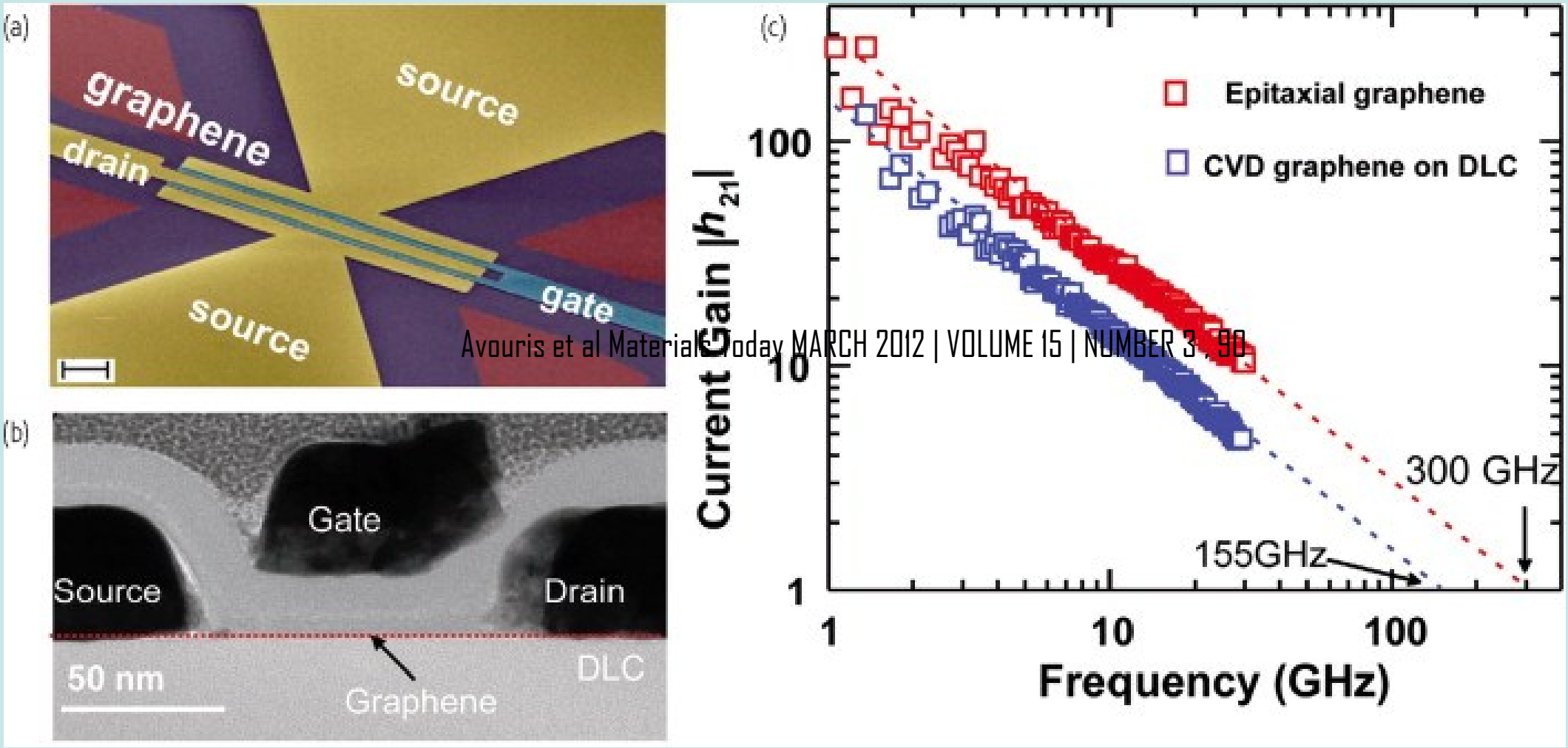
Other applications

Other applications:

- perfect barrier coating
- wideband optical sensors
- membranes for water filtration
- batteries and supercapacitors
- transparent electrodes

Avouris et al Materials Today MARCH 2012 | VOLUME 15 | NUMBER 3 , 90

Graphene FETs



Avouris et al Materials Today MARCH 2012 | VOLUME 15 | NUMBER 3 , 90

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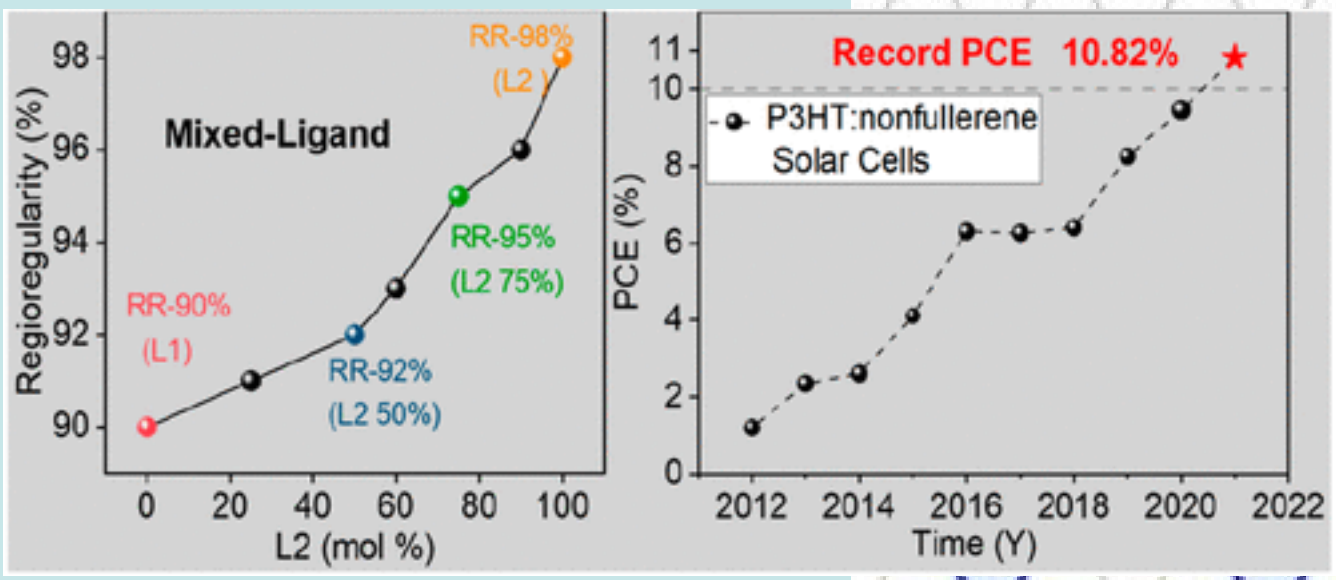
Graphene-OSC matrices



ene and Polypyrrole

Mapping Polymers

This is a useful way to map symmetry groups onto polymer strands that can ultimately determine a number of optical and electronic properties

Polyaniline

Poly(phenylene-vinylene)

Polyfluorine

Liu, Y. et al., Macromolecules 2022, 55, 8, 3078–3086
Publication Date:April 4, 2022

Summary

- ‘Wonder material’
  - ballistic charge transport
  - zero-bandgap
  - exotic phenomena in mono- and multilayers
- Challenges:
  - fabrication! impurity-free, flat, cheap and large area

Next:

Ferroelectrics