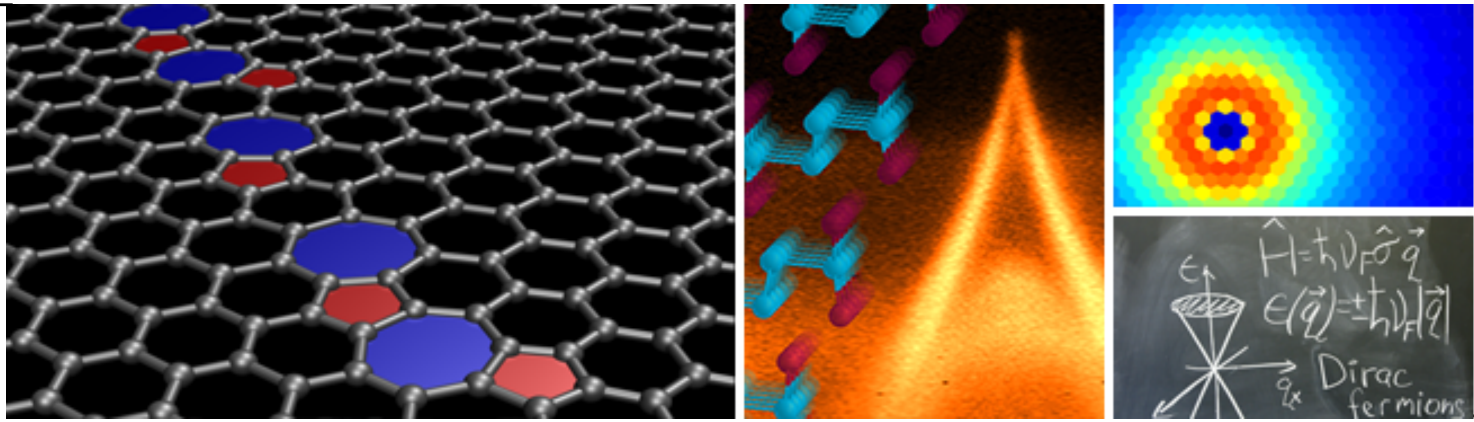
Topological defects in graphene and other 2D materials



Oleg Yazyev

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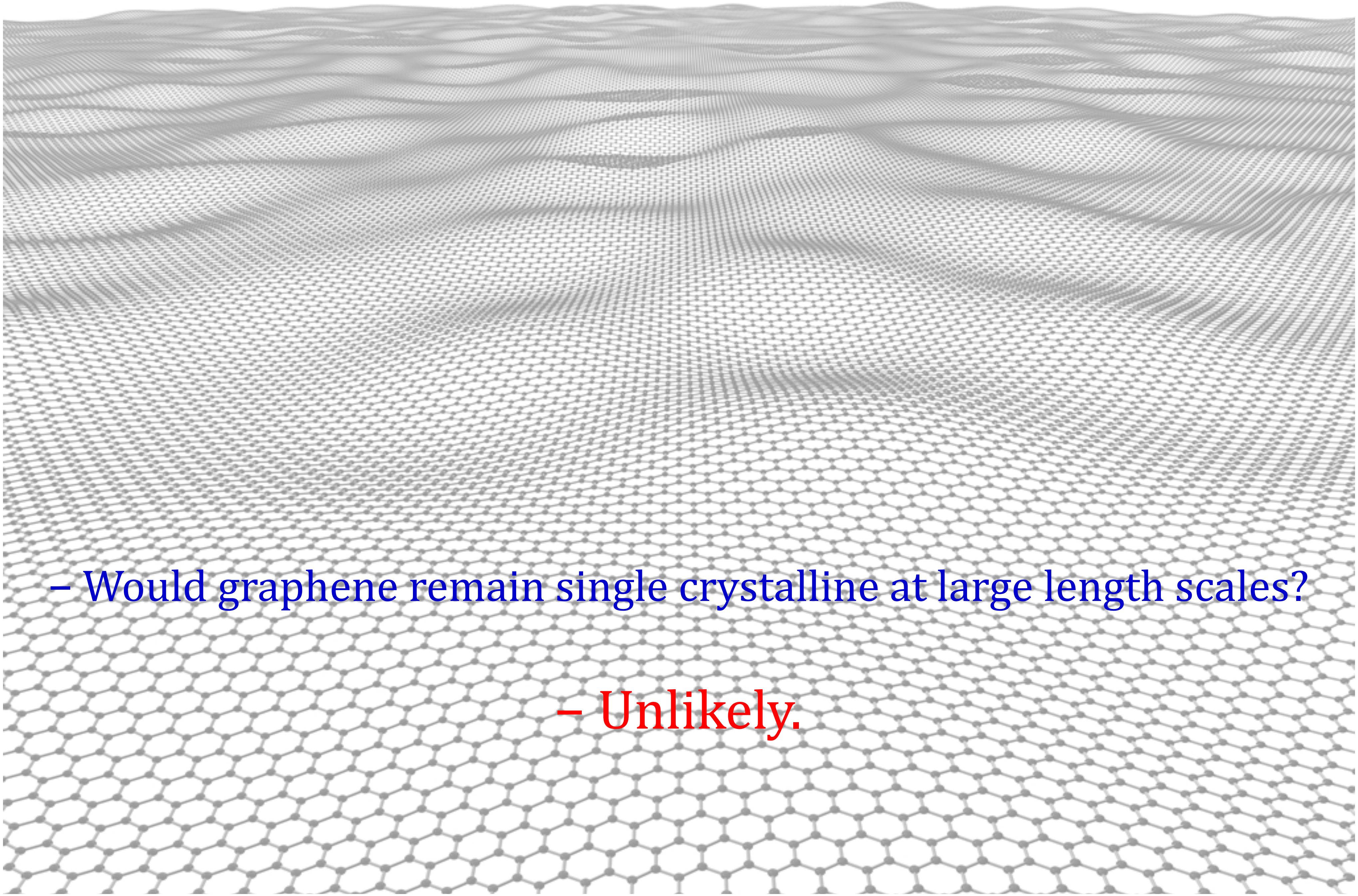
Switzerland



– Would graphene remain single crystalline at large length scales?

– Unlikely.

Outline

- Topological defects in graphene
- Experimental evidence
- Buckling transition of grain boundaries in graphene
- Electronic transport phenomena
  - Electronic transport across periodic grain boundaries
  - Dislocations as resonant scattering sources
  - Valley filtering using periodic line defects in graphene
- Topological defects in MoS_2 and other dichalcogenides
- Spin-orbit gap, spin- and valley-filtering, etc.

Further information

For review see:

nature nanotechnology

FOCUS | REVIEW ARTICLE

PUBLISHED ONLINE: 17 AUGUST 2014 | DOI: 10.1038/NNANO.2014.166

Polycrystalline graphene and other two-dimensional materials

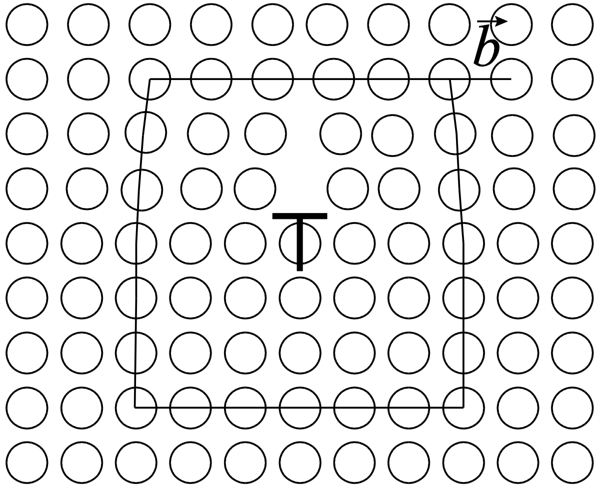
Oleg V. Yazyev[1] and Yong P. Chen[2]

Graphene, a single atomic layer of graphitic carbon, has attracted intense attention because of its extraordinary properties that make it a suitable material for a wide range of technological applications. Large-area graphene films, which are necessary for industrial applications, are typically polycrystalline — that is, composed of single-crystalline grains of varying orientation joined by grain boundaries. Here, we present a review of the large body of research reported in the past few years on polycrystalline graphene. We discuss its growth and formation, the microscopic structure of grain boundaries and their relations to other types of topological defect such as dislocations. The Review further covers electronic transport, optical and mechanical properties pertaining to the characterizations of grain boundaries, and applications of polycrystalline graphene. We also discuss research, still in its infancy, performed on other two-dimensional materials such as transition metal dichalcogenides, and offer perspectives for future directions of research.

O. V. Yazyev and Y. P. Chen, Nature Nanotechnol. **9**, 755 (2014)

Topological defects

Dislocation



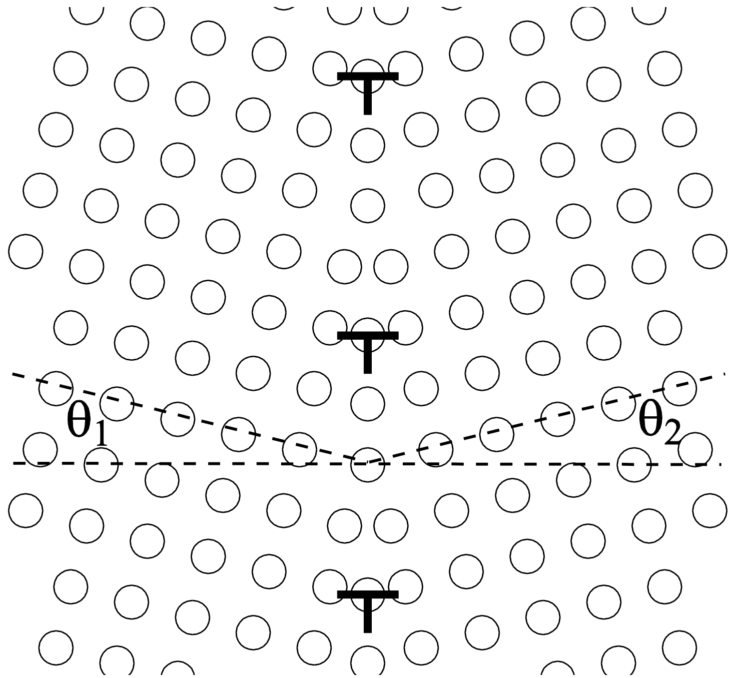
Topological invariant:

$\vec{b}$ - Burgers vector

In graphene:

In 2D only edge dislocations ($\vec{b} \perp \vec{\xi}$) are possible

Grain boundary



$\theta = \theta_1 + \theta_2$ - misoriention angle;

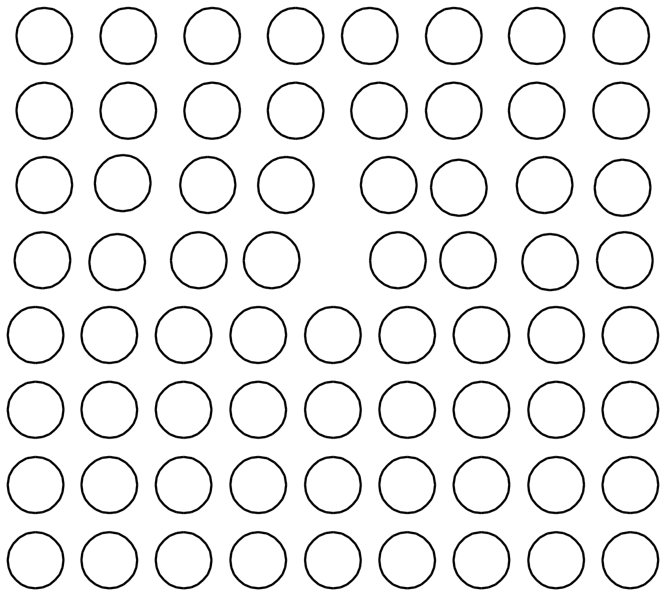
$\psi = |\theta_1 - \theta_2|$ - tilt angle

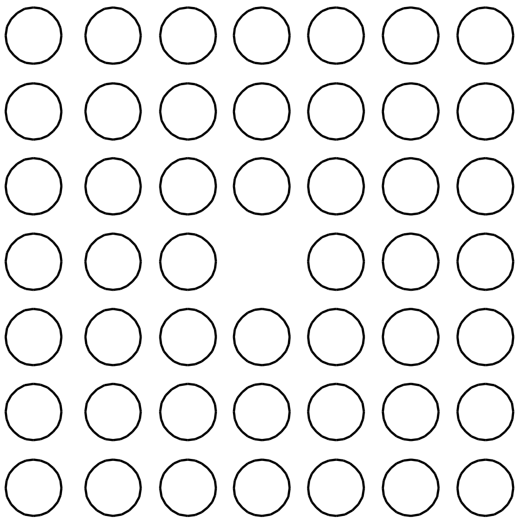
In 2D only tilt grain boundaries are possible. More specifically, in graphene

$\theta \in [0, 60^\circ], \psi \in [0, \theta]$

Non-locality of topological disorder

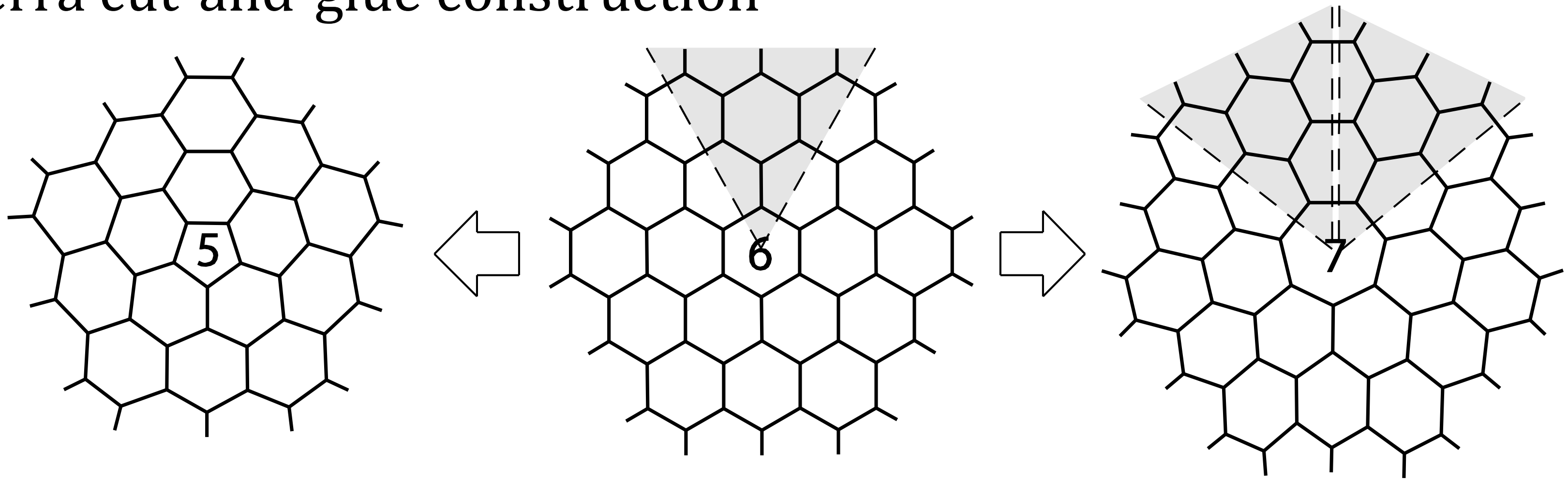
Dislocations **vs.** **point defects**





Disclinations in graphene

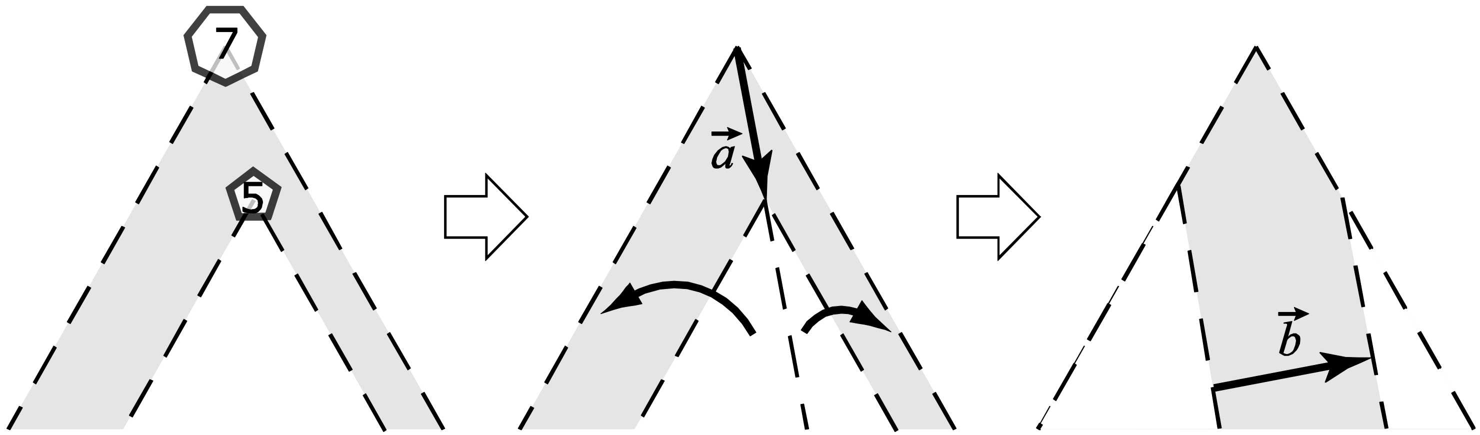
Volterra cut-and-glue construction



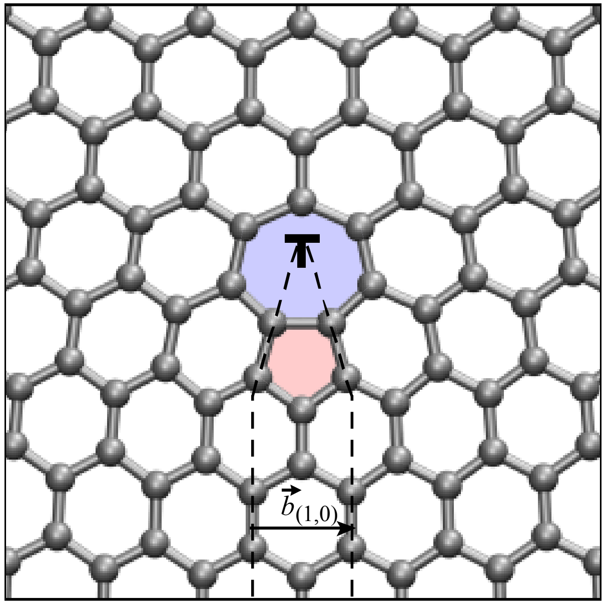
positive disclination $s = 60^o$ | ideal graphene | negative disclination $s = -60^o$

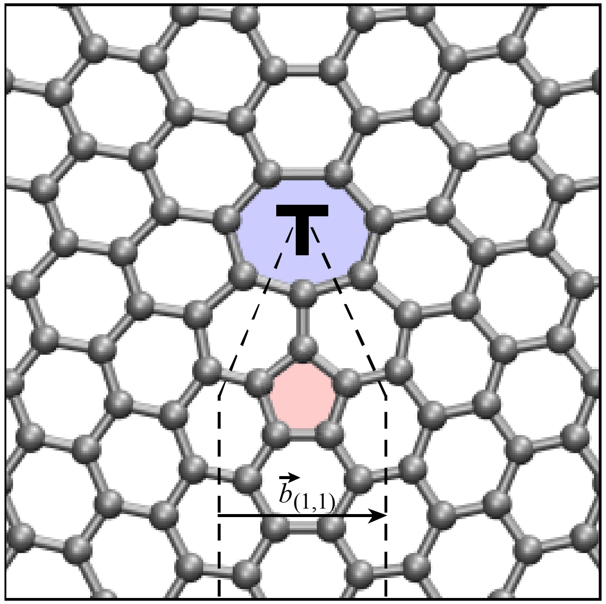
Seung & Nelson, 1988

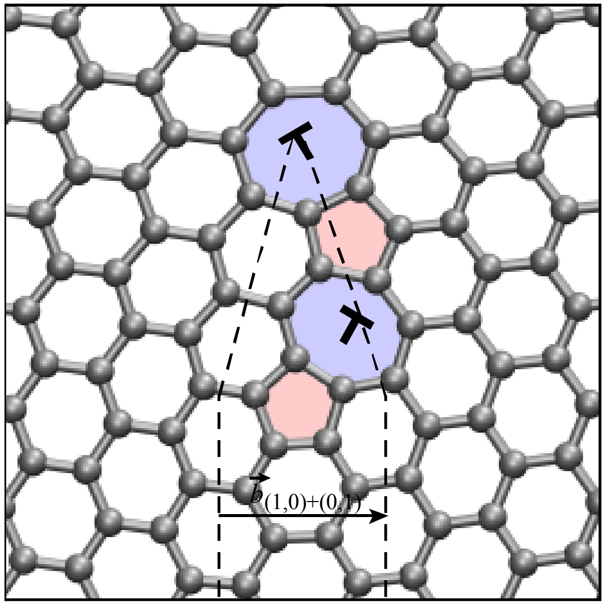
Dislocation = pair of disclinations



Dislocations in graphene







(1,0) dislocation

$$|\vec{b}| = \sqrt{3}d_{\mathrm{CC}} = 2.46\text{Å}$$

(1,1) dislocation

$$|\vec{b}| = 3d_{\mathrm{CC}} = 4.23\text{Å}$$

(1,0)+(0,1) dislocation

$$|\vec{b}| = 3d_{\mathrm{CC}} = 4.23\text{Å}$$

Yazyev & Louie, Phys. Rev. B **81**, 195420 (2010)

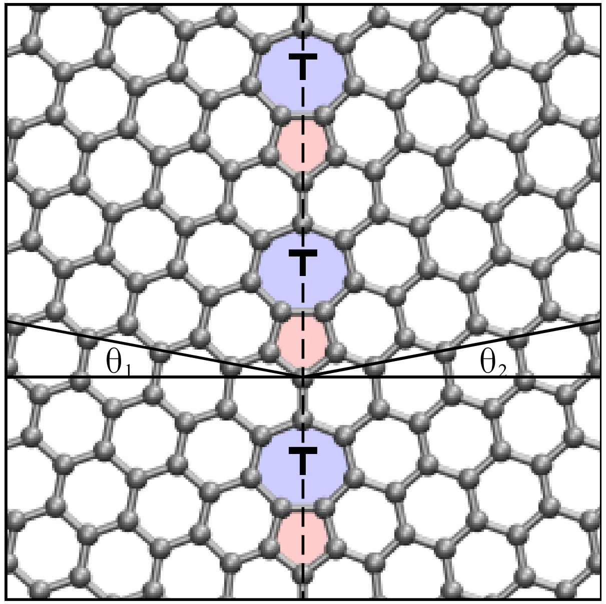
Large-angle symmetric grain boundaries in graphene

Frank's equations:

GB's along armchair direction:

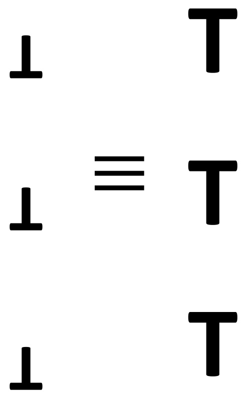
$$\theta = 2\arcsin\frac{|\vec{b}_{(1,0)}|}{2d_{(1,0)}}$$

$$0^\circ < \theta < 21.8^\circ$$



LAGB I

$\theta = 21.8^\circ$

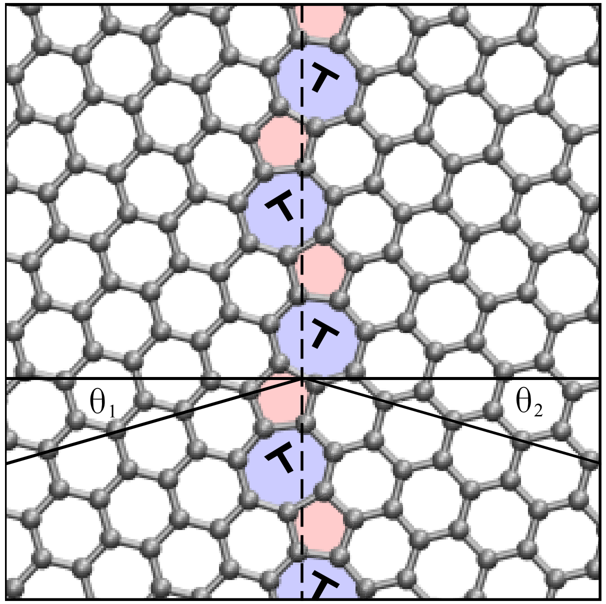


(1,0) (1,1)

GB's along zigzag direction:

$$\theta = 60^\circ - 2\arcsin\frac{|\vec{b}_{(1,1)}|}{2d_{(1,1)}}$$

$$21.8^\circ < \theta < 60^\circ$$



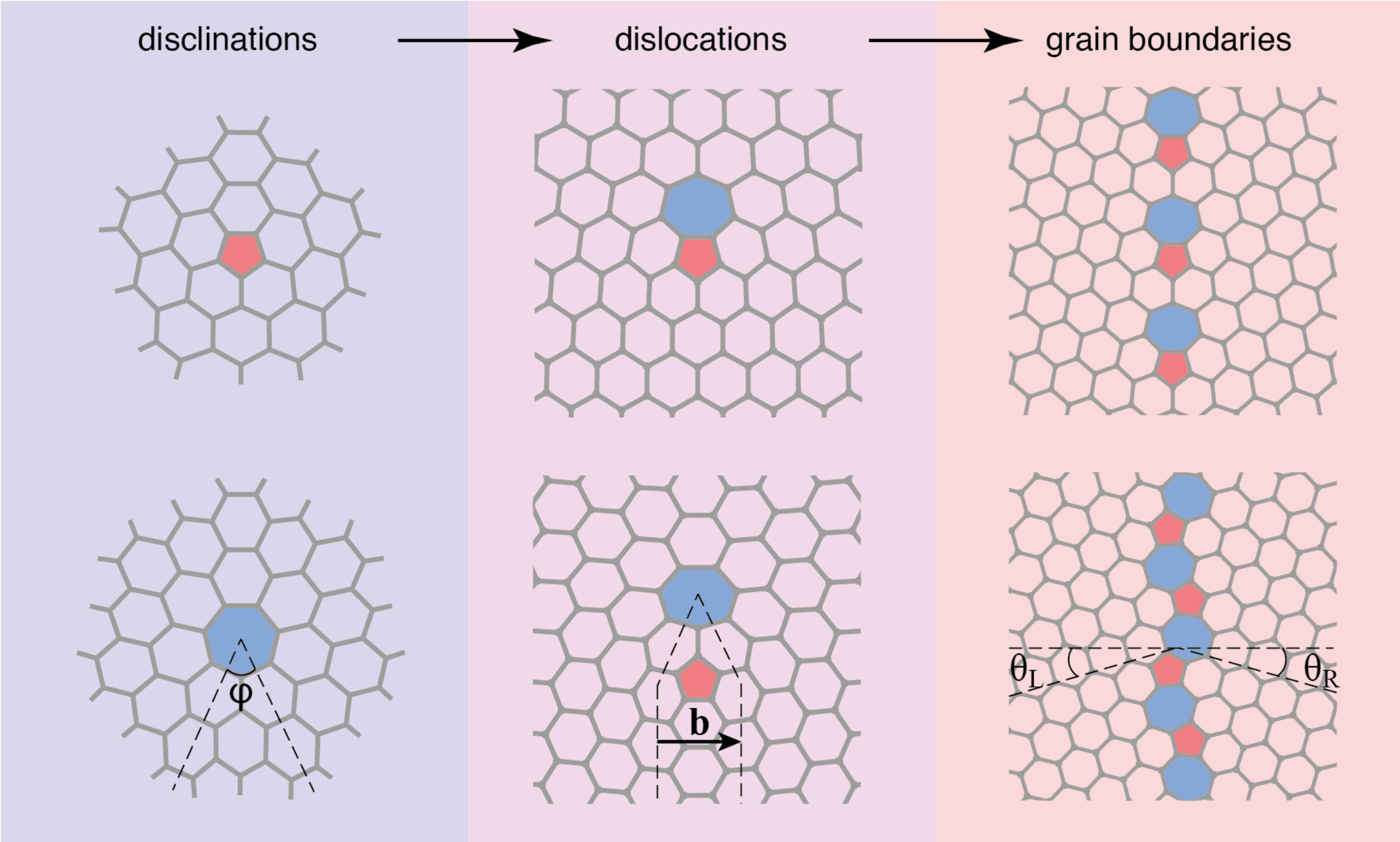
LAGB II

$\theta = 32.2^\circ$

(1,0)+(0,1)

Yazyev & Louie, Phys. Rev. B **81**, 195420 (2010)

Polycrystalline graphene and topological defects



disclination strength
φ

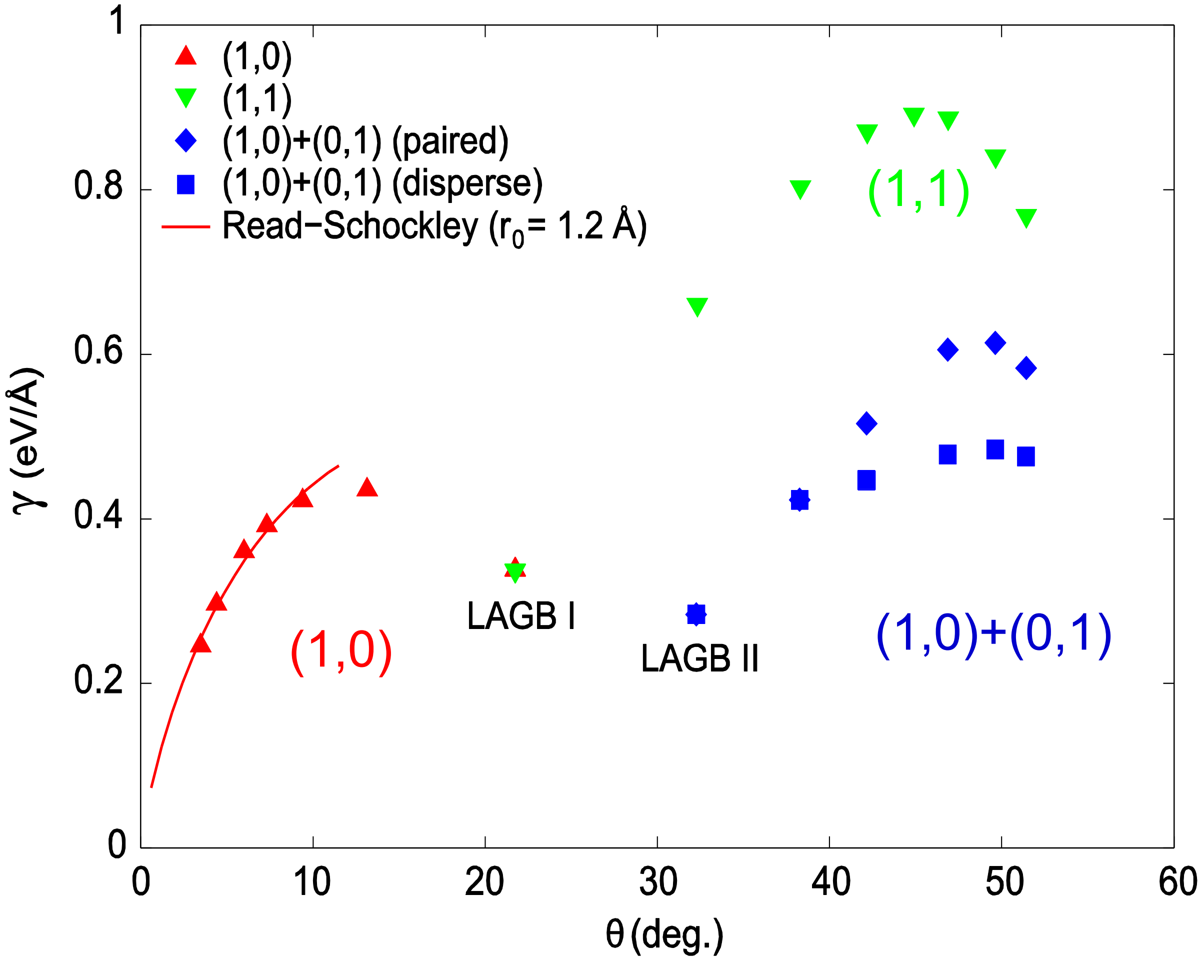
Burgers vector
b

misorientation angle
$\theta = \theta_L + \theta_R$

Yazyev & Louie, Phys. Rev. B **81**, 195420 (2010); also results by group of Yakobson

Grain boundary energetics (flat)

DFT-GGA results



Flat regime (bulk-like):
Read-Shockley equation

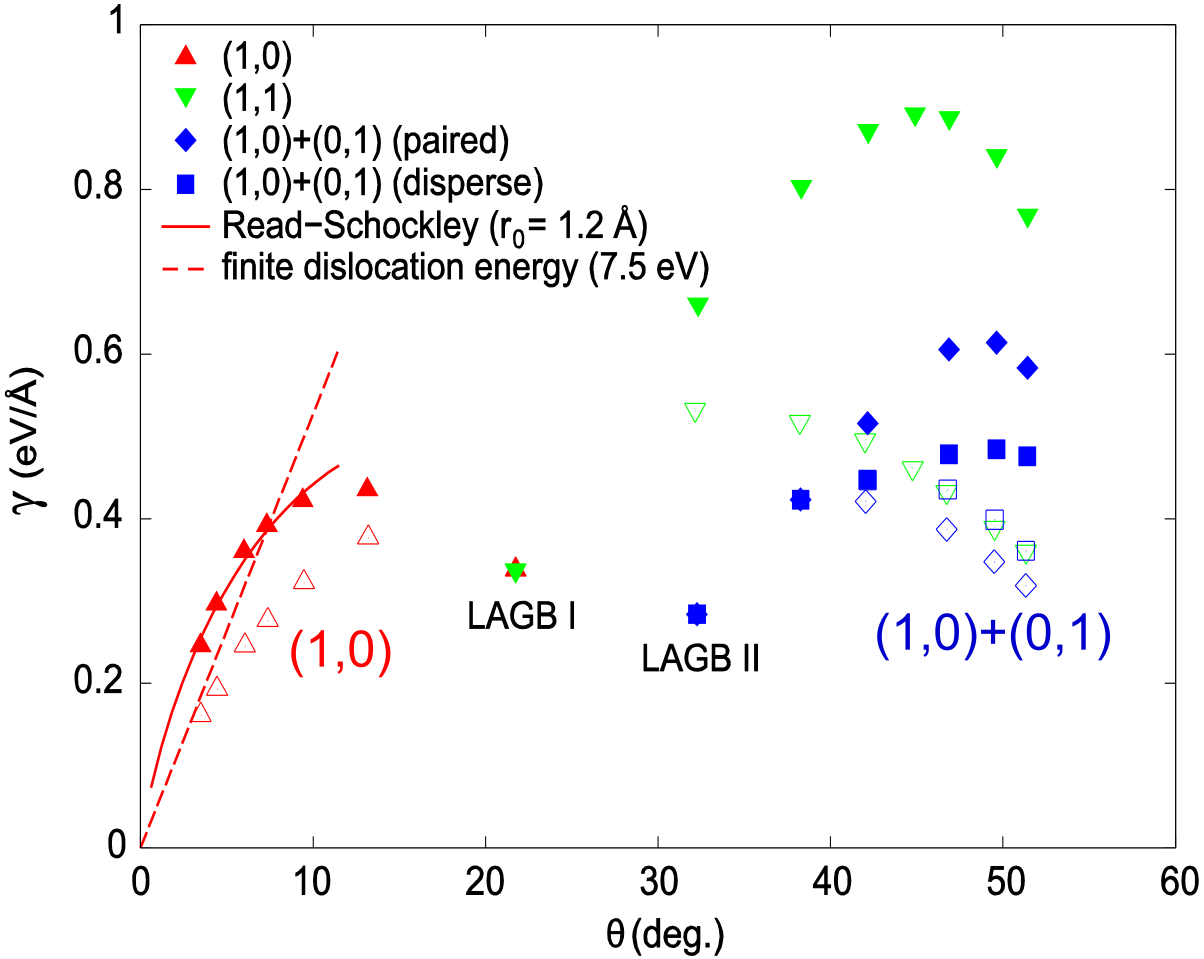
$$\gamma(\theta) = \frac{\mu|\vec{b}|}{4\pi(1-\nu)}\theta(A-\ln\theta)$$

$$A = 1+\ln\left(\frac{|\vec{b}|}{2\pi r_0}\right) \quad r_0 = 1.2\ \text{Å}$$

Yazyev & Louie, Phys. Rev. B **81**, 195420 (2010)

Grain boundary energetics (buckled)

DFT-GGA results



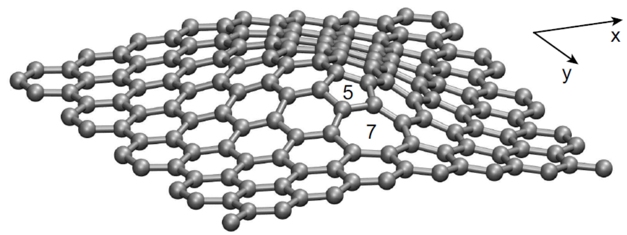
Flat regime (bulk-like):
Read-Shockley equation

$$\gamma(\theta) = \frac{\mu|\vec{b}|}{4\pi(1-\nu)}\theta(A - \ln\theta)$$

$$A = 1 + \ln\left(\frac{|\vec{b}|}{2\pi r_0}\right) \qquad r_0 = 1.2\ \text{Å}$$

Buckled regime (membrane)
Finite dislocation energy

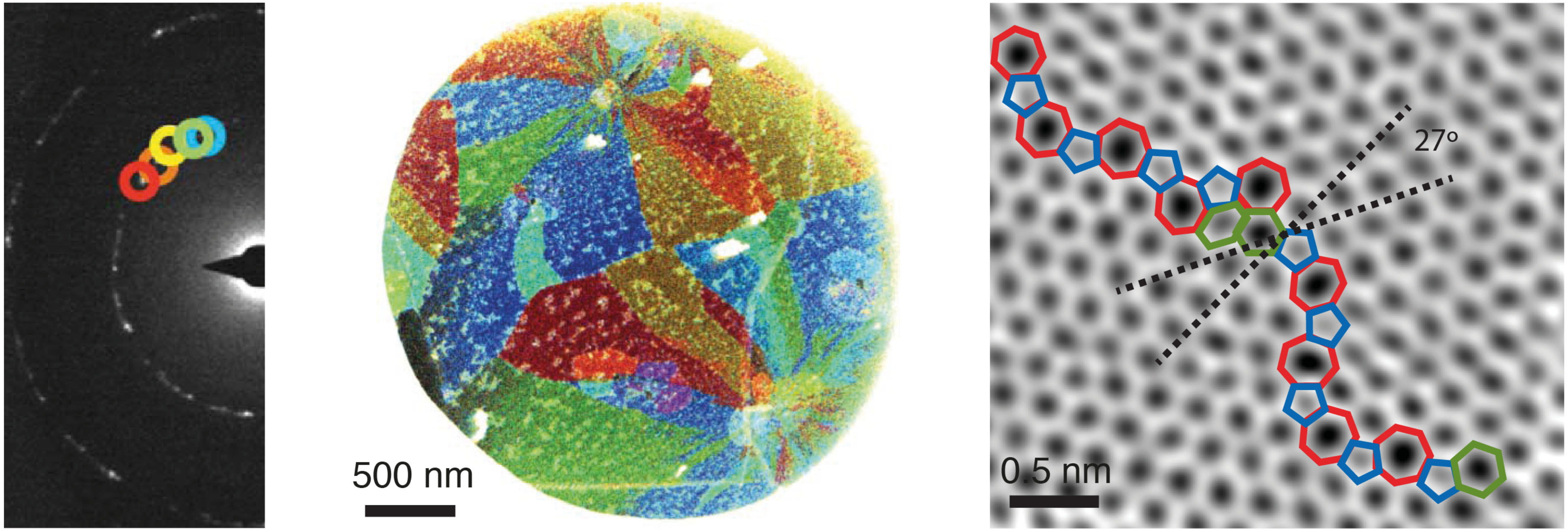
$$\gamma(\theta) = \frac{E_f\theta}{|\vec{b}|} \qquad E_f = 7.5\ \text{eV}$$



Yazyev & Louie, Phys. Rev. B **81**, 195420 (2010)

Experimental evidence

Epitaxial graphene grown on Cu substrates

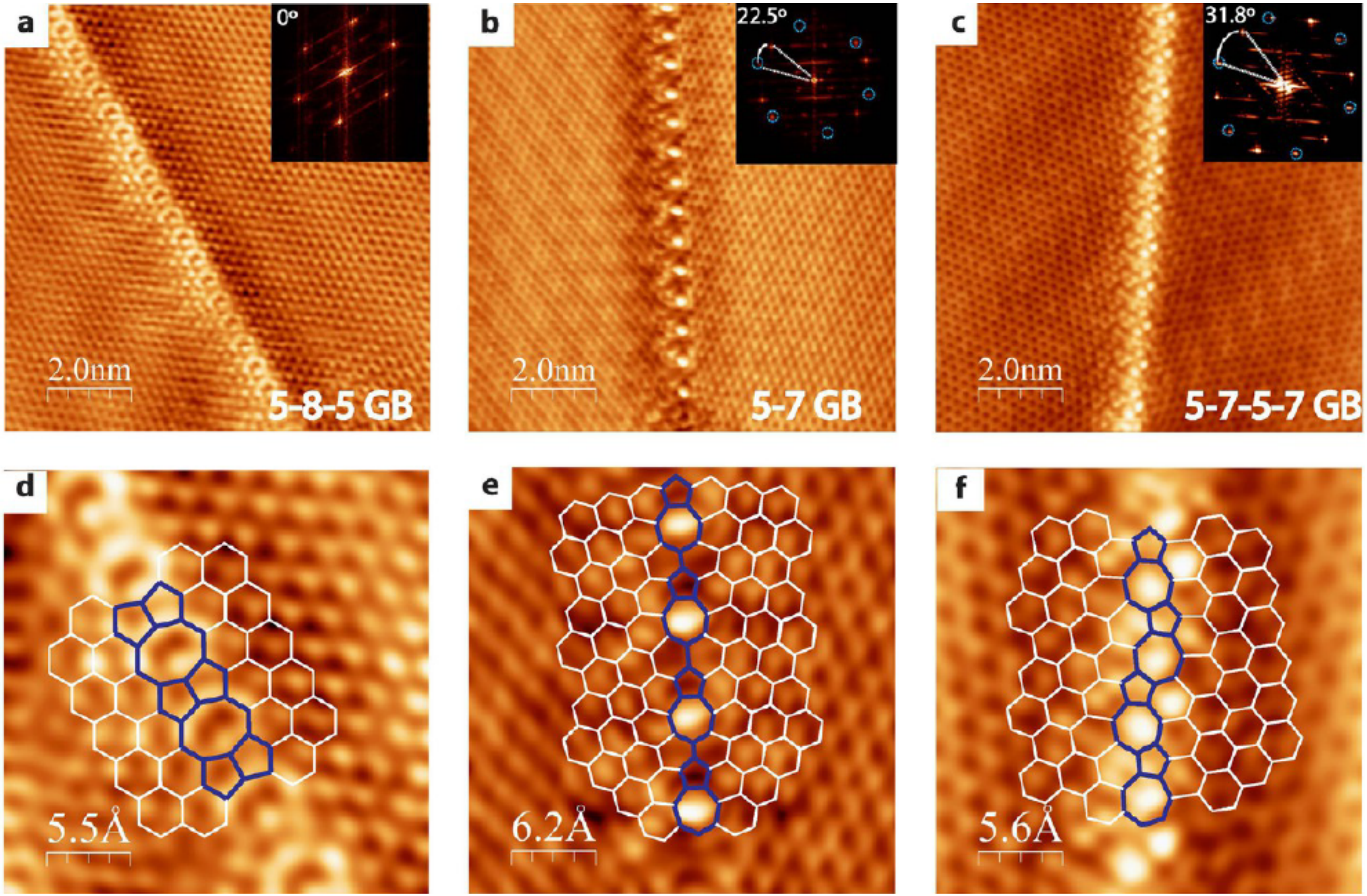


Reproduced from Huang *et al.*, Nature **469**, 389 (2011).

Almost simultaneously reported in
Kim *et al.*, ACS Nano **5**, 2142 (2011),
An *et al.*, ACS Nano **5**, 2433 (2011),
followed by many others.

Ordered GBs in graphene

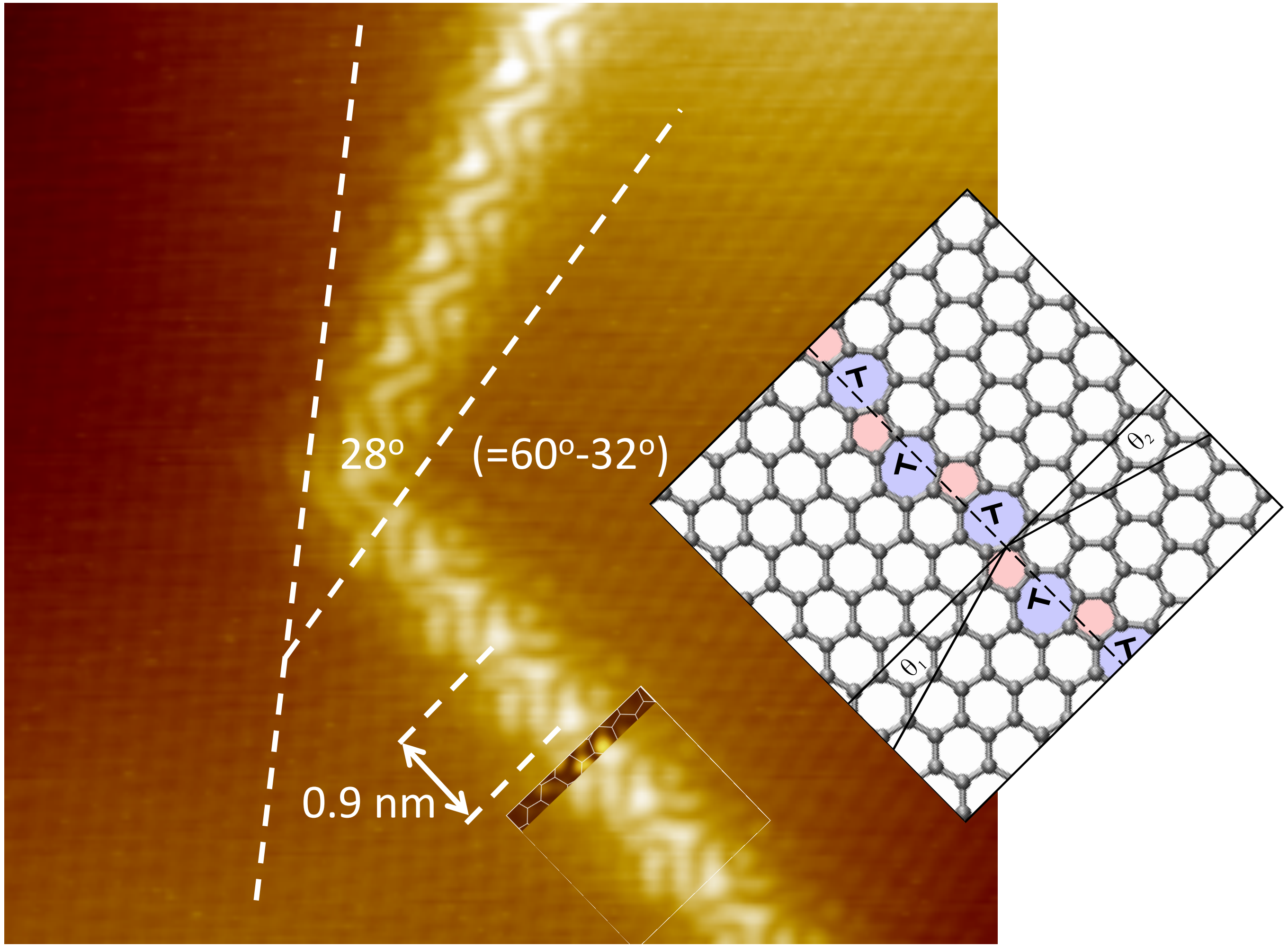
Annealed CVD graphene



B. Yang *et al.*, JACS **136**, 12041 (2014)

Experimental evidence

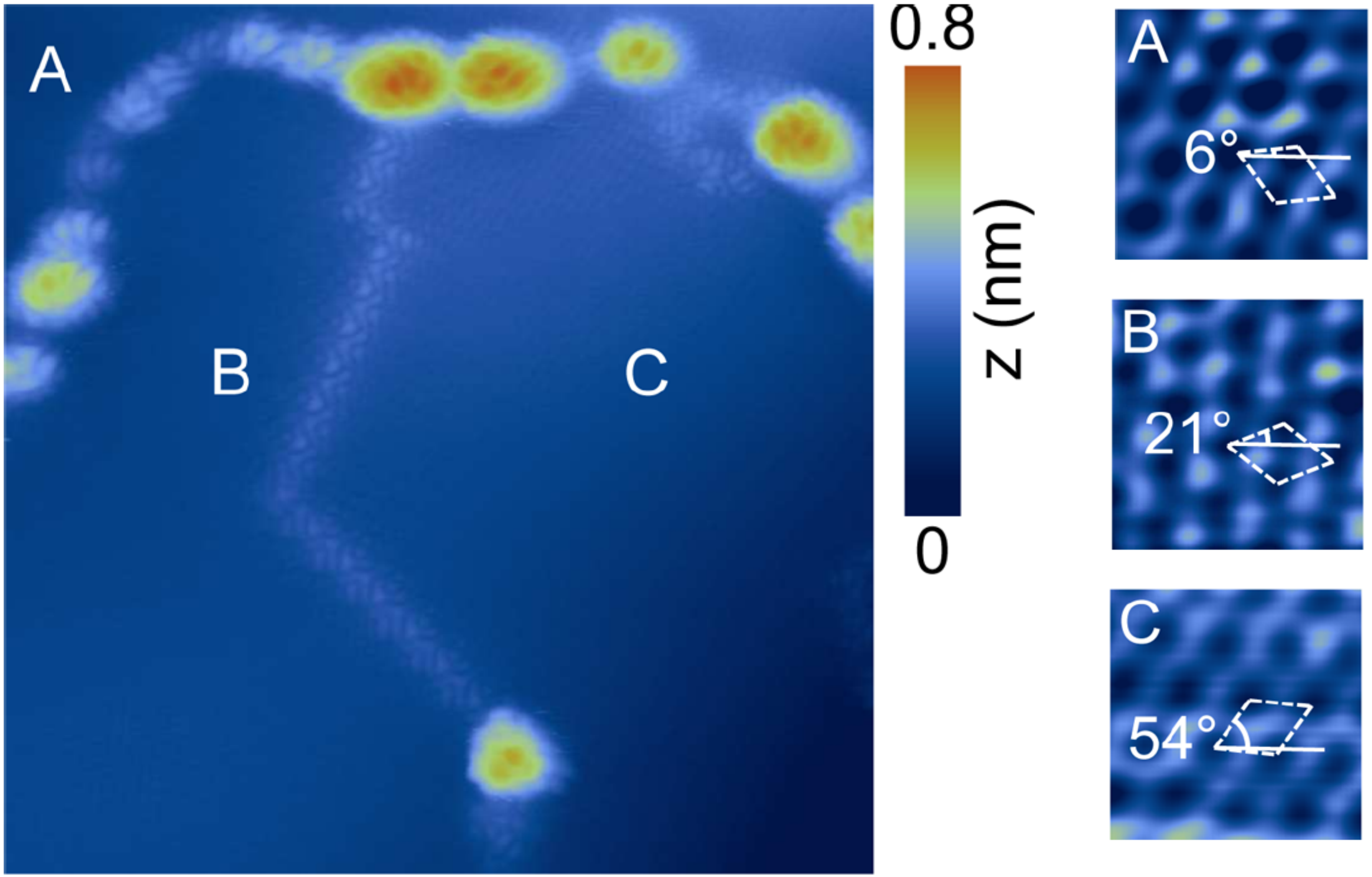
Large-angle GB in epitaxial graphene on SiC(000-1).



Experiments: Vincent Repain (Paris VII); theory: Yazyev group (EPFL)

Y. Tison *et al.*, Nano Lett. **14**, 6382 (2014)

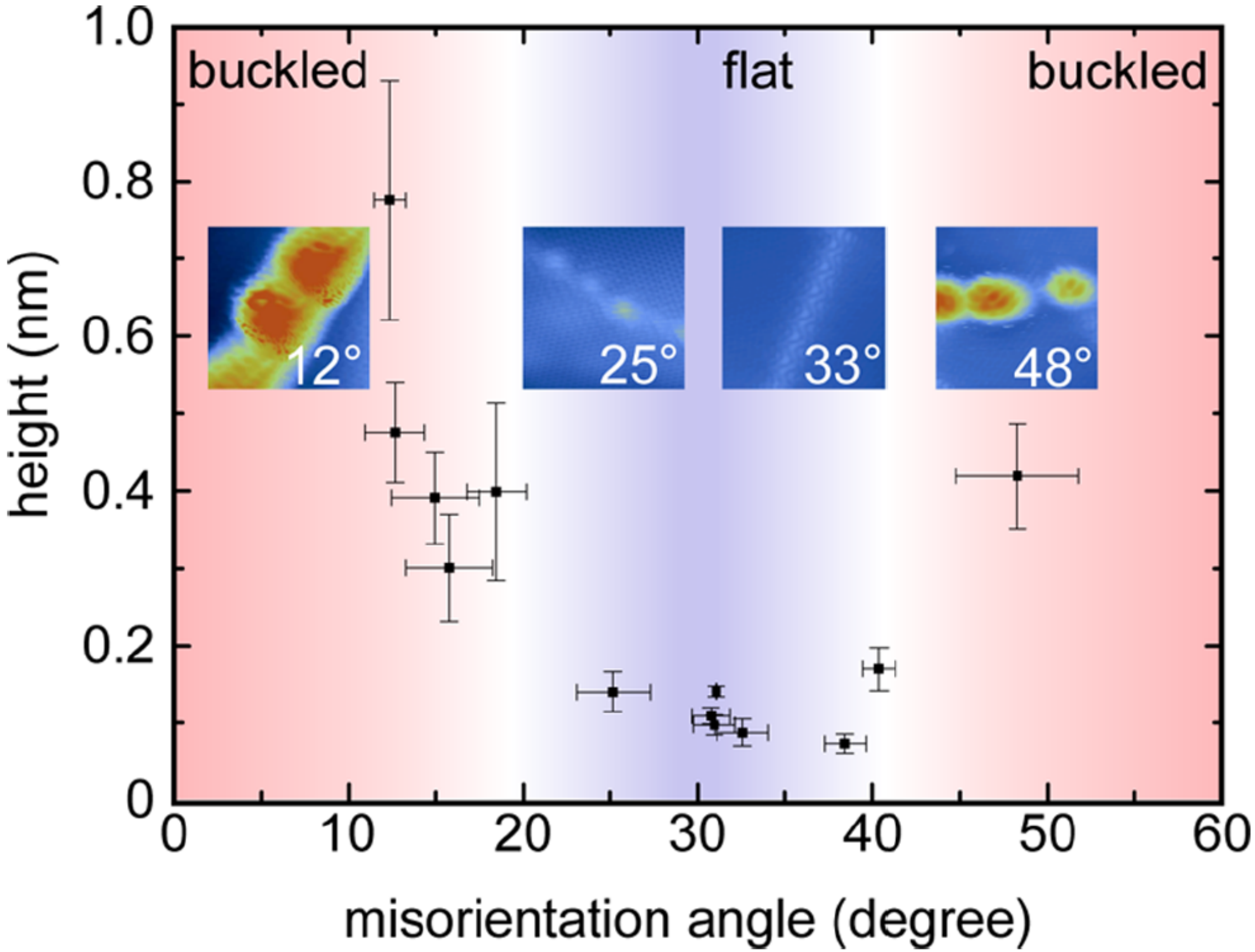
Buckling transition of GBs in graphene



Y. Tison *et al.*, Nano Lett. **14**, 6382 (2014)

Buckling transition of GBs in graphene

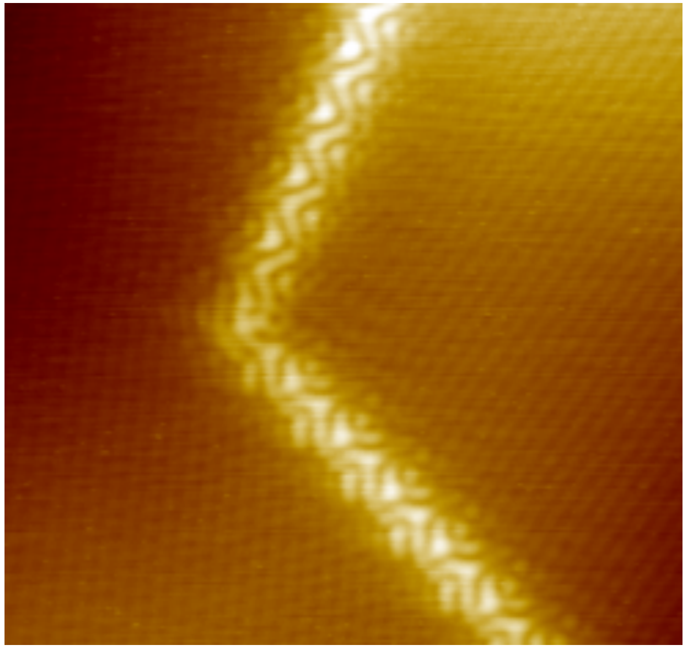
Buckling transition $\theta_c = 19^\circ \pm 1^\circ$ (and symmetrically $\theta_c = 41^\circ \pm 1^\circ$)



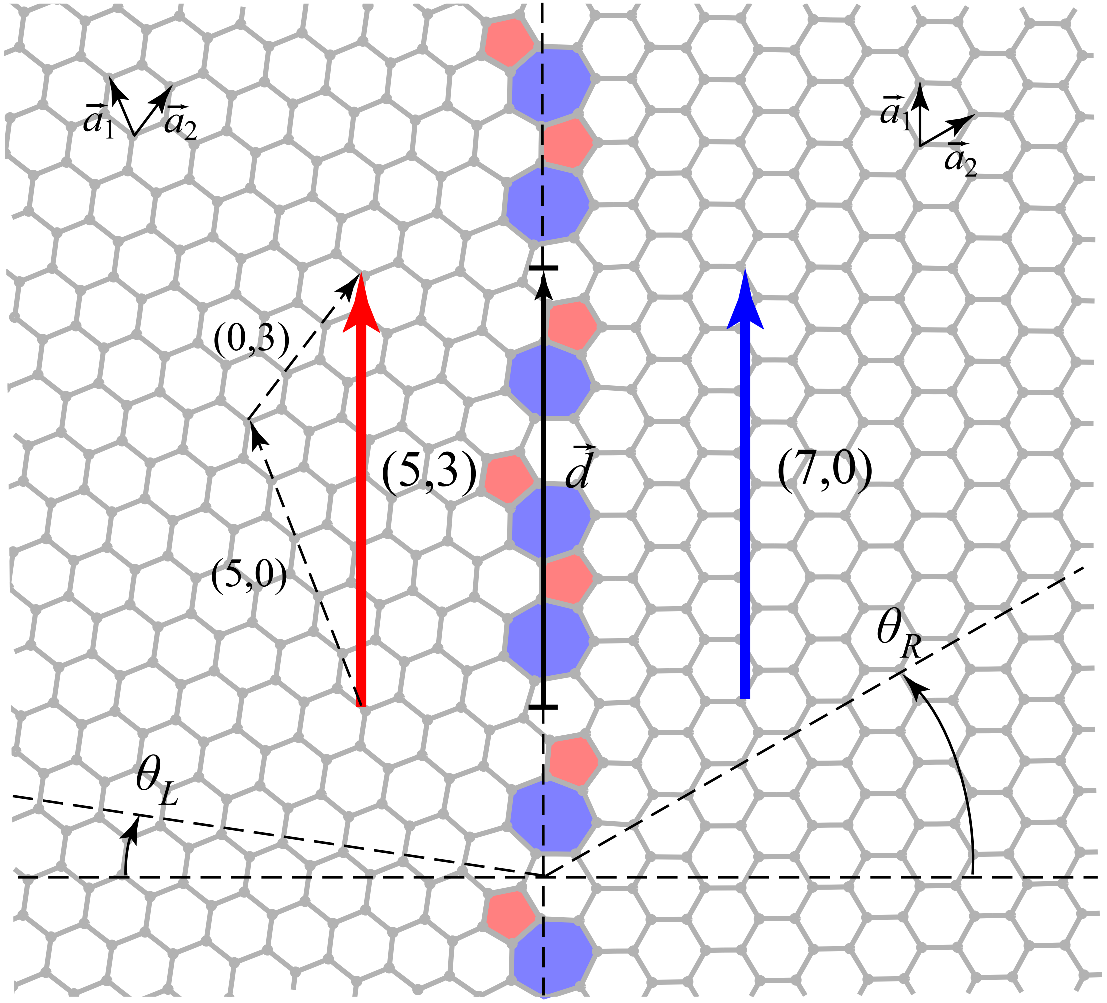
Y. Tison *et al.*, Nano Lett. **14**, 6382 (2014)

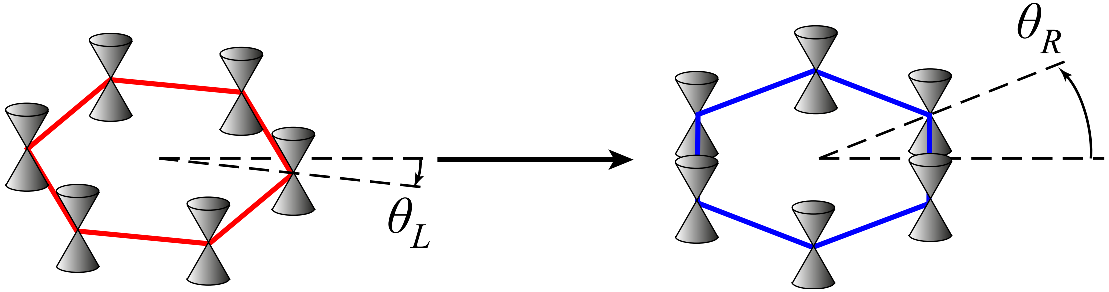
I. Transport across periodic grain boundaries in graphene:

Momentum conservation

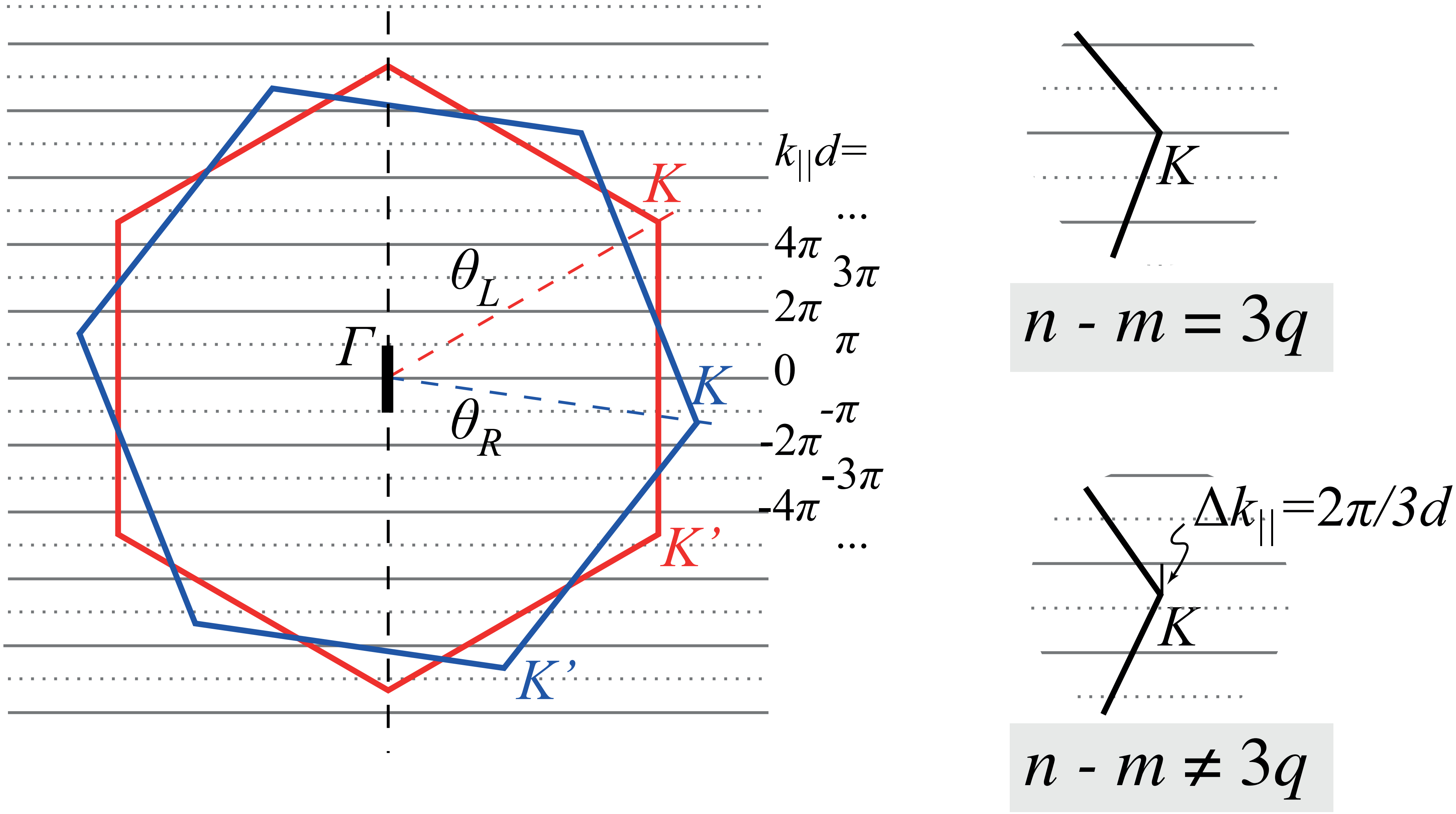


Electronic transport in polycrystalline graphene



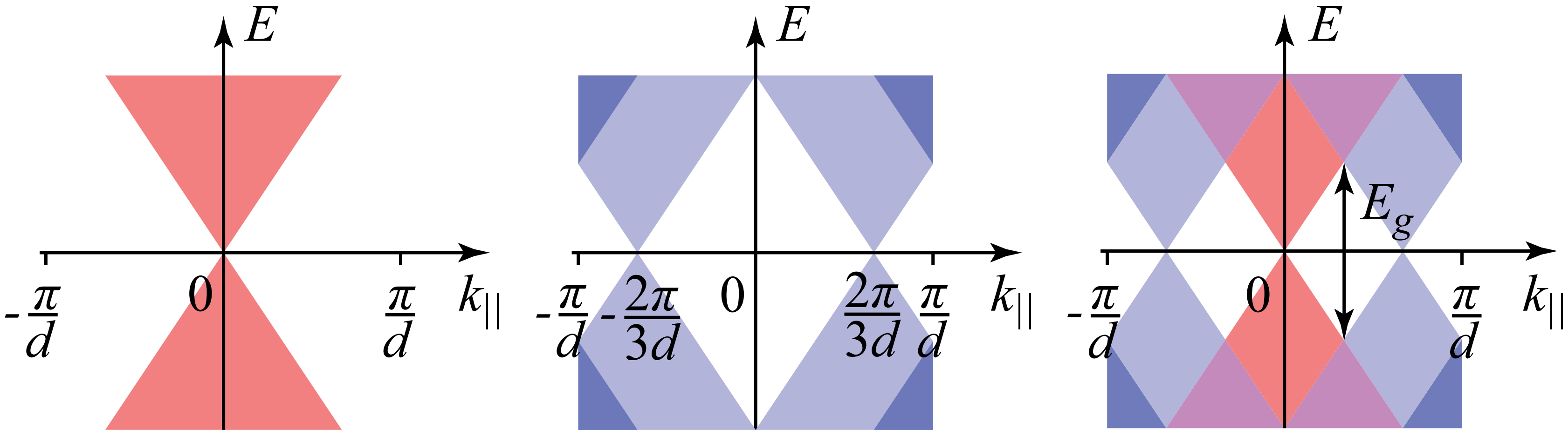


Zone-folding approach



Yazyev & Louie, Nature Mater. **9**, 806 (2010)

Two distinct transport behaviors of periodic GBs



Transmission allowed: Ia Ib II

Ia	Ib	II
n_L-m_L = $3q$ n_R-m_R = $3q$	n_L-$m_L \neq 3q$ n_R-$m_R \neq 3q$	n_L-m_L = $3q$, n_R-$m_R \neq 3q$ or n_L-$m_L \neq 3q$, n_R-m_R = $3q$

Transport gap:

$$E_g = 0$$

$$E_g = 0$$

$$E_g = \hbar v_F \frac{2\pi}{3d} \approx \frac{1.38}{d[\mathrm{nm}]}[\mathrm{eV}]$$

Yazyev & Louie, Nature Mater. **9**, 806 (2010)

Non-equilibrium Green's function results (ballistic regime)

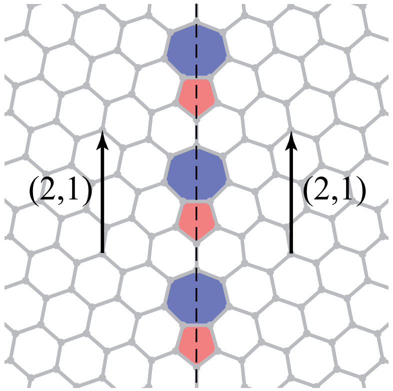
Transmission: $T = \mathrm{Tr}\left(\Gamma_{\mathrm{L}} G_{\mathrm{S}}^{\dagger} \Gamma_{\mathrm{R}} G_{\mathrm{S}}\right)$

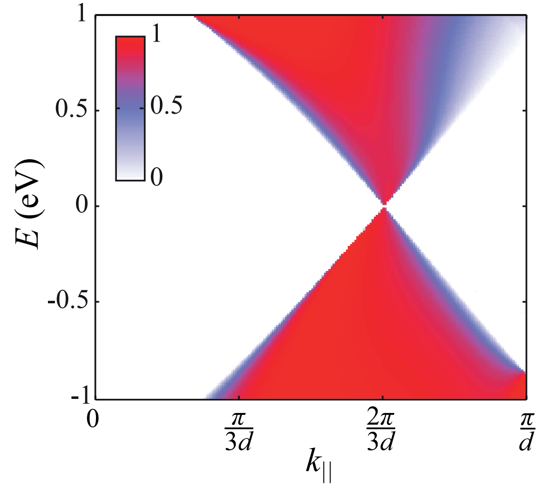
Green's function (scatt. region): $G_{\mathrm{S}} = \left(E^{+} I - \mathrm{H}_{\mathrm{S}} - \Sigma_{\mathrm{L}} - \Sigma_{R}\right)^{-1}$

Coupling matrices (contacts): $\Gamma_{\mathrm{L(R)}} = i\left(\Sigma_{\mathrm{L(R)}} - \Sigma_{\mathrm{L(R)}}^{\dagger}\right)$

Class I (2,1)|(2,1)
Θ = 21.8° (symmetric)

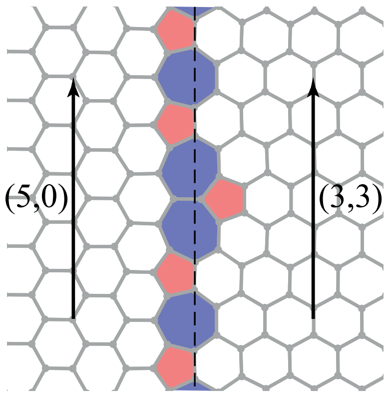
- highly transparent
- valleys separated in $k_{||}$

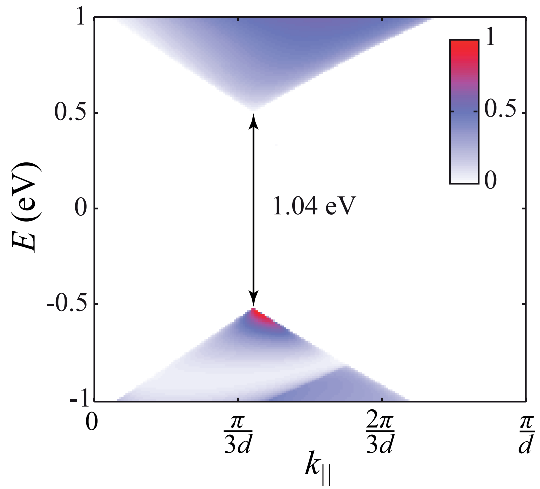




Class II (5,0)|(3,3)
Θ = 30.0° (asymmetric)

- large transport gap (1 eV)
- asymmetric, with misfit





Yazyev & Louie, Nature Mater. **9**, 806 (2010)

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Class I (2,1)|(2,1)
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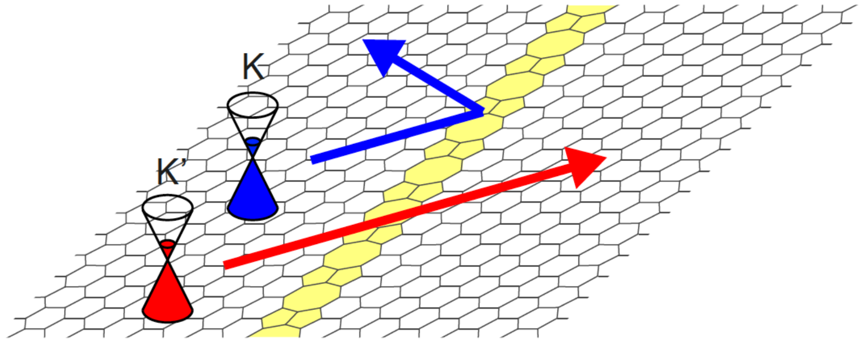
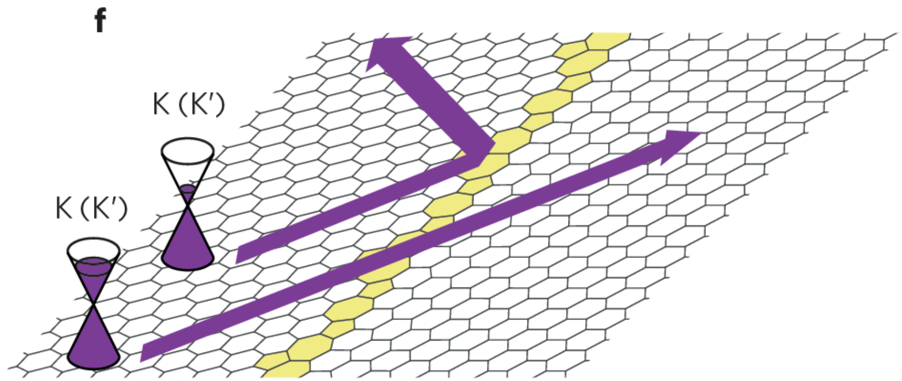
- highly transparent
- valleys separated in $k_{||}$ (valley filtering)





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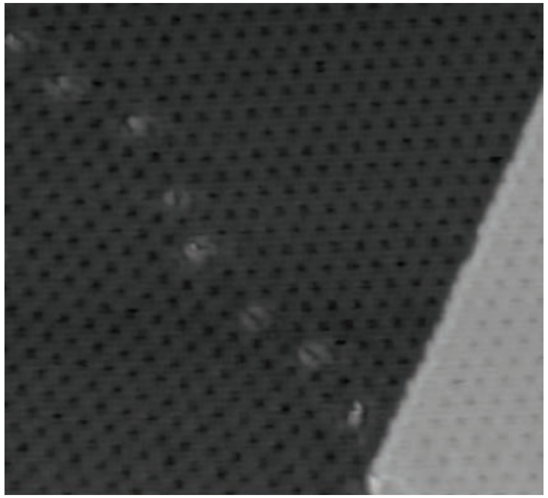
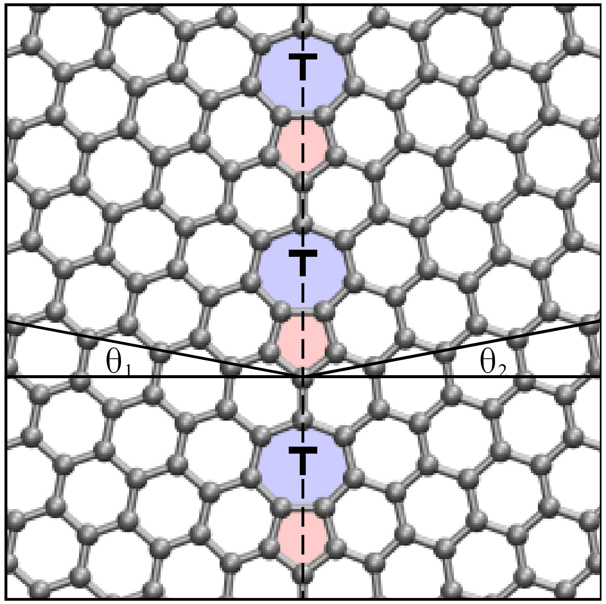
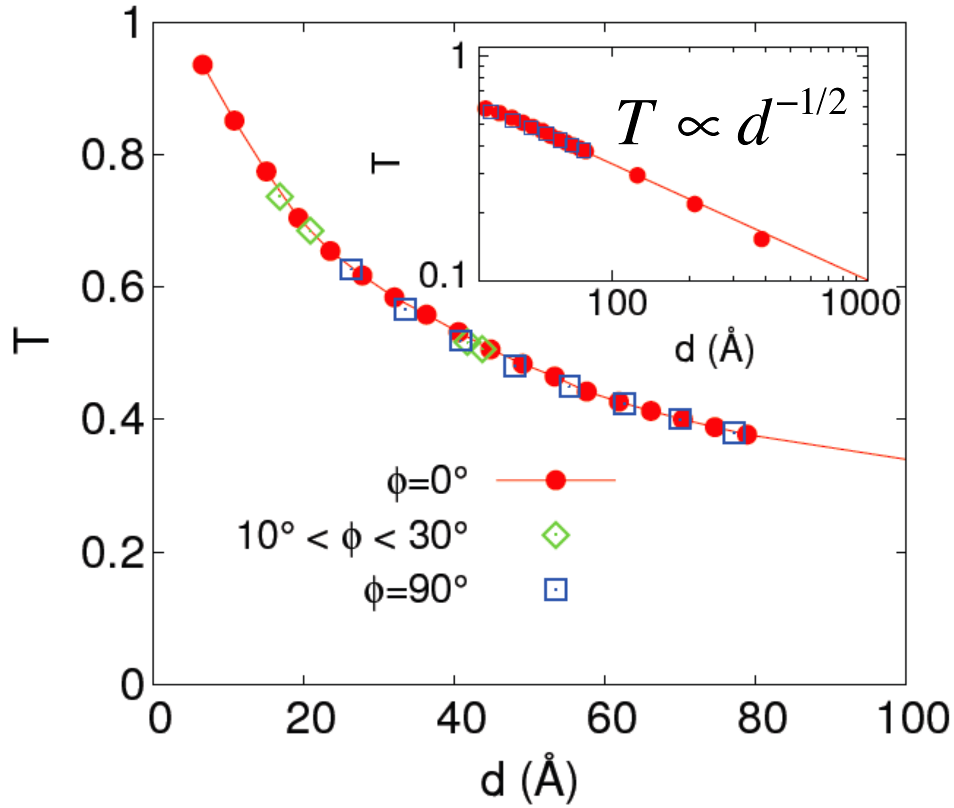
Yazyev & Louie, Nature Mater. **9**, 806 (2010)

II. Dislocations as resonant scattering centers



Transport anomaly at low energies





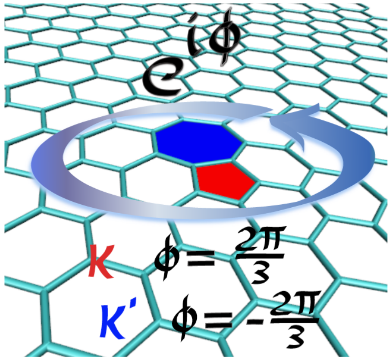
Transmission at E = 0 decreases (!) as separation between dislocations increases.

Dislocations cannot be described in terms of scattering cross-sections, topological aspects are important

Gargiulo & Yazyev, Nano Lett. **14**, 250 (2014)

Topological aspects in electronic transport

Gauge field associated with dislocations



$$\varphi = \oint \mathbf{A}\, d\mathbf{r} = \mathbf{k}\cdot\mathbf{b}$$

Iordanskii & Koshelev, Sov. Phys. JETP **63**, 820 (1986)

$\mathbf{b} = (1,0)$ dislocations (or any $n - m \neq 3q$) are non-trivial ($\mathbf{k}\cdot\mathbf{b} = \frac{2\pi}{3}$)
$\mathbf{b} = (1,1)$ dislocations (or any $n - m = 3q$) are trivial ($\mathbf{k}\cdot\mathbf{b} = 0$)

Analogy with Aharonov-Bohm effect (for the 1st case)

$$\Phi = 1/3\ \Phi_0\ (-1/3\ \Phi_0) \text{ for } \tau = +1\ (\tau = -1)$$

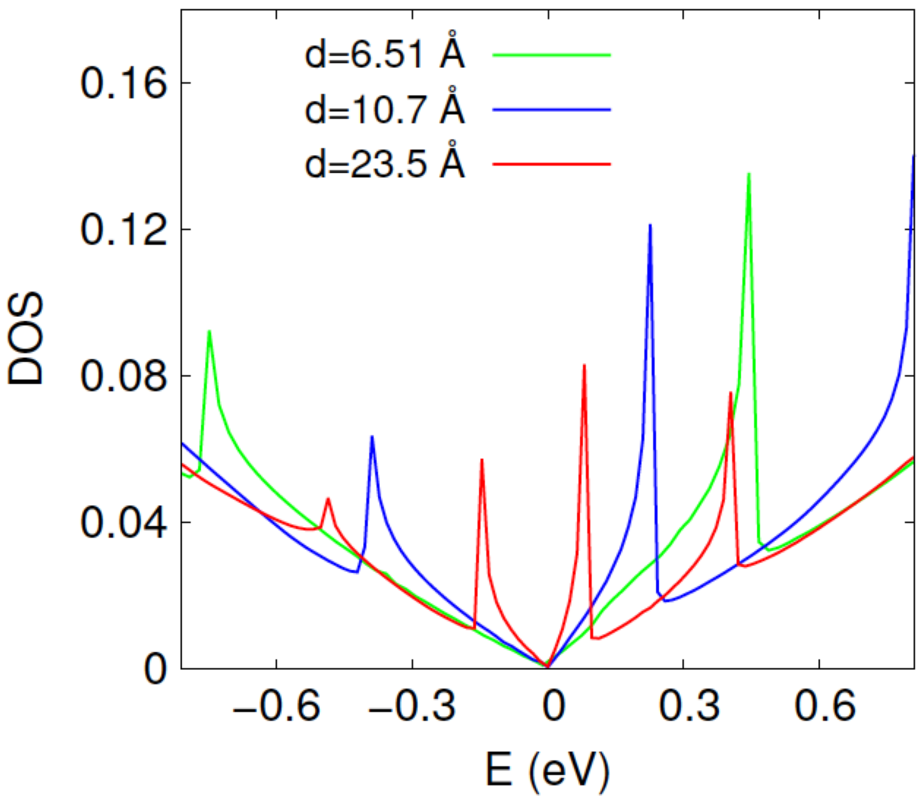
Give rise to zero-energy modes

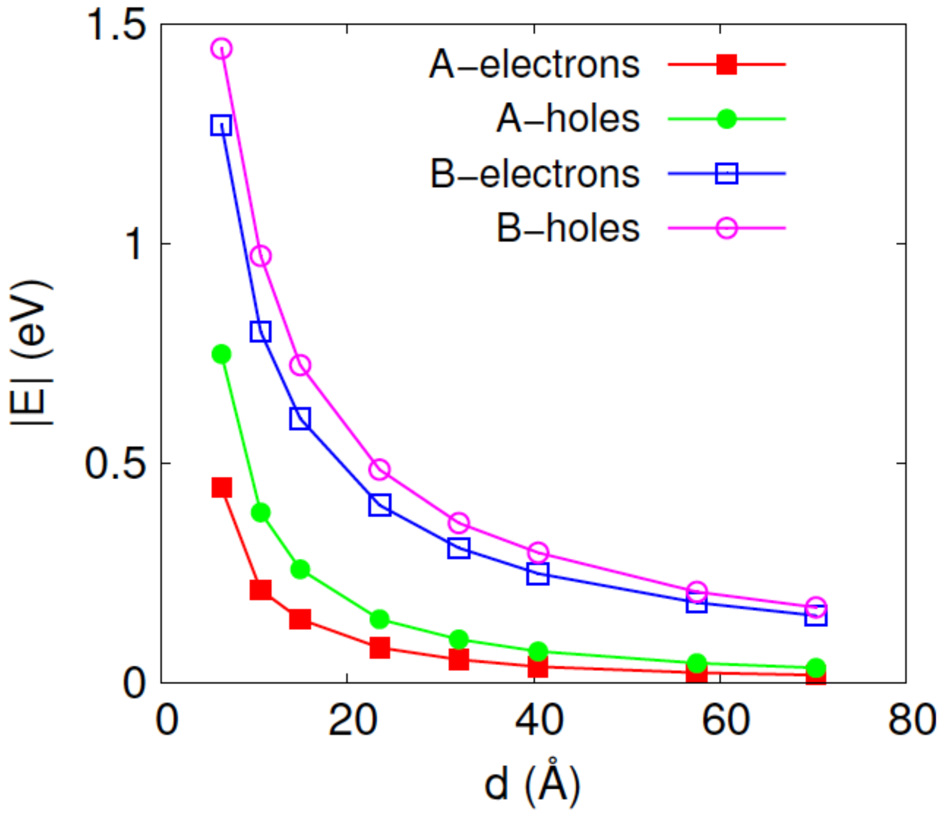
$$LDOS(r,E) \propto r^{-4/3}\,|E|^{-1/3}$$

Mesaros *et al.*, PRB **82**, 205119 (2010)

Hybridization of zero-modes

Resonant backscattering on zero-energy states



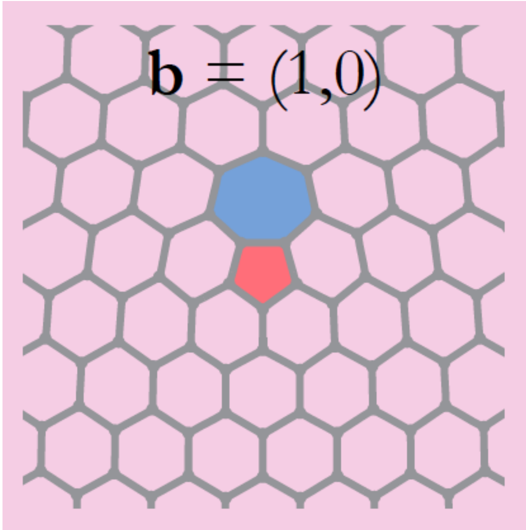


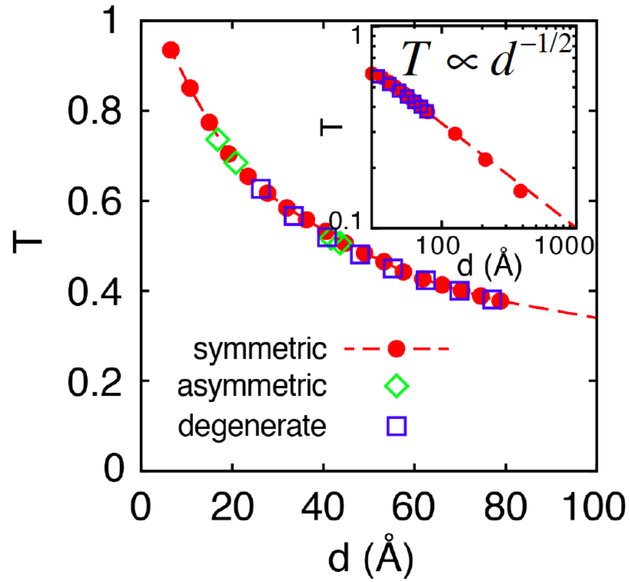
Gargiulo & Yazyev, Nano Lett. **14**, 250 (2014)

Topological aspects: numerical results

b = (1,0) dislocations:

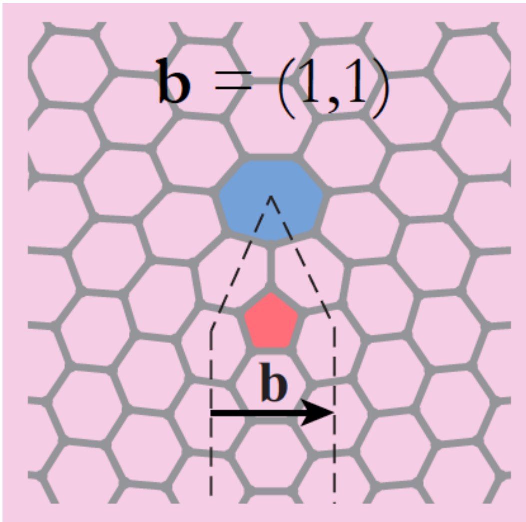
- resonant scattering sources at $E = 0$
- anomalous dependence of conductance on dislocation density

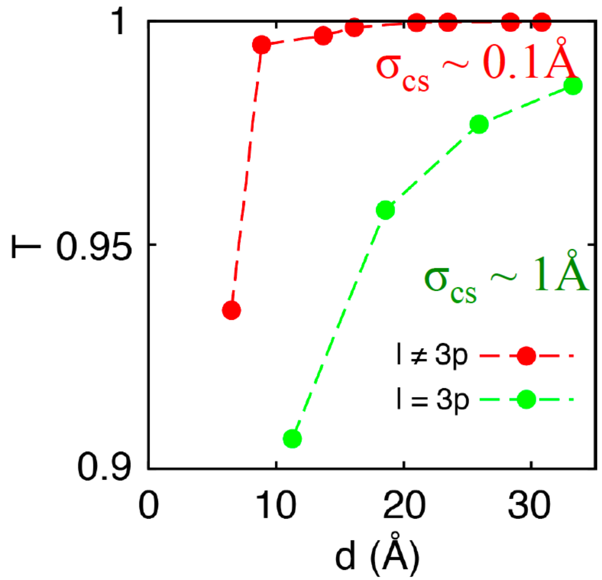




b = (1,1) dislocations:

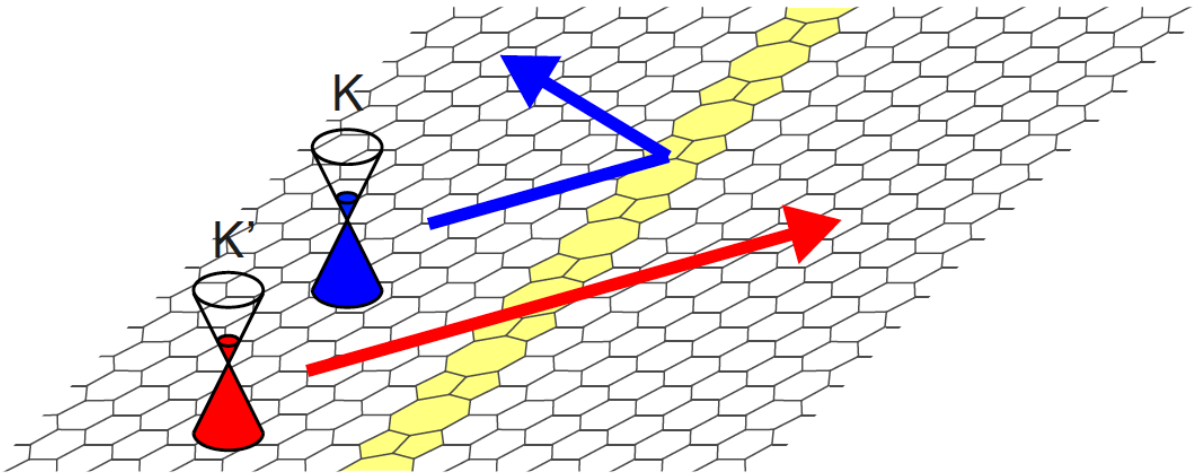
- small scattering cross-sections
- behave like point defects (topologically trivial)



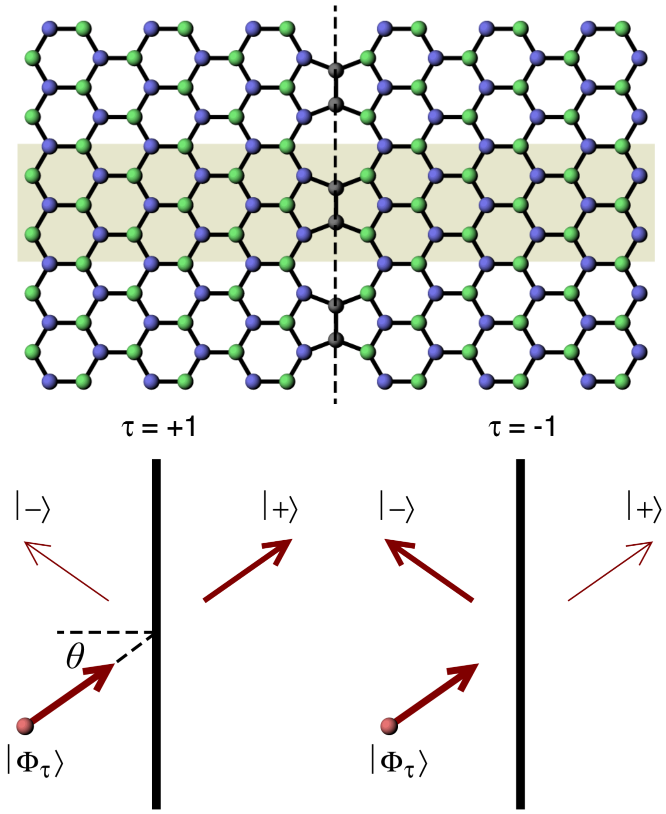


Gargiulo & Yazyev, Nano Lett. **14**, 250 (2014)

III. Valley filtering with line defects



Valley filtering with 5-5-8 line defect



Gunlycke & White, PRL **106**, 136806 (2011)

Eigenstates in graphene:

$$|\Phi_\tau\rangle = \frac{1}{\sqrt{2}}\left(|A\rangle + ie^{-i\tau\theta}|B\rangle\right)$$

In the symmetry-adapted basis:

$$|\Phi_\tau\rangle = \frac{1+ie^{-i\tau\theta}}{2}|+\rangle + \frac{1-ie^{-i\tau\theta}}{2}|-\rangle$$

where

$$|\pm\rangle = \frac{1}{\sqrt{2}}\left(|A\rangle \pm |B\rangle\right)$$

Transmission:

$$T_\tau = \left|\langle + |\Phi_\tau\rangle\right|^2 = \frac{1}{2}\left(1+\tau\sin\theta\right)$$

Valley polarization

$$P_\tau = \frac{T_\tau - T_{-\tau}}{T_\tau + T_{-\tau}} = \tau\sin\theta$$

In general, all periodic defects with $k_{||}(K) \neq k_{||}(K')$ (e.g. class-Ib GBs) are expected to show valley filtering, because

$$T_\tau(\theta) = T(k_{||}) = T(-k_{||}) = T_{-\tau}(-\theta) \neq T_{-\tau}(\theta)$$

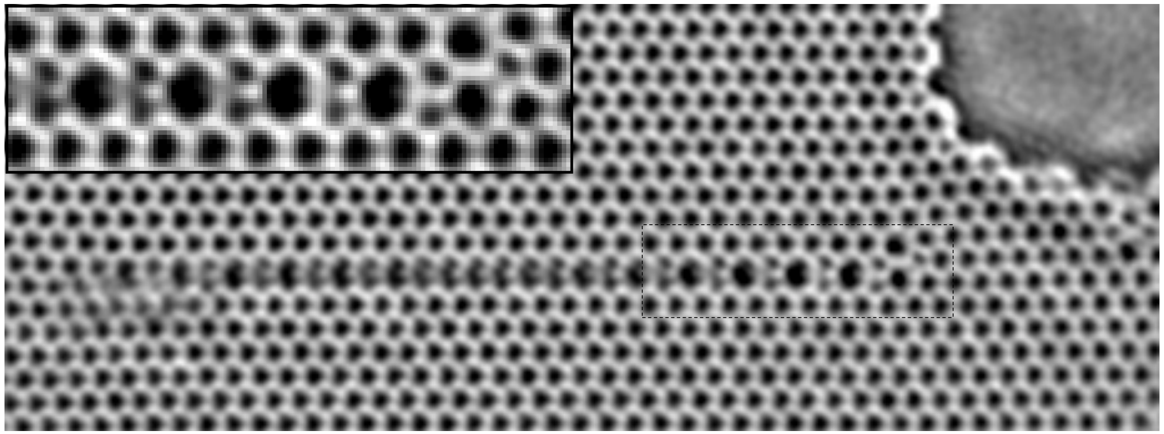
Why bother? Valleytronics!

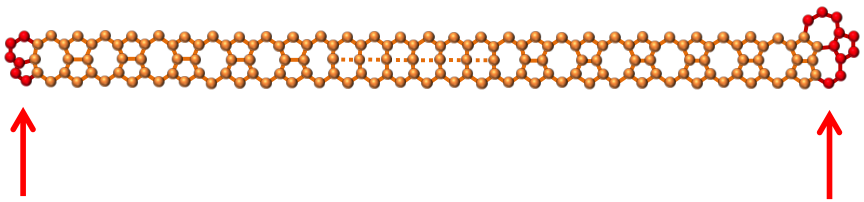
Rycerz, Tworzydlo & Beenakker, Nature Phys. **3**, 172 (2007)

Controlled production of 5-5-8 line defect

Controlled production in TEM microscope + electric current:

- Starts at the edge of a hole and proceeds via carbon atom removal;
- Combination of knock-on damage and electromigration (?)

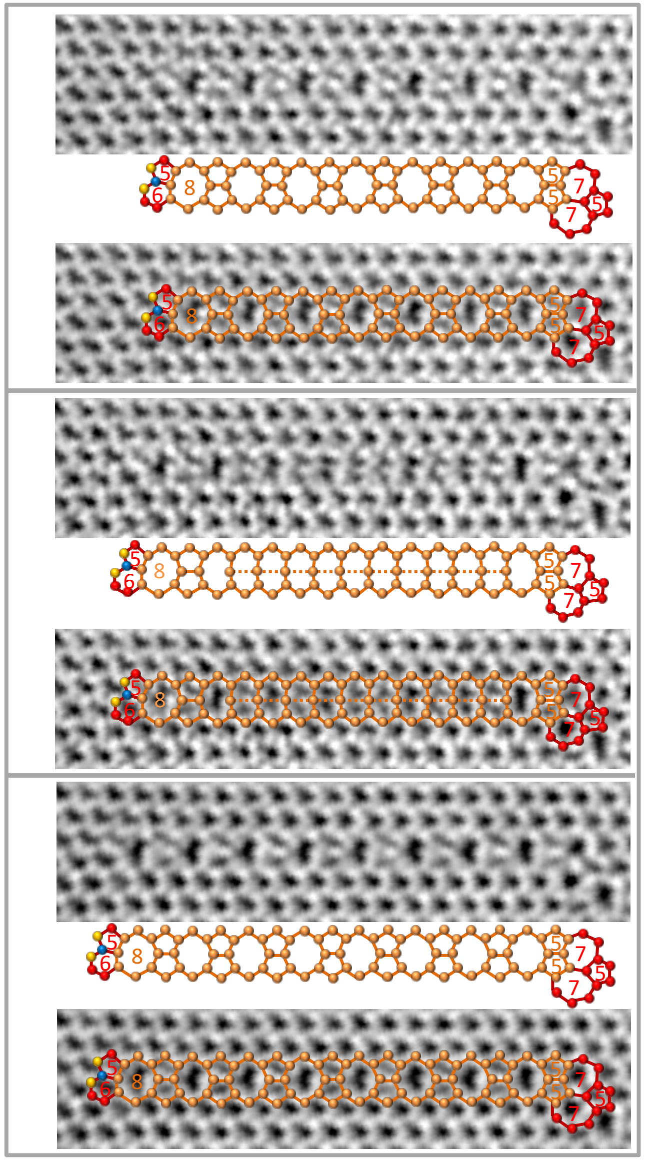




mobile end
E_{term} = 18 eV

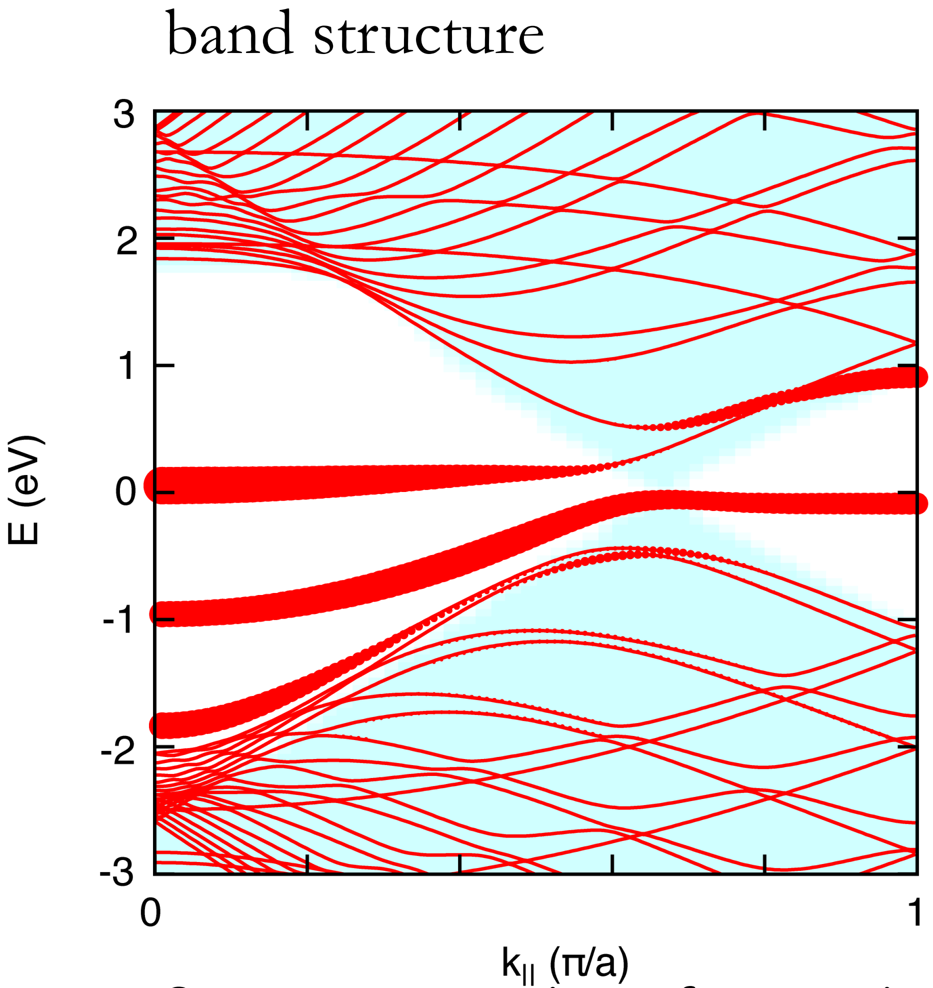
pinned end
E_{term} = 15 eV

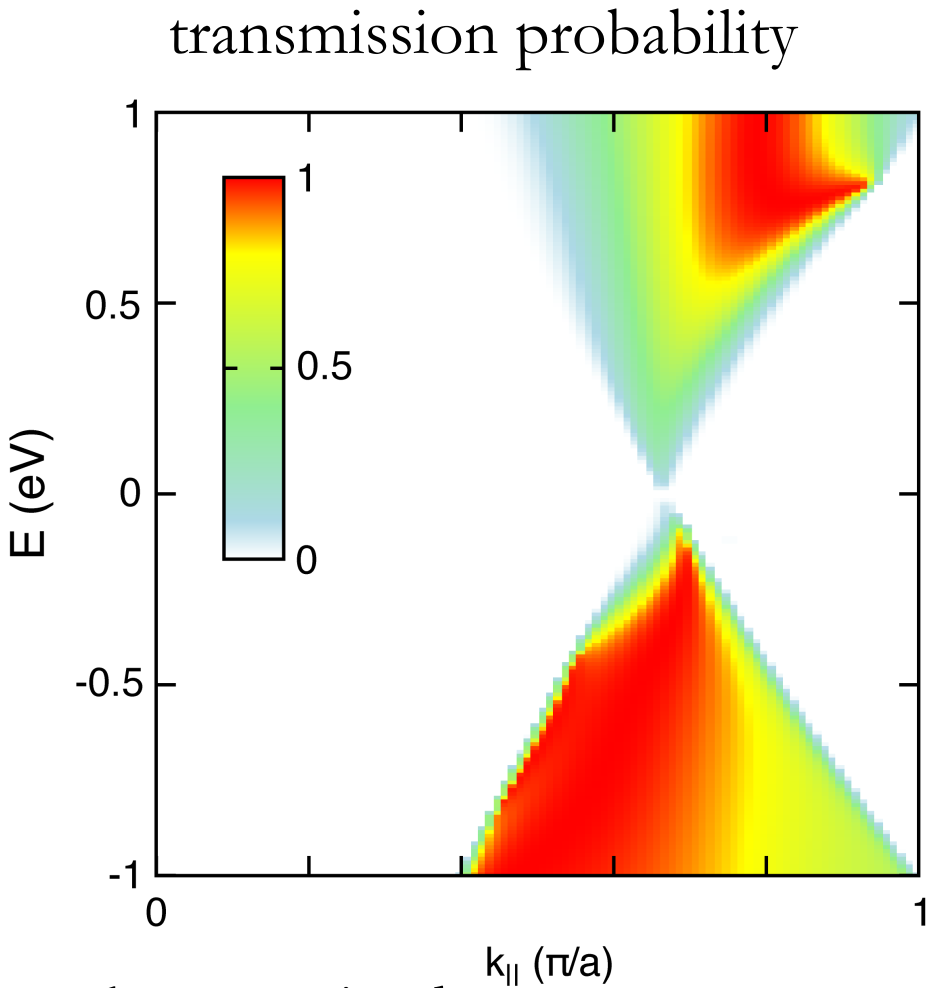
Growth dynamics:



Experiments: Zettl group (UC Berkeley)

First-principles results



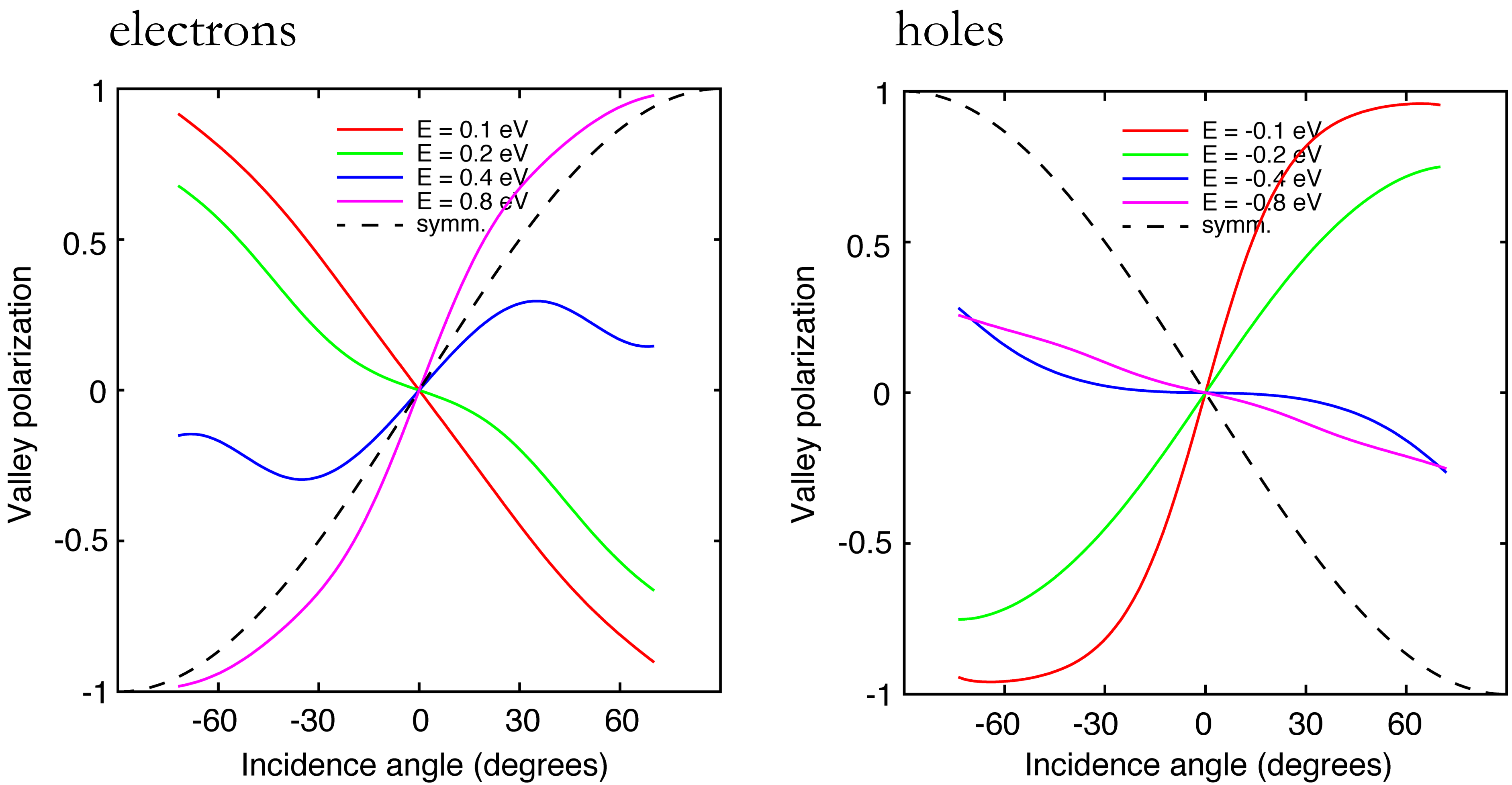


Strong suppression of transmission at low energies due to resonant backscattering on localized states

Calculations: Yazyev group (EPFL)

Chen *et al.*, Phys. Rev. B **89**, 121407 (2014)

Valley filtering from first-principles

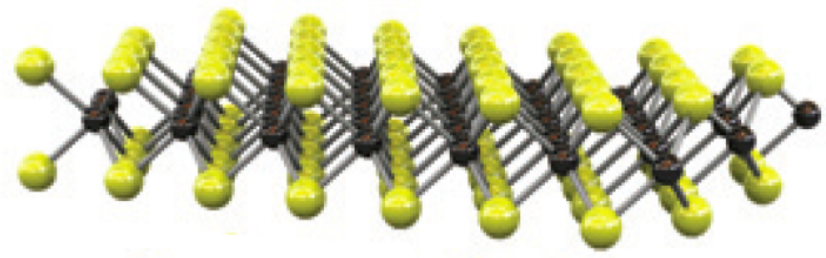


Strong energy dependence of valley polarization on charge-carrier energy

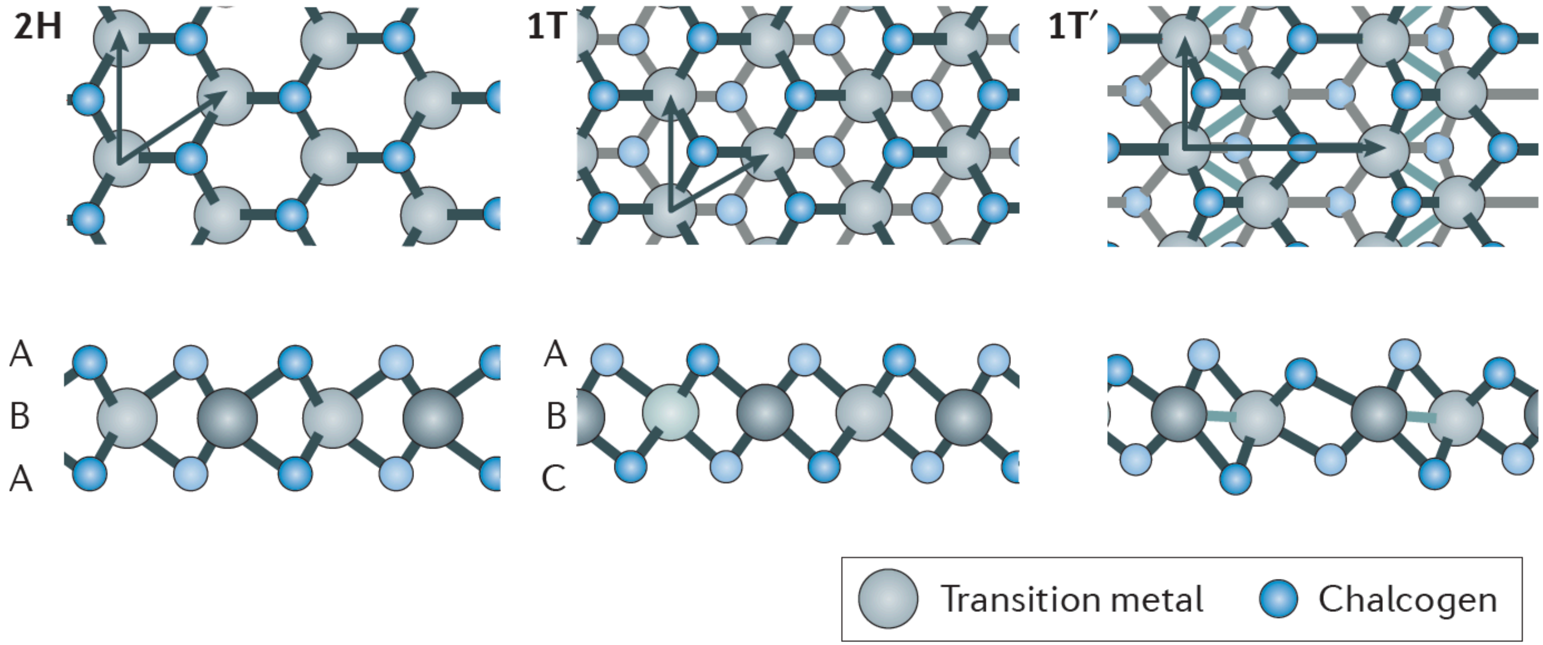
Calculations: Yazyev group (EPFL)

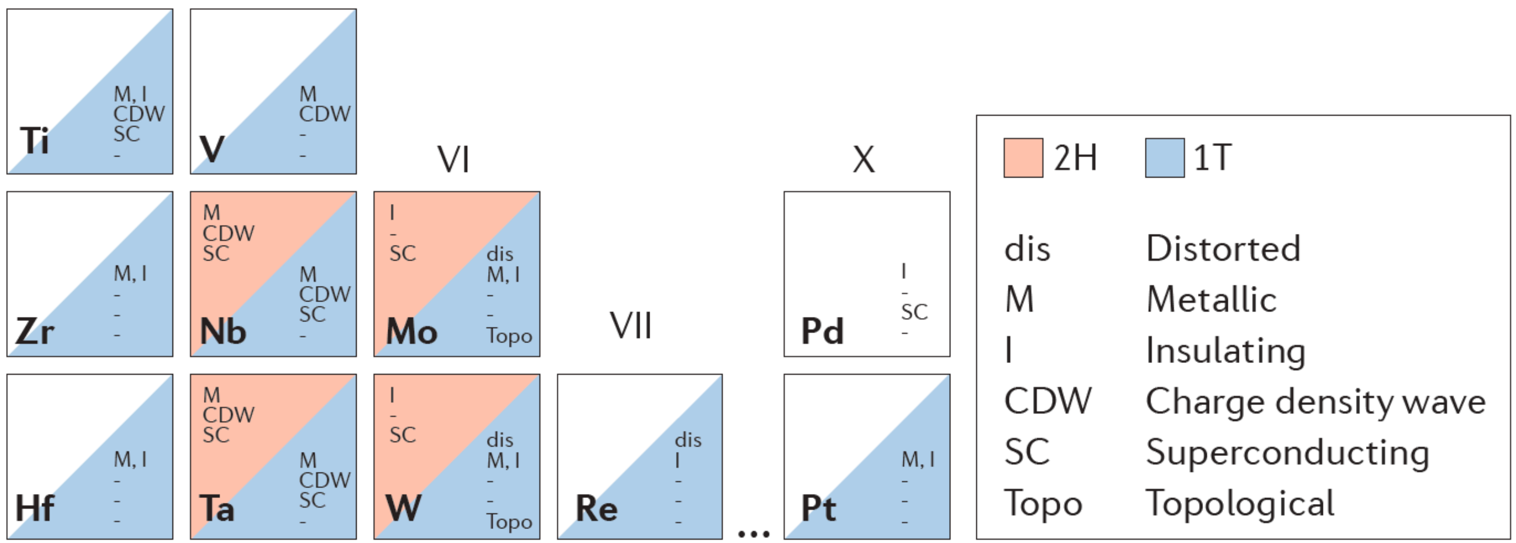
Chen *et al.*, Phys. Rev. B **89**, 121407 (2014)

IV. Valley/spin filtering in TMDs



2D transition metal dichalcogenides (TMDs)

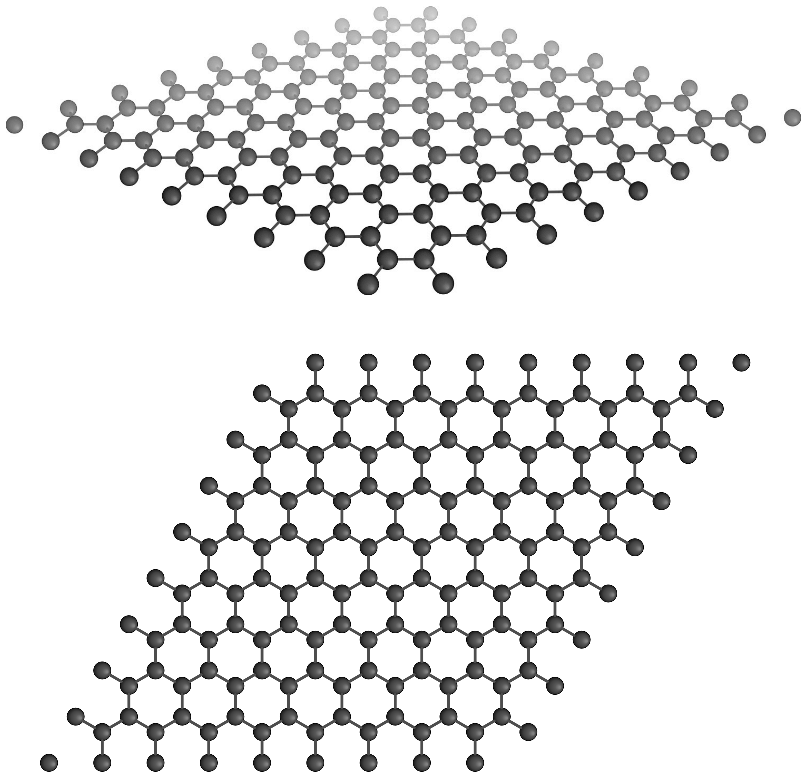




Manzeli, Ovchinnikov, Pasquier, Yazyev & Kis, Nature Review Materials **2**, 17033 (2017)

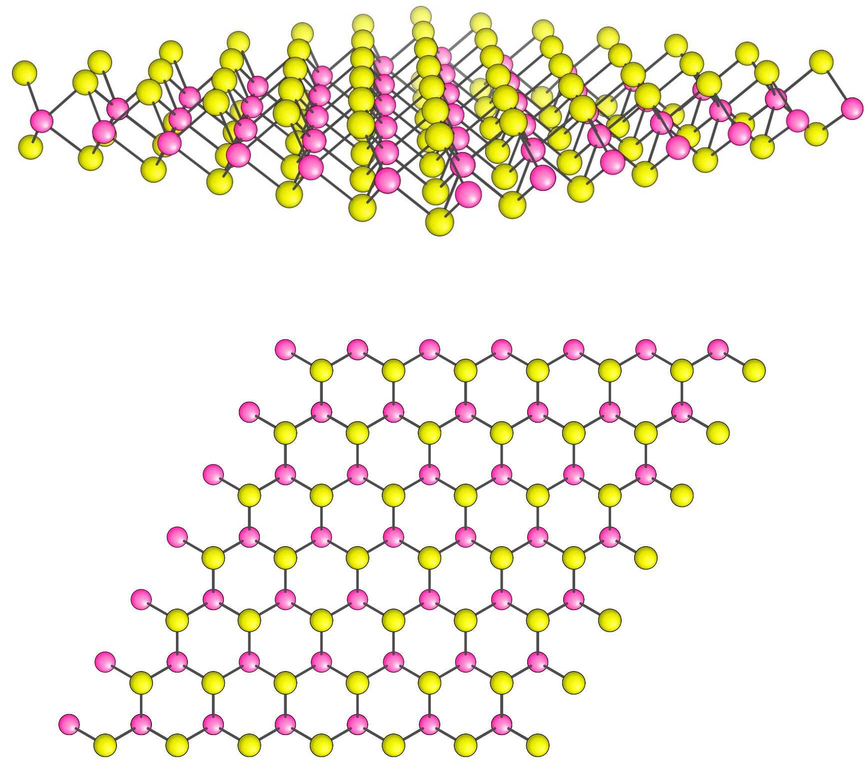
Graphene vs. TMDs: atomic structure

graphene



- hexagonal symmetry
- equivalent sublattices
- centrosymmetric

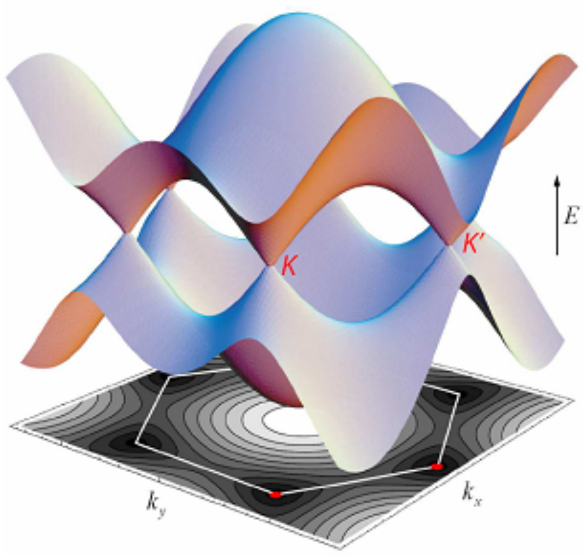
monolayer 2H MoS_2



- hexagonal symmetry
- inequivalent “sublattices”
- non-centrosymmetric

Graphene vs. TMDs: electronic structure

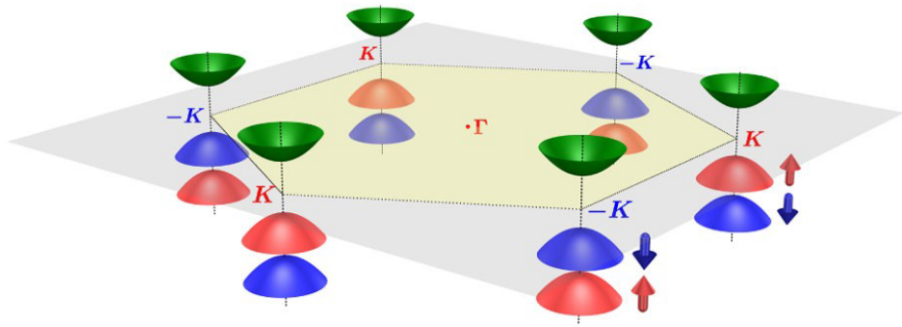
graphene



- semi-metal (E_g = ~ 0 eV)
- 2 valleys (points K and K')
- very weak spin-orbit coupling ($\Delta_{SO} = 2.4 \times 10^{-5}$ eV)

Gmitra *et al*, Phys. Rev. B **80**, 235431 (2009)

monolayer 2H MoS_2

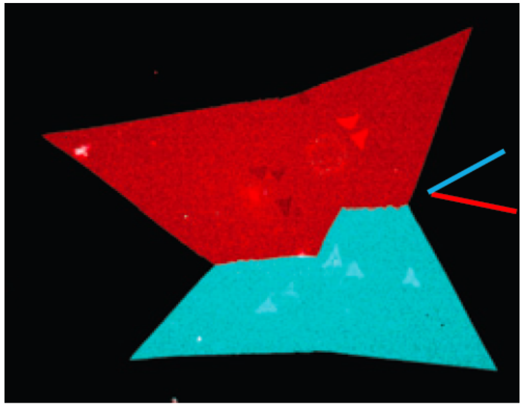


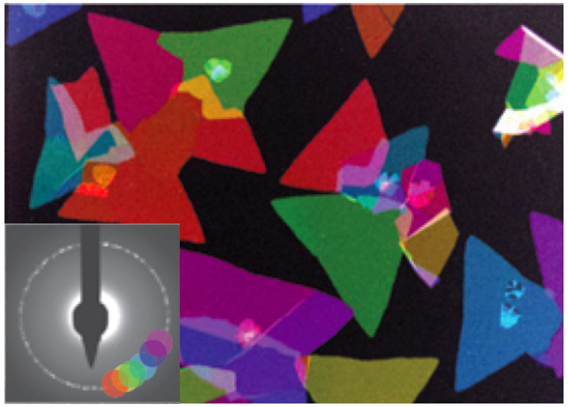
- semiconductor (E_g = 1.9 eV, DFT)
- 2 valleys (points K and K')
- strong spin-orbit coupling (Δ_{SO} = 0.15 eV for MoS_2, Δ_{SO} = 0.46 eV for WSe_2)

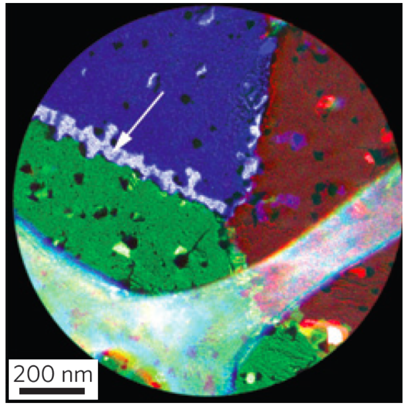
Zhu *et al*, Phys. Rev. B **84**, 153402 (2011)

Polycrystalline TMDCs

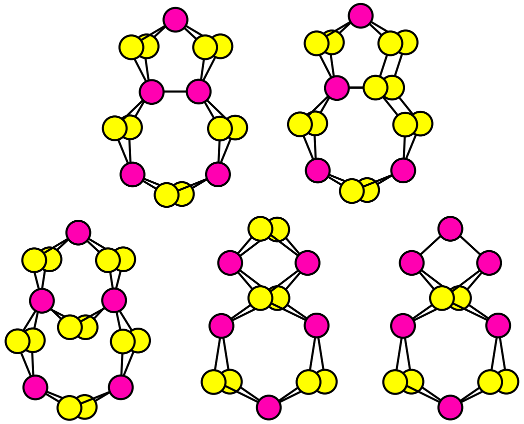
Aperture filtered DF-TEM images of CVD grown MoS_2



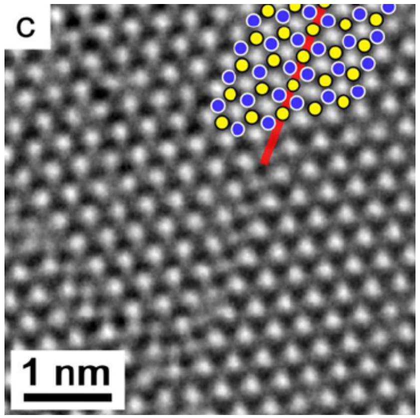


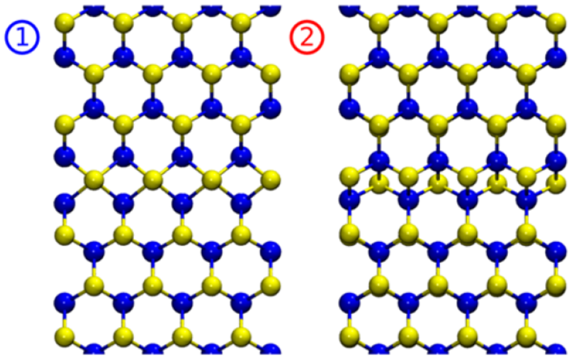


van der Zande *et al.*, Nature Mater. **12**, 554 (2013);
Najmaei *et al.*, Nature Mater. **12**, 754 (2013).



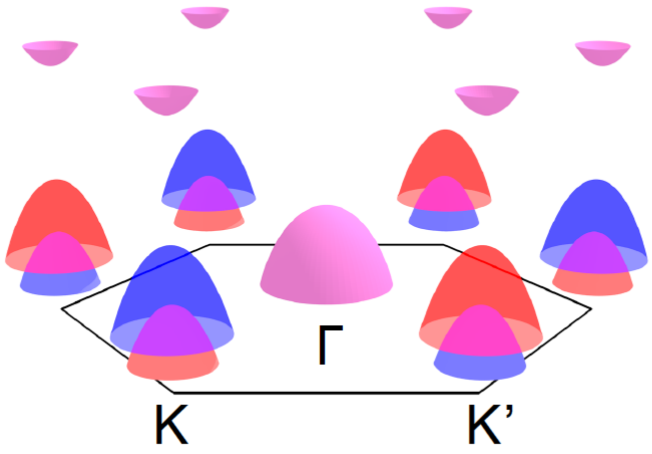
- Highly faceted grain boundaries
- Many different structures possible
- Abundance of inversion domain boundaries



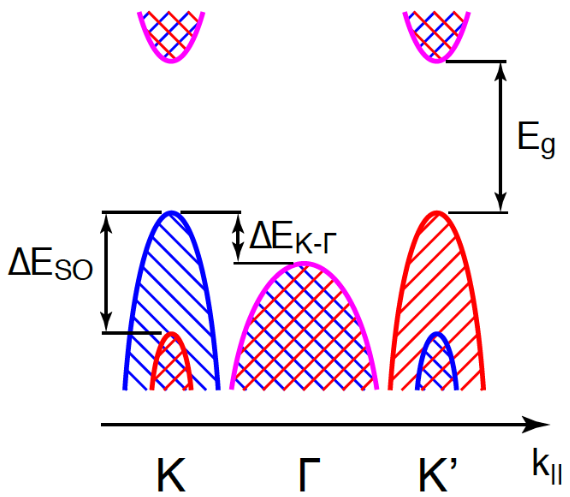


Zhou *et al.*, Nano Lett. **13**, 2615 (2013);
Lin *et al.*, Nature Nanotech. **9**, 391 (2014)
Lehtinen et al, ACS Nano **9**, 3274 (2015).

Possible transport scenarios

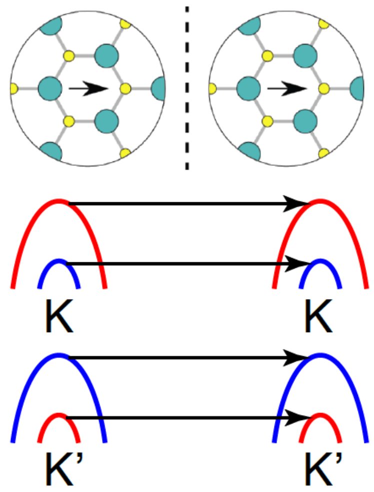


Band structure projected on lattice vector direction



Trivial scenario:

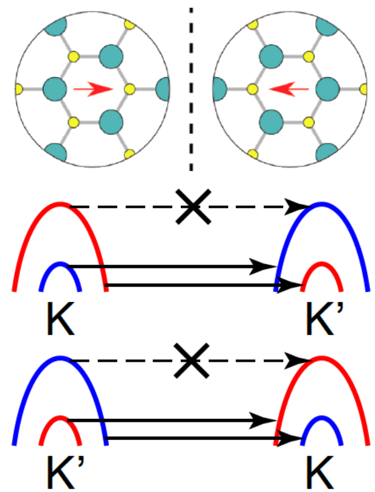
valley/spin filtering



Inversion domain boundary:

valley/spin filtering

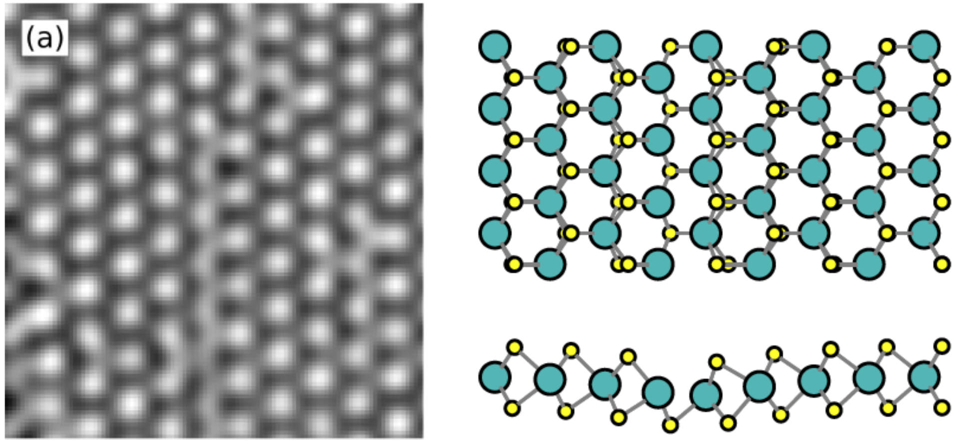
+ transport gap



Pulkin & Yazyev, PRB **93**, 041419(R) (2016)

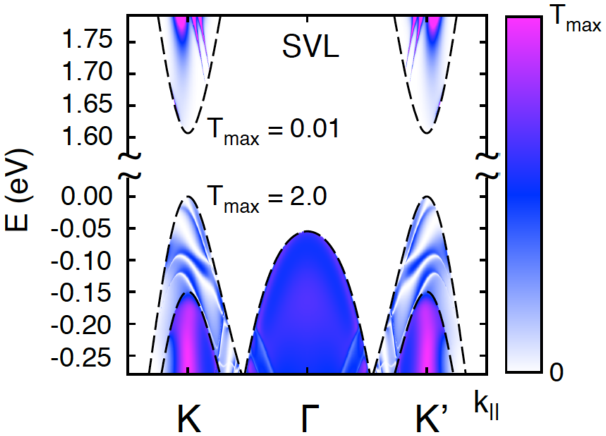
Trivial scenario

Ordered sulfur vacancy lines

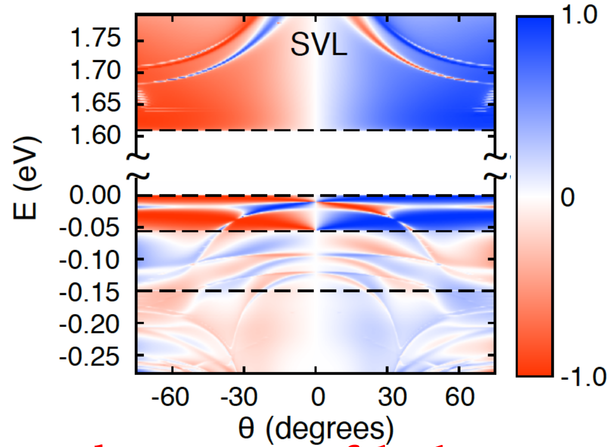


Komsa *et al.*, PRB **88**, 035301 (2013)

Transmission:



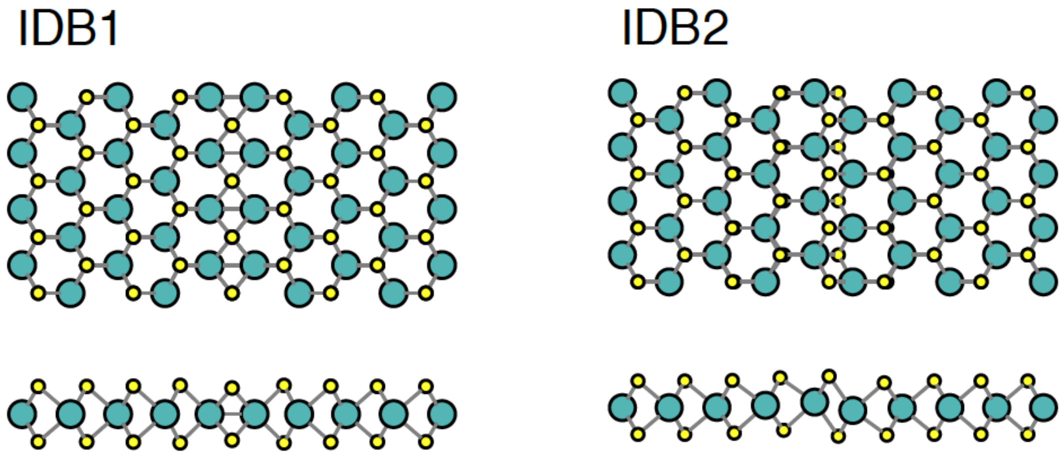
Valley/spin polarization:



- nearly 100% spin polarization and large conductances of holes;
- contrasting transmissions asymmetry of electrons and holes

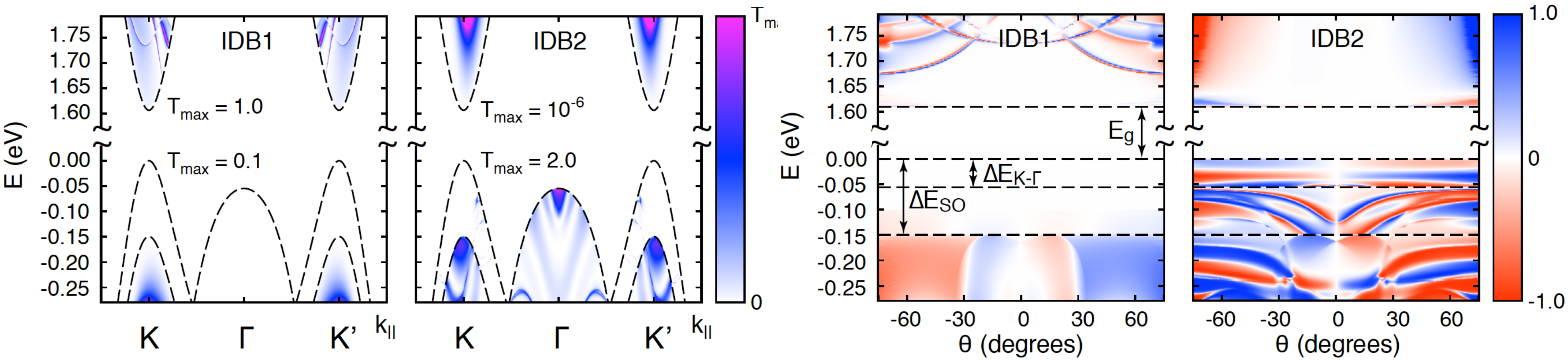
Pulkin & Yazyev, PRB **93**, 041419(R) (2016)

Inversion domain boundaries



Transmission:

Valley/spin polarization:



- spin-orbit transport gap of G-K offset magnitude
- contrasting transmissions asymmetry of electrons and holes

Pulkin & Yazyev, PRB **93**, 041419(R) (2016)

Acknowledgements

My group

Fernando Gargiulo

Artem Pulkin

Gabriel Autès

and

Steve Louie, Alex Zettl (UC Berkeley),
Jérôme Lagoute, Vincent Repain (Paris VII),
Andras Kis (EPFL), O. Lehtinen (Ulm)
H.-P. Komsa, A. Krasheninnikov (Helsinki)

Funding:

FNSNF
SWISS NATIONAL SCIENCE FOUNDATION

European Research Council
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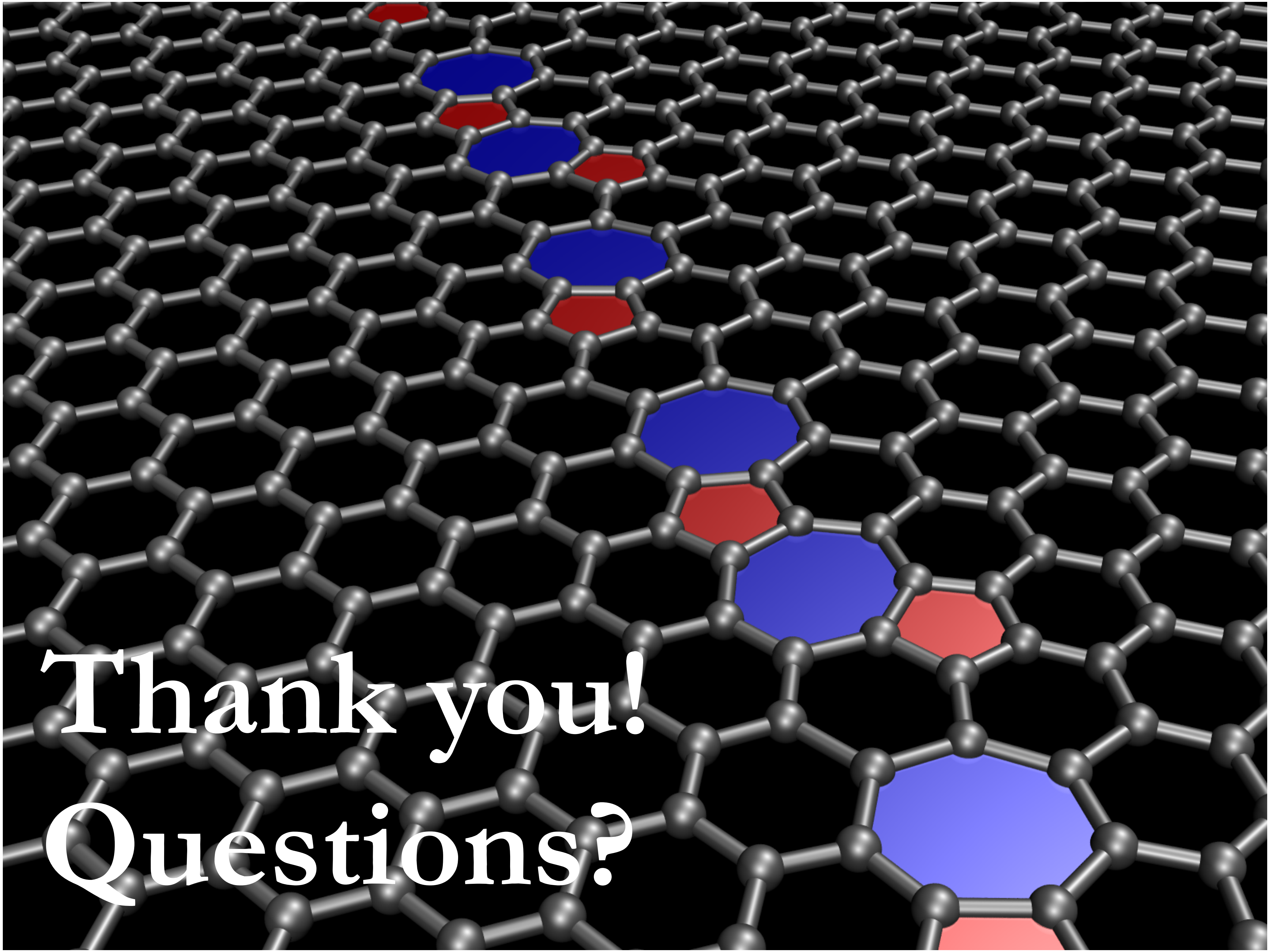
Thank you!
Questions?