Dislocation accommodation mechanisms in monolayer and bilayer graphene

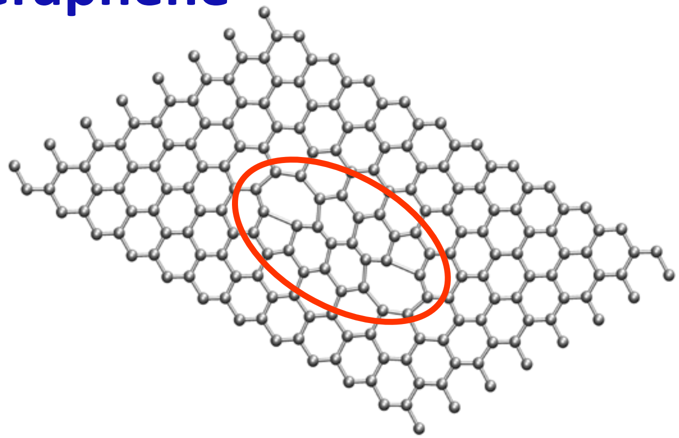
Pilar Ariza
Universidad de Sevilla

In collaboration with: **M. Ortiz**, **J.P. Méndez**, **F. Arca**, **J. Ramos**

Theory and Computation for 2D Materials
JANUARY 13 - 17, 2020

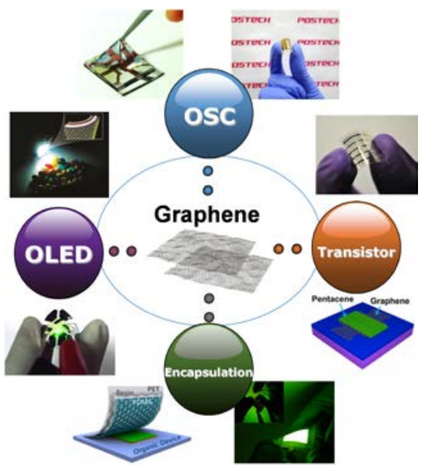
Motivation

Graphene



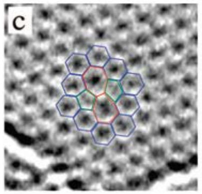
- Graphene is a truly 2D material
- Fabricated by:
  - *Mechanical/ chemical exfoliation*
  - *Epitaxial growth*
  - Chemical vapor deposition
- Electronic, thermal, chemical and mechanical properties **sensitive to lattice imperfections**

Key material: Next generation electronic devices



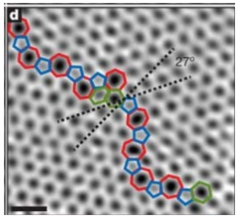
Graphene-based flexible electronic devices.
T.H. Han et al. *Materials Science Engineering: R:reports*, 118 (2017)

- Changes in **electronic properties** due to:
  - *Presence of point defects: dislocation arrangements, vacancies, etc.*



J. C. Meyer et al.
Nano Lett., 2008

  - *Geometry or linear defects: grain boundary structures, armchair or zig-zag nanoribbons, etc.*
  - *Doping elements.*



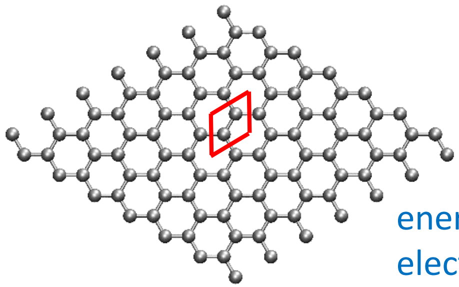
P. Y. Huang et al.
Nature, 1-4 (2010)

TIGHT BINDING POTENTIALS

- Stability of defects due to **thermal loading**

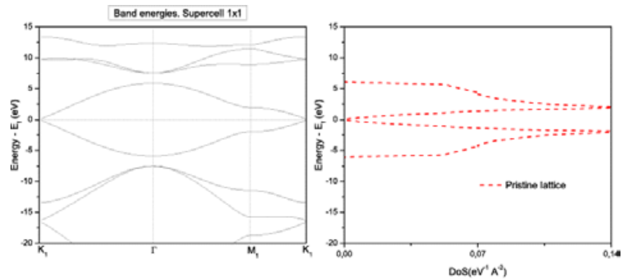
Graphene: electronic properties

Graphene lacks energy band gaps



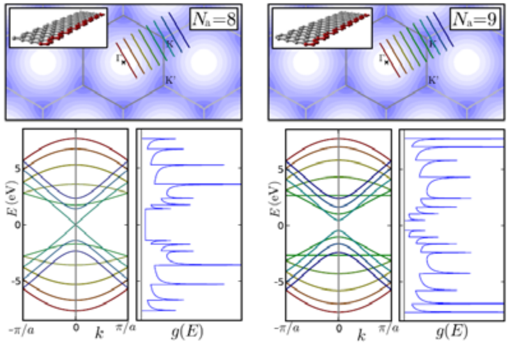
energy range where no
electron states can exist

Band Structures & Density of State (unit cell)



Nanoribbons

(armchair conf.)

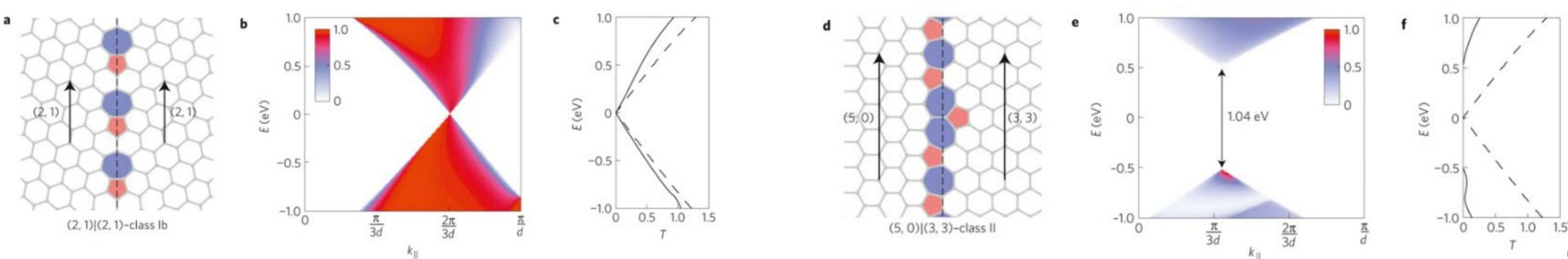


N. Nemec. Dr. Rer. Nat. Thesis.
Univeristy of Regensburg (2007)

Grain boundaries

Band gap: 0 eV

Band gap: ~ 1 eV



O.V. Yazyev & S.G. Louie. Nature Materials 9, 806–809 (2010)

DFT studies

Defects in graphene – Our Approach

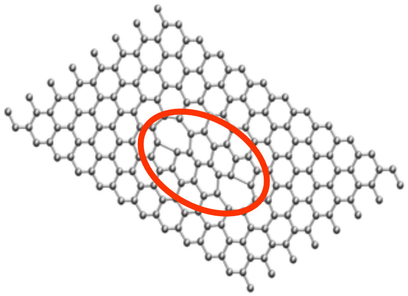
Main issues of interest:

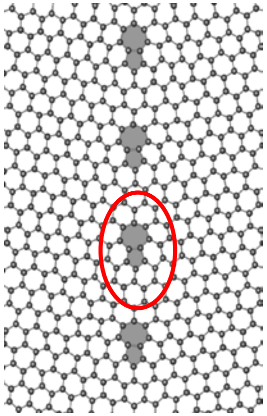
- Properties of individual defects: Core structure, core energies, limiting behaviors (dilute, continuum…)

Ariza and Ortiz, ARMA (2005), JMPS (2010)

Our harmonic approach:

✓ Discrete lattice elasticity, discrete defects
✓ Discrete dislocations as eigendeformations
✓ Discrete Fourier transform, closed-form solutions (**u** and E)





- Stability of defects: Relaxed core structures, thermal stability,…

1. Anharmonic approach:

Gallego and Ortiz (1993) Mod. Simul. Mater. Sci. Eng., 1:417–436

✓ Extension of the Discrete Dislocation theory

2. Molecular dynamics: LAMMPS code

thermal effects

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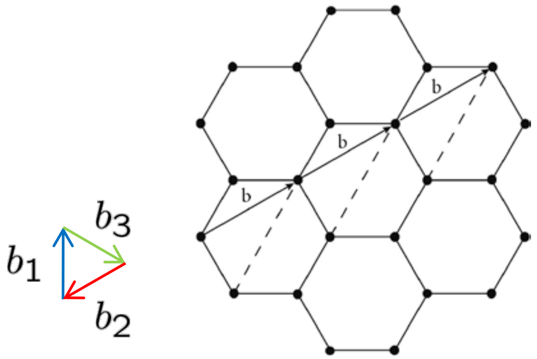
Discrete Dislocation Theory

- Harmonic energy of defective graphene:

$$E_H(u,\beta) = \frac{1}{2}\langle B(du-\beta),(du-\beta)\rangle - \langle f,u\rangle$$

$u \equiv$ displacement field
$\beta \equiv$ eigendeformations

$du \equiv$ bond deformation
$f \equiv$ applied forces



$$\beta(e_1) \in b_1\mathbb{Z} + b_2\mathbb{Z} + b_3\mathbb{Z}$$

- Displacement equilibrium problem:

$$E_H(\beta) = \min_u E_H(u,\beta) \;\Rightarrow\; u_H^* = A^{-1}(f^E + f)$$

$$\boxed{DE(u_H^*) \neq 0}$$

Gallego and Ortiz (1993) Mod. Simul. Mater. Sci. Eng., 1:417–436

- Non-equilibrium anharmonic energy function $E(u_H^*)$:

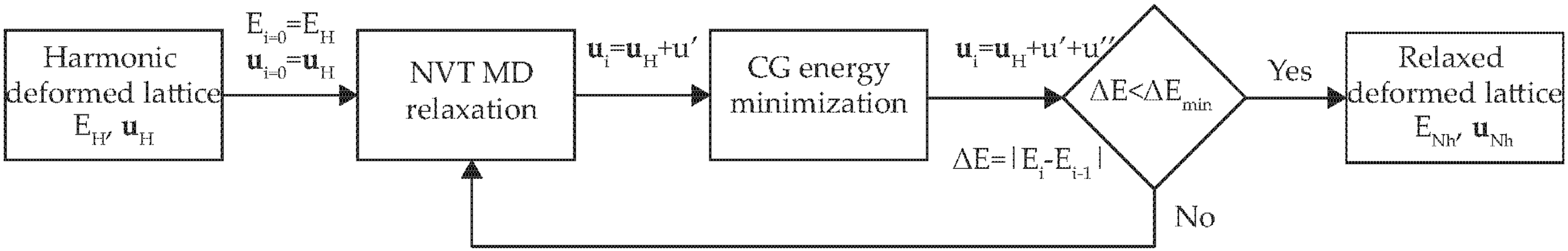
$$f^{(k+1)} = f^{(k)} - \alpha_k \cdot \delta DE(A^{-1}(f^E + f^{(k)}))$$

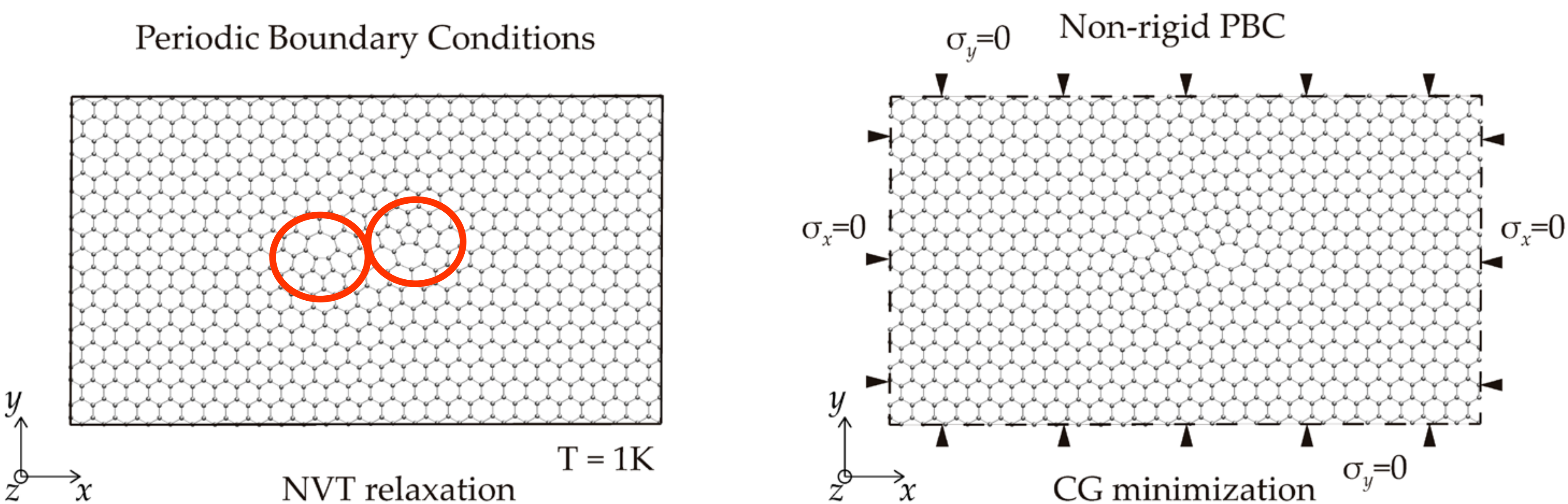
Fixed point iteration method

$$DE(A^{-1}(f^E + f^{(k)} - \alpha_k \delta DE(A^{-1}(f^E + f^{(k)})))) = 0$$

$$\boxed{u^* = A^{-1}(f^E + f^*)}$$

Energy minimization





Graphene: interatomic potentials

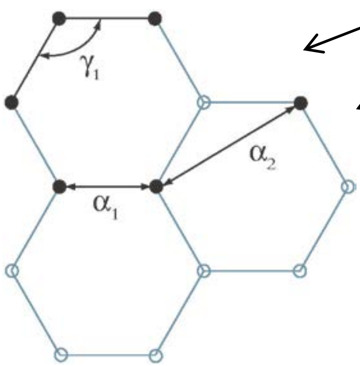
Harmonic potentials

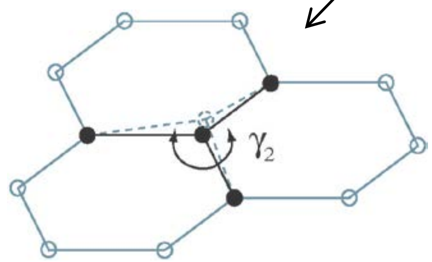
interaction with substrate

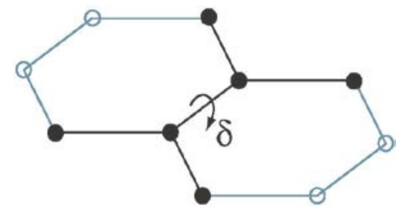
$$E(u) = V_1 + V_2 + V_3 + V_4 + V_5 + V_6$$

$\alpha_1, \alpha_2, \gamma_1, \gamma_2, \delta, \alpha_s$

$$\Psi\begin{pmatrix} l \\ \alpha,\beta \end{pmatrix}$$





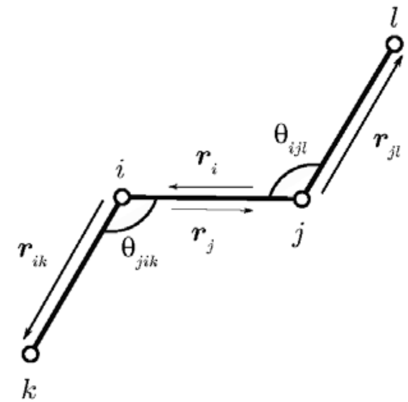


Aizawa, T. et al., “Bond Softening in Monolayer Graphite Formed on Transition-Metal Carbide Surfaces” Phys. Rev. B, 42(18) (1990)11469--11478

Bond order potentials

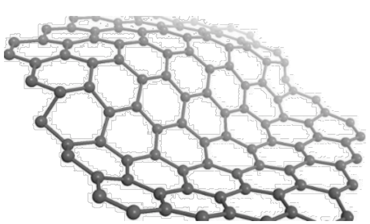
Stuart SJ, Tutein AB, Harrison JA
J Chem Phys 112(14):6472–6486

$$E = \frac{1}{2}\sum_i \sum_{j\neq i}\left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k\neq i,j}\sum_{l\neq i,j,k} E_{kijl}^{tors}\right]$$



AIREBO potential

LCBOP potential



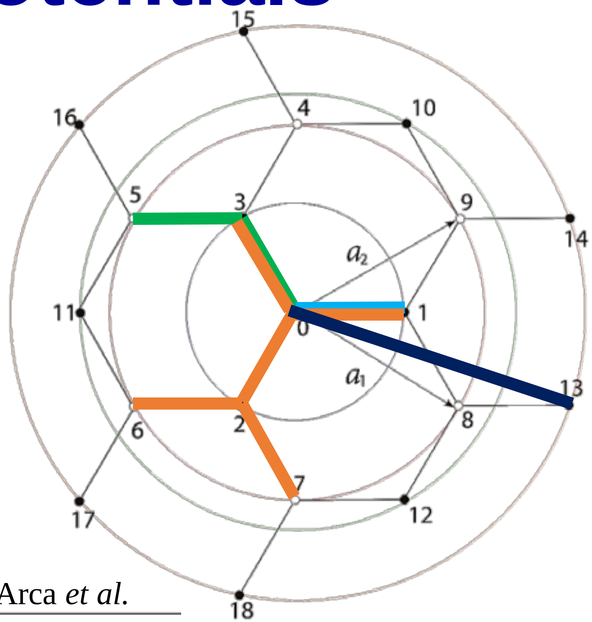
$$E_b = \frac{1}{2}\sum_{i,j}^{N_{at}}\left(S_{sr,ij}^{down}V_{ij}^{sr} + S_{sr,ij}^{up}V_{ij}^{lr} + \frac{1}{Z_i^{mr}}S_{mr,ij}^{up}V_{ij}^{mr}\right)$$

Jan H. Los et al.
Phys. Rev. B, 2005

Graphene: interatomic potentials

Tight-binding potentials

Xu, C. H. et al.,
J. Mech. Phys.: Condens. Matter, 4(28) (1992) 6047



	Wirtz *et al.*	Tewary *et al.*	Ariza *et al.*	Ariza *et al.*	Mendez *et al.*	Arca *et al.*
α_1	399.0	409.7	364.0	527.7	497.2	423.6
β_1	135.7	145.0	247.0	68.1	173.7	144.3
δ_1	292.8	98.9	100.5	118.3	106.9	75.7
α_2	-79.6	-40.8	-30.8	5.8	-41.43	-6.5
β_2	67.8	74.2	72.3	32.7	58.1	29.9
γ_2	39.2	-9.1	-17.8	26.7	-3.0	-23.7
δ_2	0.9	-8.2	-11.5	-16.9	-15.9	-8.8
α_3	0.0	-33.2		0.0	-20.64	4.0
β_3	0.0	50.1		0.0	34.51	-0.8
δ_3	-34.3	5.8		3.7	9.1	-0.8
α_4	0.0	10.5		0.0		0.3
β_4	0.0	5.0		0.0		0.0
γ_4	0.0	2.2		0.0		0.1
τ_4	0.0	-2.2		0.0		0.1
δ_4	17.1	-5.2		-1.8		0.0

Wirtz et al.
Solid State Comm., 2004

Tewary et al.
Phys. Rev. B, 2009

Ariza et al.
JPMS, 2010

Ariza et al.
Met. Num. Cal., 2011

Mendez et al.
JPMS, 2016

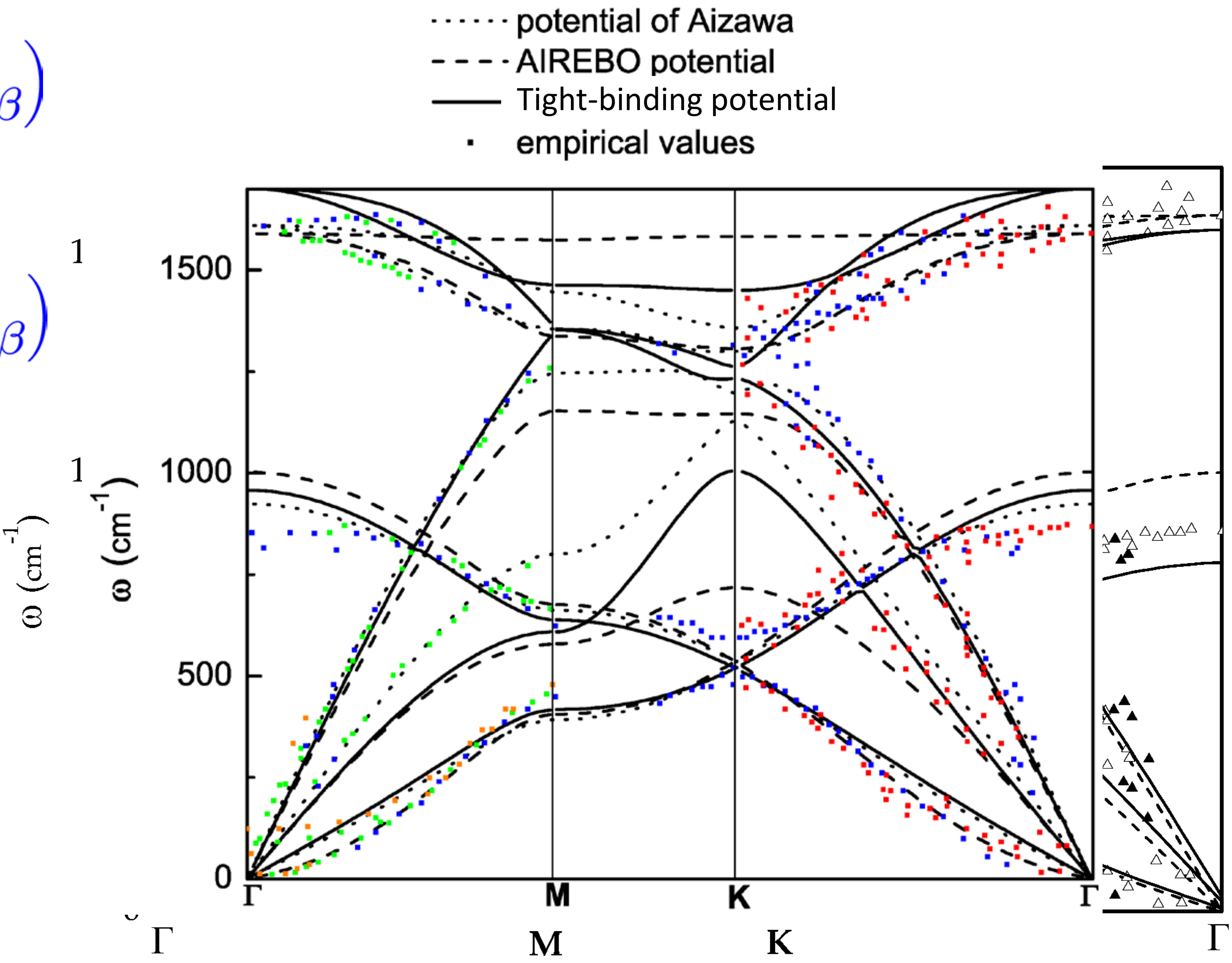
Arca et al.
Acta Materialia, 2019

Graphene: interatomic potentials

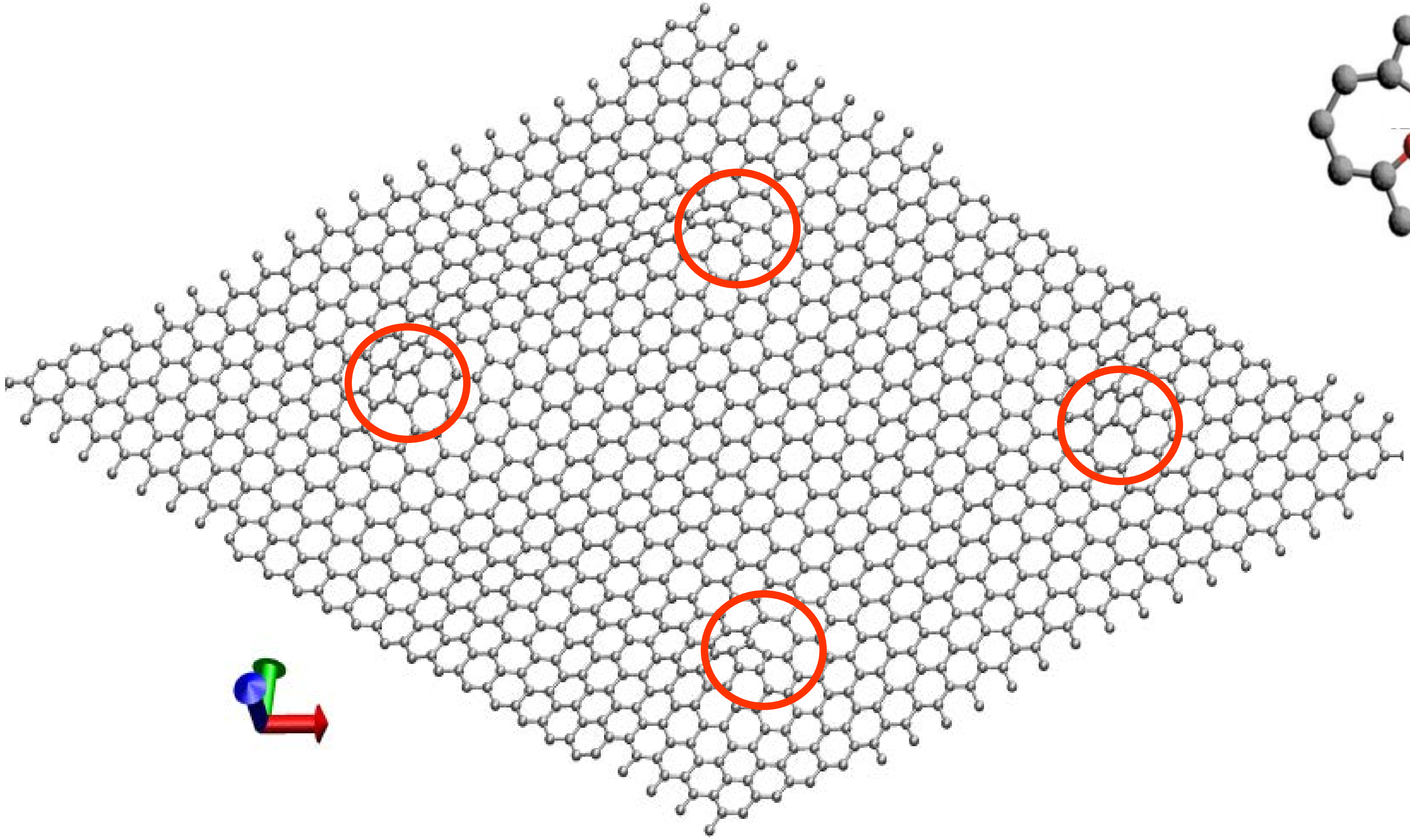
$$\Psi\binom{l}{\alpha,\beta}$$

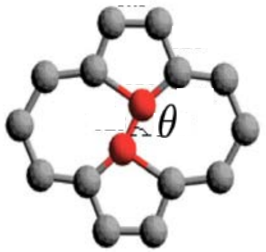
↓

$$\Phi\binom{l}{\alpha,\beta}$$



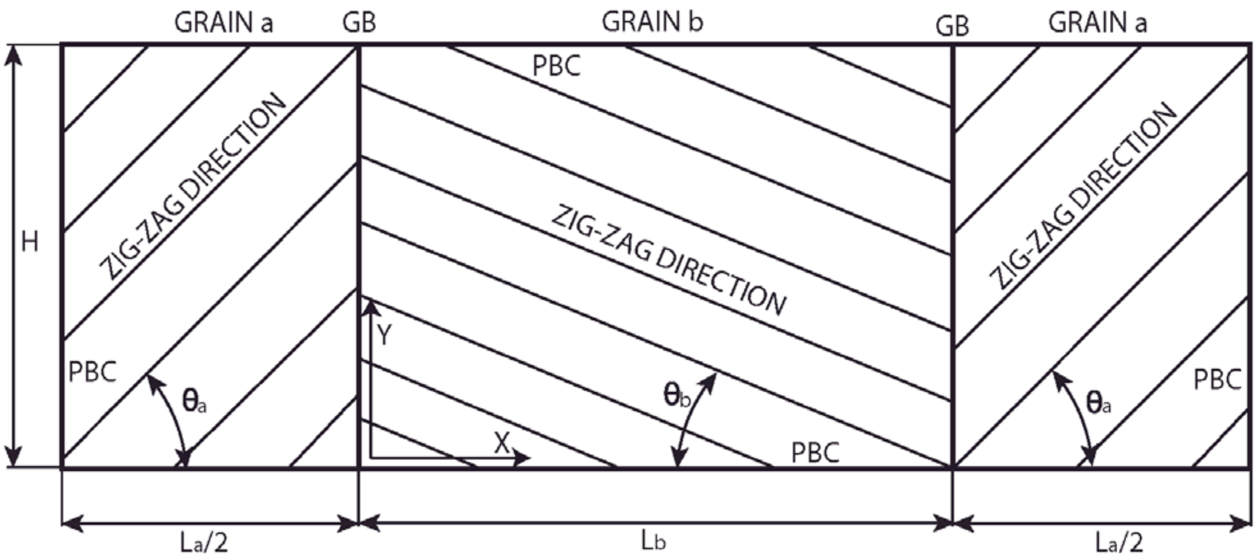
Our approach – Stability of core structures

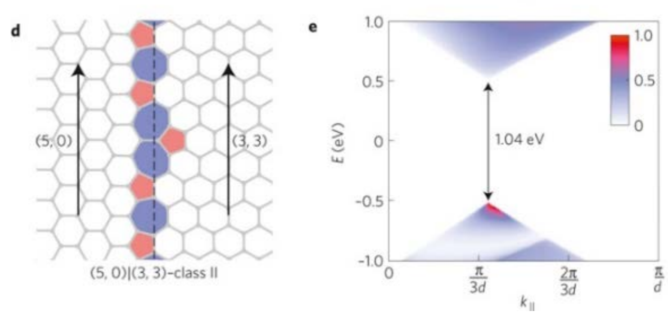




- Dislocation cores predicted by the discrete-dislocation are stable with respect to fully non-linear potentials and in agreement with observation and first-principles calculations
- Dislocation cores appear stable up to high temperatures (2500 K)

Linear defects: grain boundaries in graphene





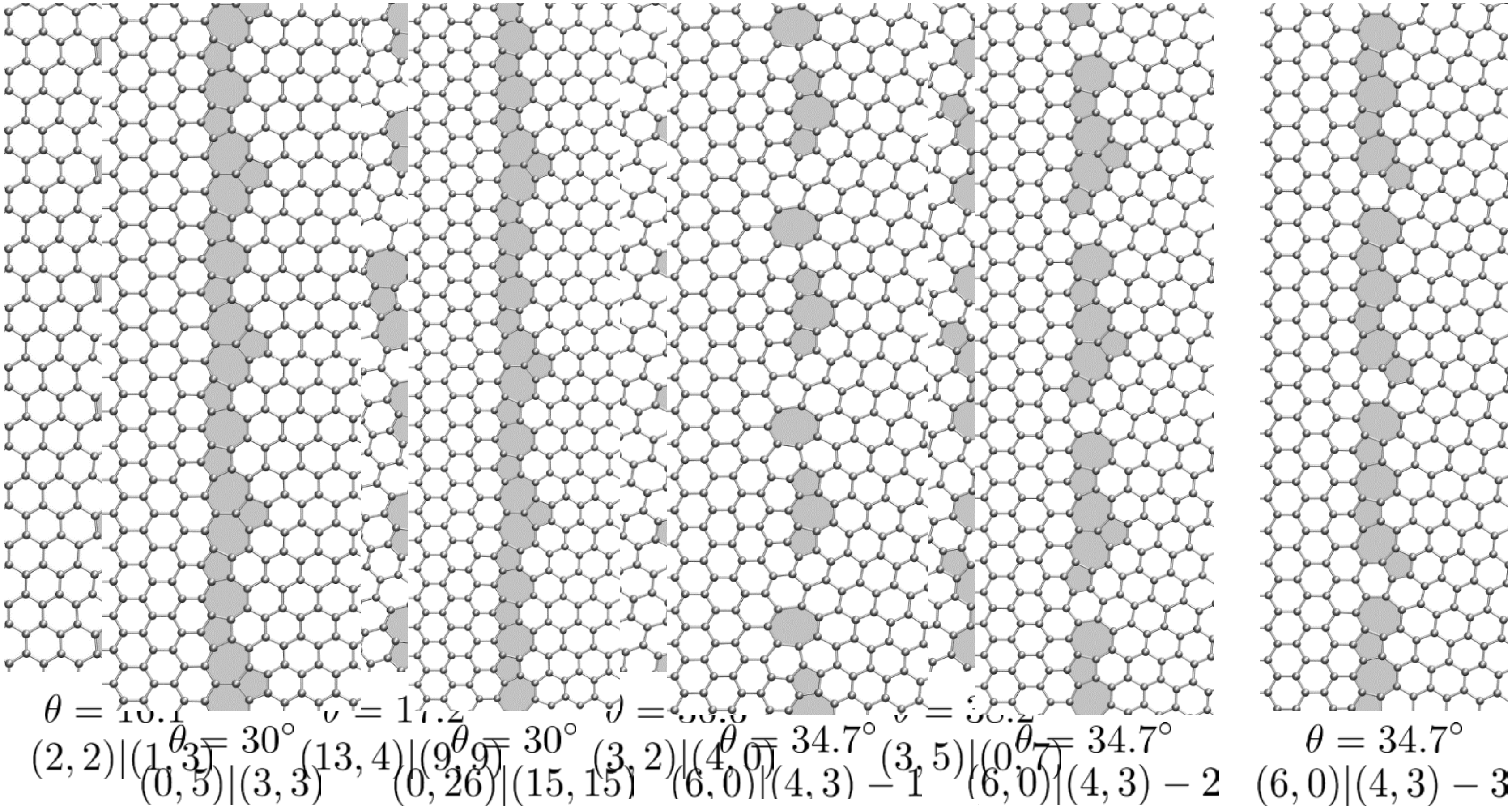
O. V. Yazyev et al.
Nature Materials, 2010

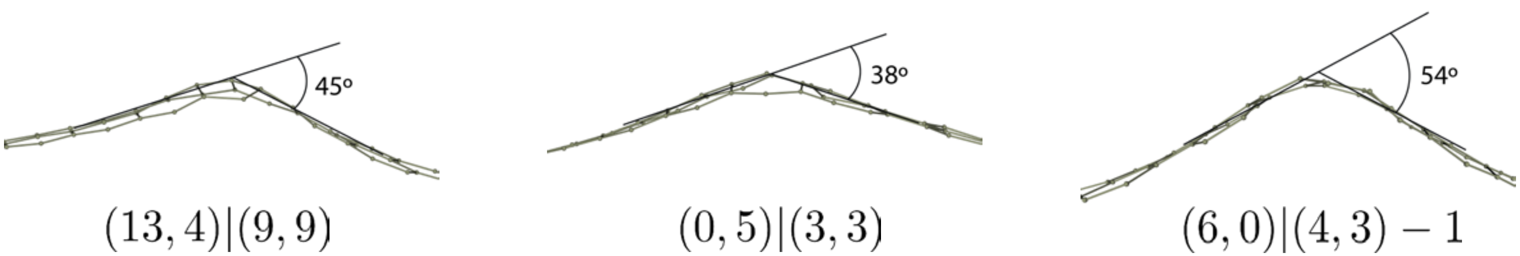
Angle θ	θ_a	θ_b	GB configuration (n_a,m_a) | (n_b,m_b)	H (Å)	Energy (eV/Å)	Energy (eV/Å)
16.1°	16.1°	0°	(2,2)|(1,3)	8.5	0.427	0.482
17.2°	0°	17.2°	(13,4)|(9,9)	37.6	0.499	
36.6°	30°	6.6°	(4,0)|(3,2)	9.9	0.548	0.591
38.2°	8.2°	30°	(3,5)|(0,7)	16.9	0.483	0.457
30°	0°	30°	(0,5)|(3,3)-1	12.2	0.531	0.503
30°	0°	30°	(0,5)|(3,3)-2	62.8	0.505	
34.7°	30°	4.7°	(6,0)|(4,3)-1	14.6	0.451	
34.7°	30°	4.7°	(6,0)|(4,3)-2	14.6	0.535	0.575
34.7°	30°	4.7°	(6,0)|(4,3)-3	14.6	0.476	0.472

J. Zhang et al.
Carbon, 2013

Stable ASYMMETRIC grain boundaries

Cell sizes: 380 – 9772 atoms

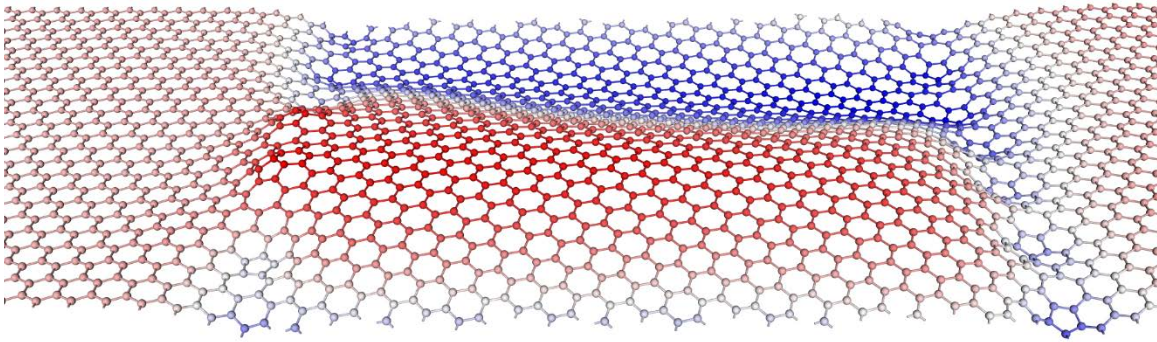


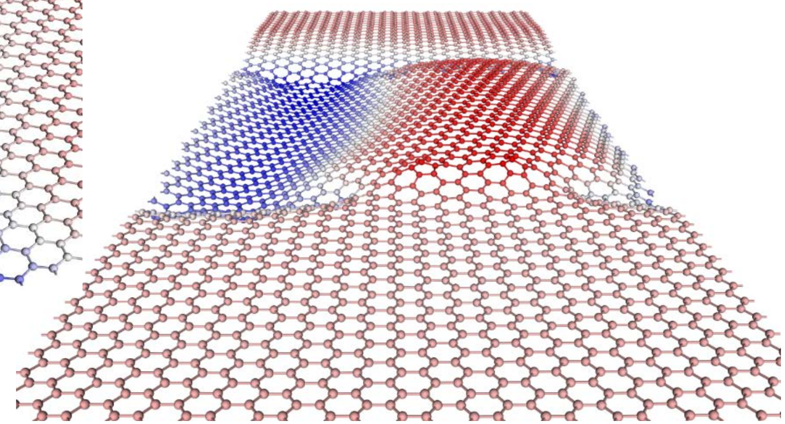


Local wrinkle structures

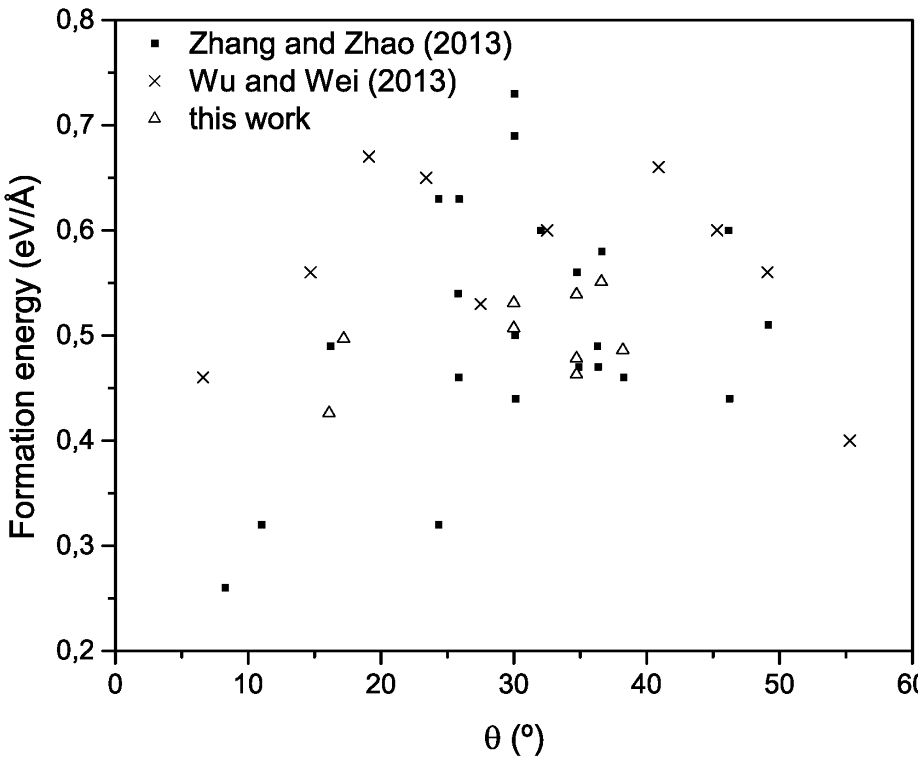
Stable ASYMMETRIC grain boundaries

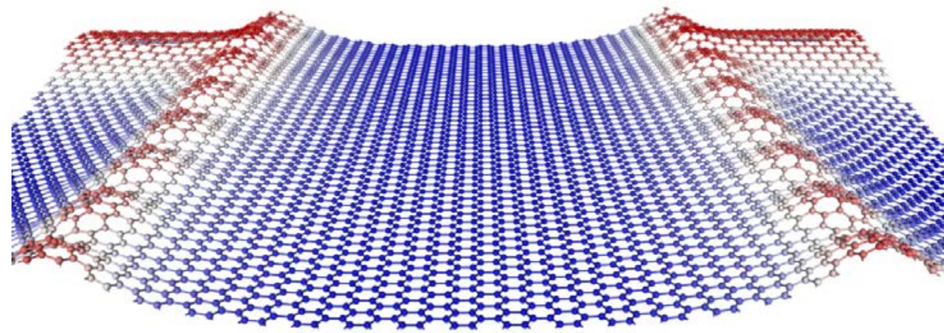
Together with secondary wrinkle structure.





(2,2)|(1,3), θ = 16.1°



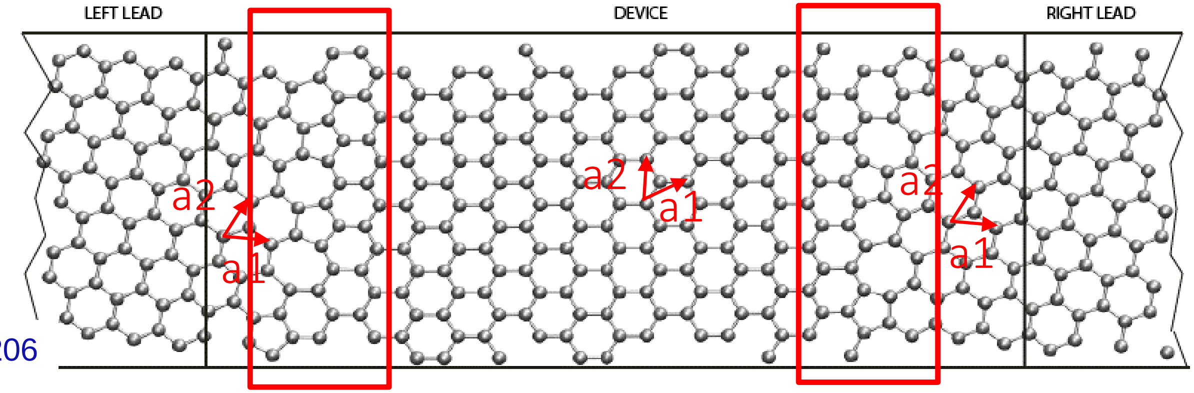


(6,0)|(4,3)-1, θ = 34.7°

Wu and Wei, JMPS 511, 61 (2013) 1421–1432
Zhang and Zhao, Carbon 55 (2013) 151–159
Mendez et al. Acta Materialia 154 (2018) 199–206

Transport properties across grain boundaries

A tight binding model (C.H. Xu et al., 1992) and the Landauer-Büttiker formalism

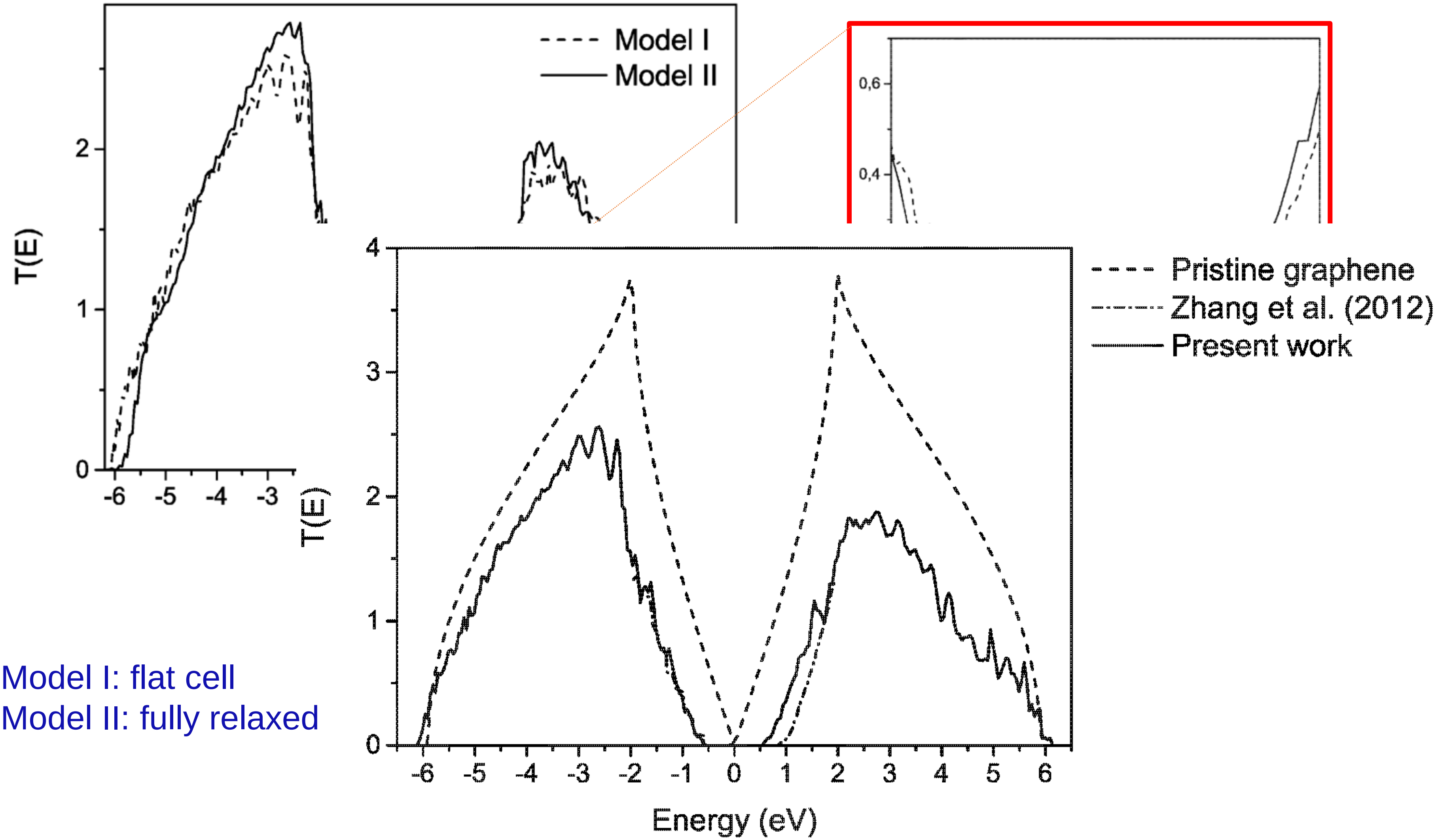


Mendez et al. Acta Materialia 154 (2018) 199–206

GB configuration	Transport gap (eV)	H (Å)	$\|\Delta d\|/d_{min}$ (%)
(2,2)|(1,3)	1.15	8.5	4.08
(13,4)|(9,9)	0.29	37.6	1.26
(4,0)|(3,2)	0.24	9.9	8.96
(3,5)|(0,7)	0.0	16.9	0.0
(0,5)|(3,3)-1	0.88	12.2	3.92
(0,5)|(3,3)-2	0.59	62.8	0.07
(6,0)|(4,3)-1	0.72	14.6	1.40
(6,0)|(4,3)-2	0.77	14.6	1.40
(6,0)|(4,3)-3	0.68	14.6	1.40

Correlation between transport gap and lattice mismatch |Δd|/dmin

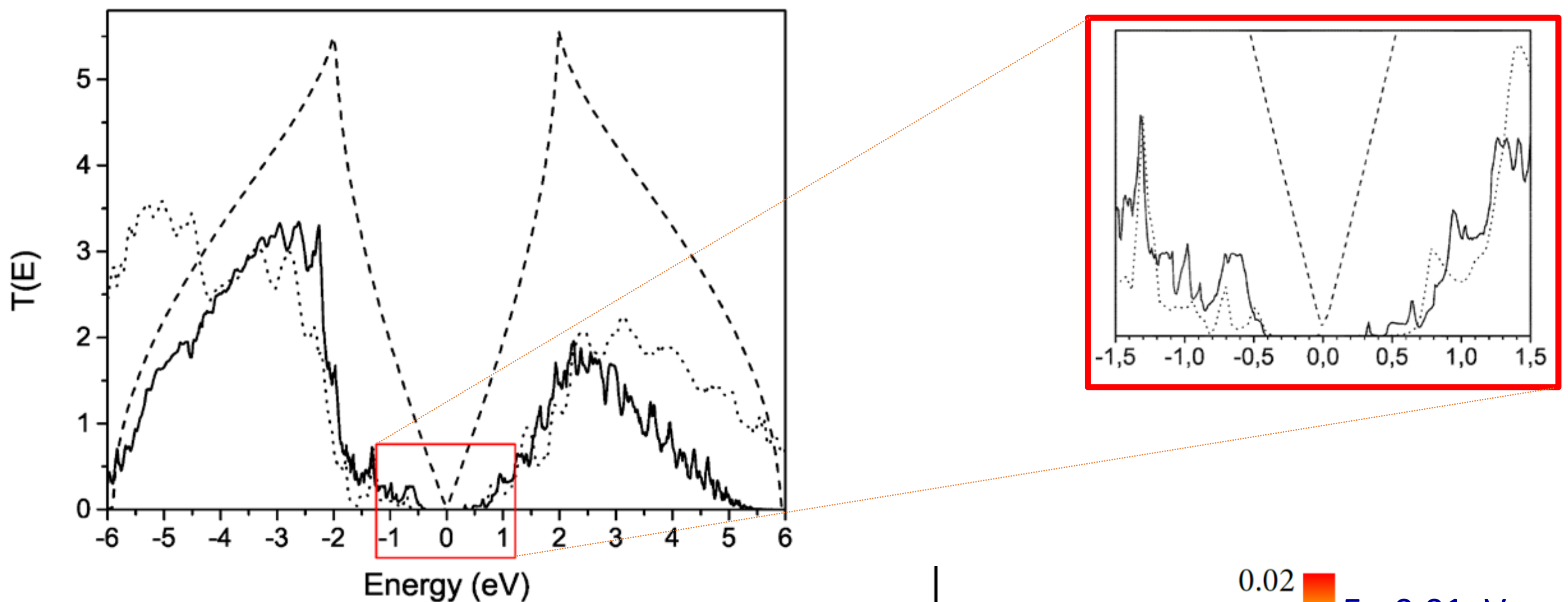
Transport properties across grain boundaries



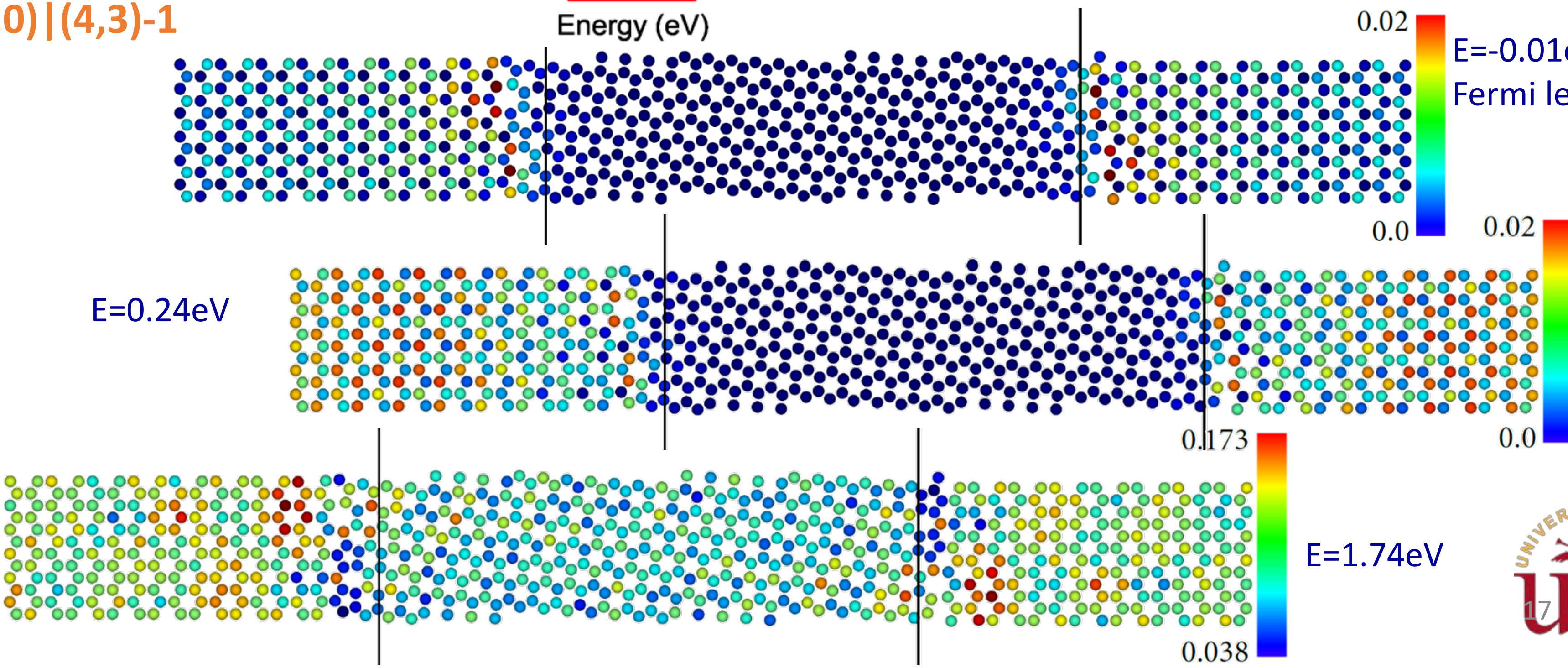
Model I: flat cell
Model II: fully relaxed

Mendez et al. Acta Materialia 154 (2018) 199–206

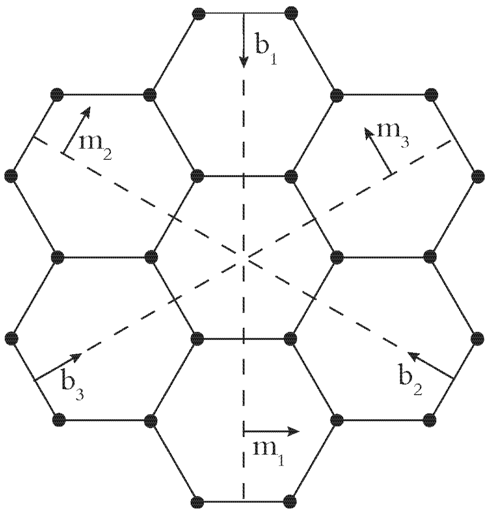
Transport properties across grain boundaries



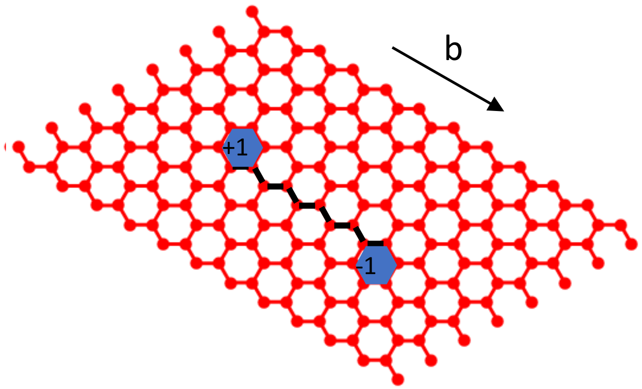
(6,0)|(4,3)-1



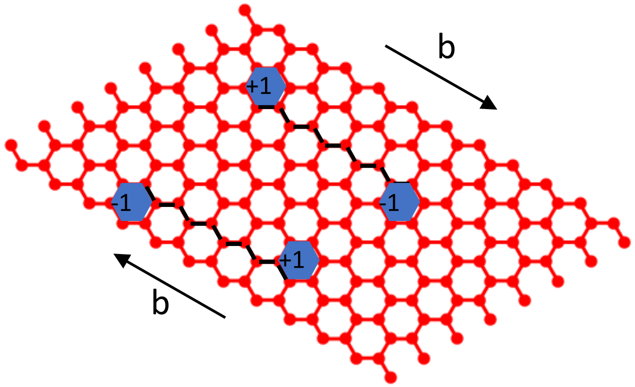
Point defects: dislocations in graphene



periodic arrangement of dislocations

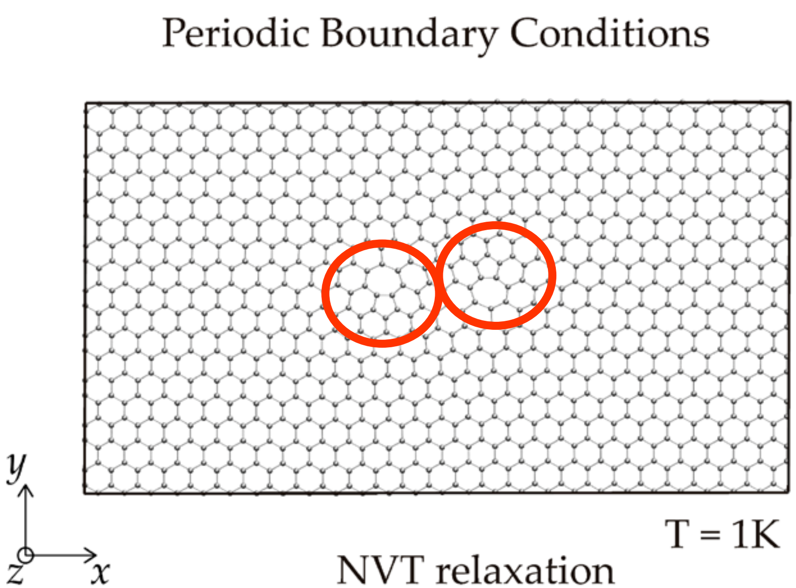


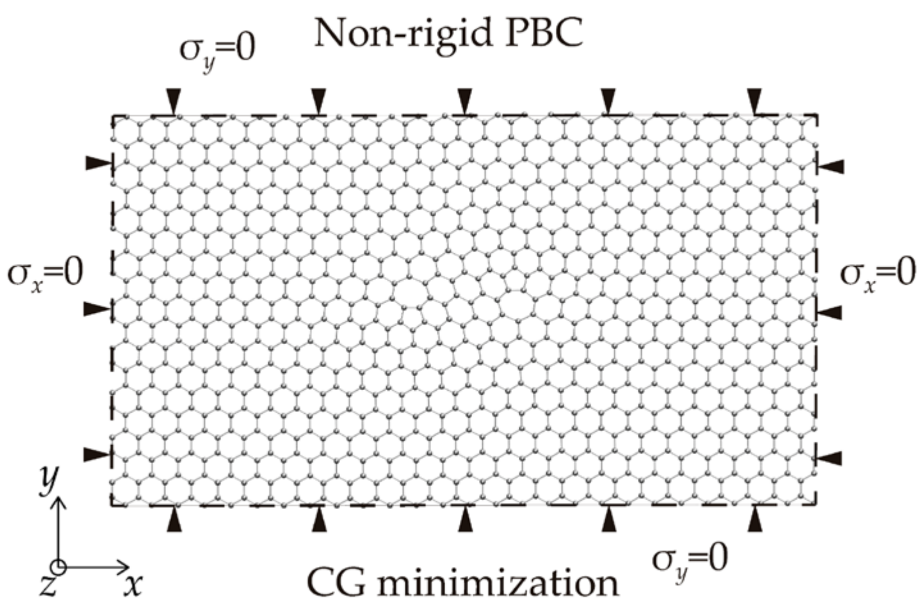
dipoles



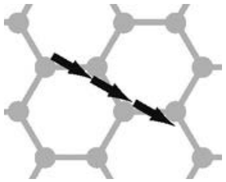
quadrupoles

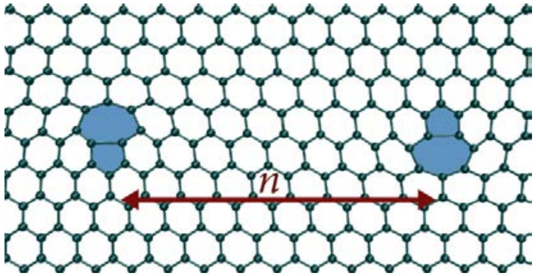
Slip systems

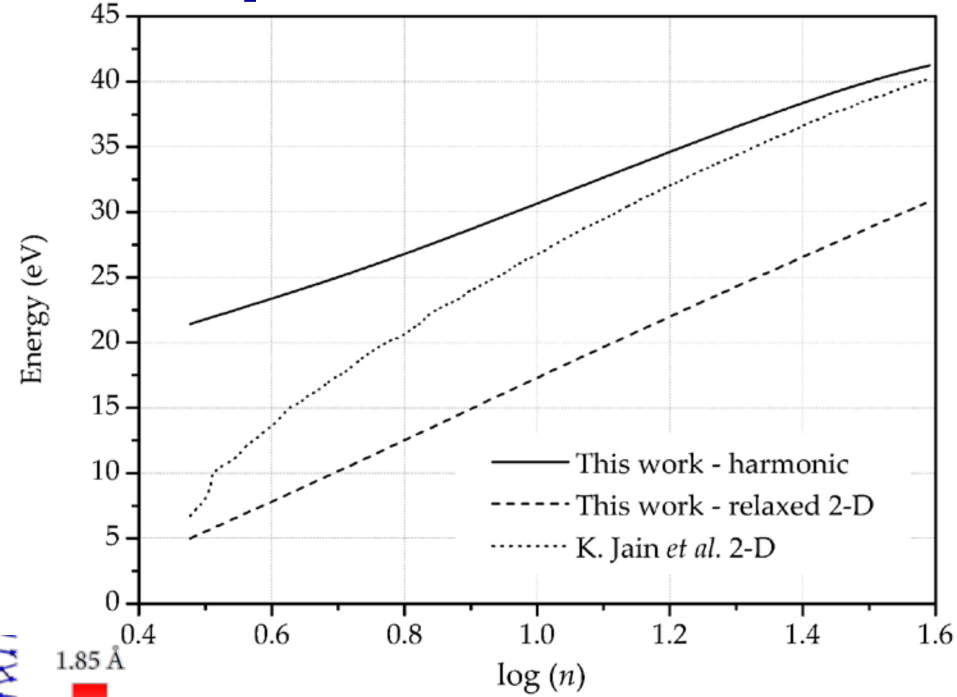




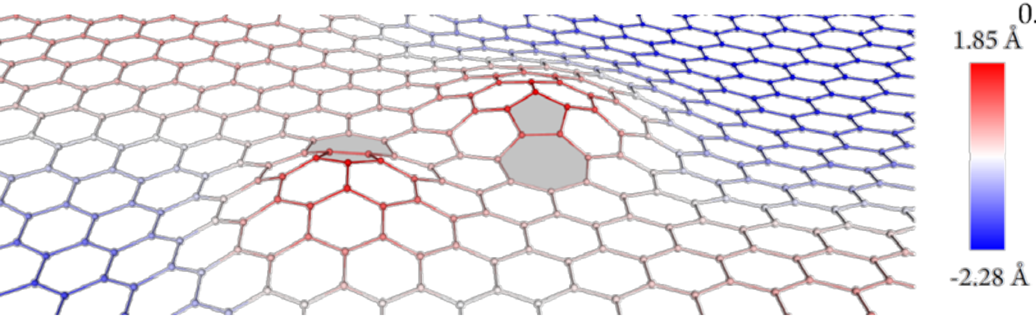
Dislocation dipoles





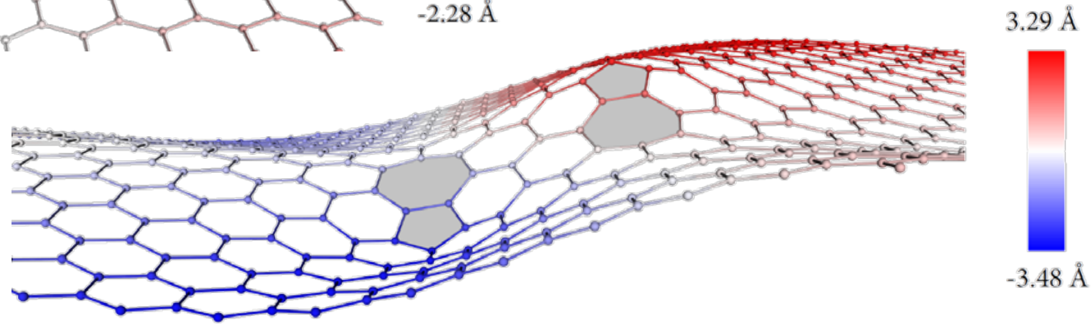


S. T. Jain et al. J. Physical Chemistry, (2011)
Arca et al. Nanomaterials **9** (2019) 1012



Symmetric (metaestable)

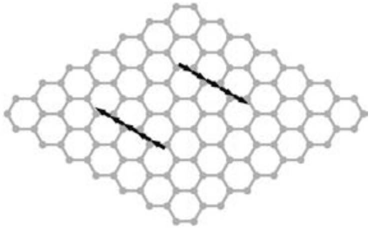
E = 9.46eV

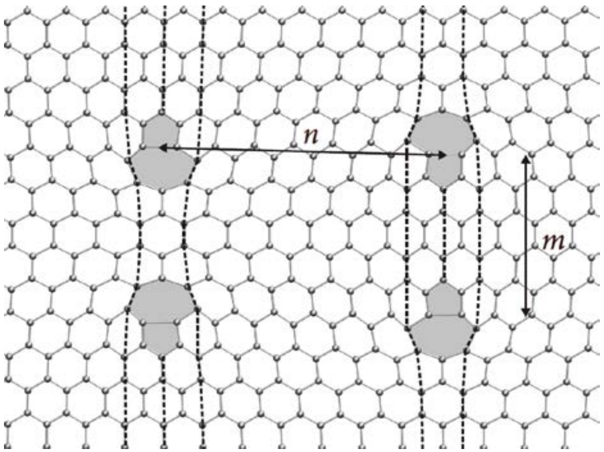


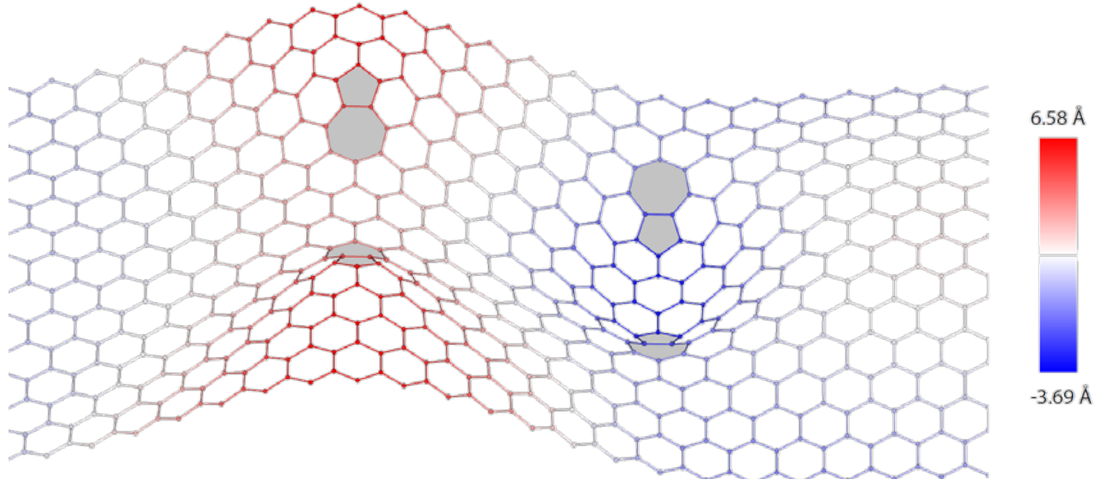
Asymmetric

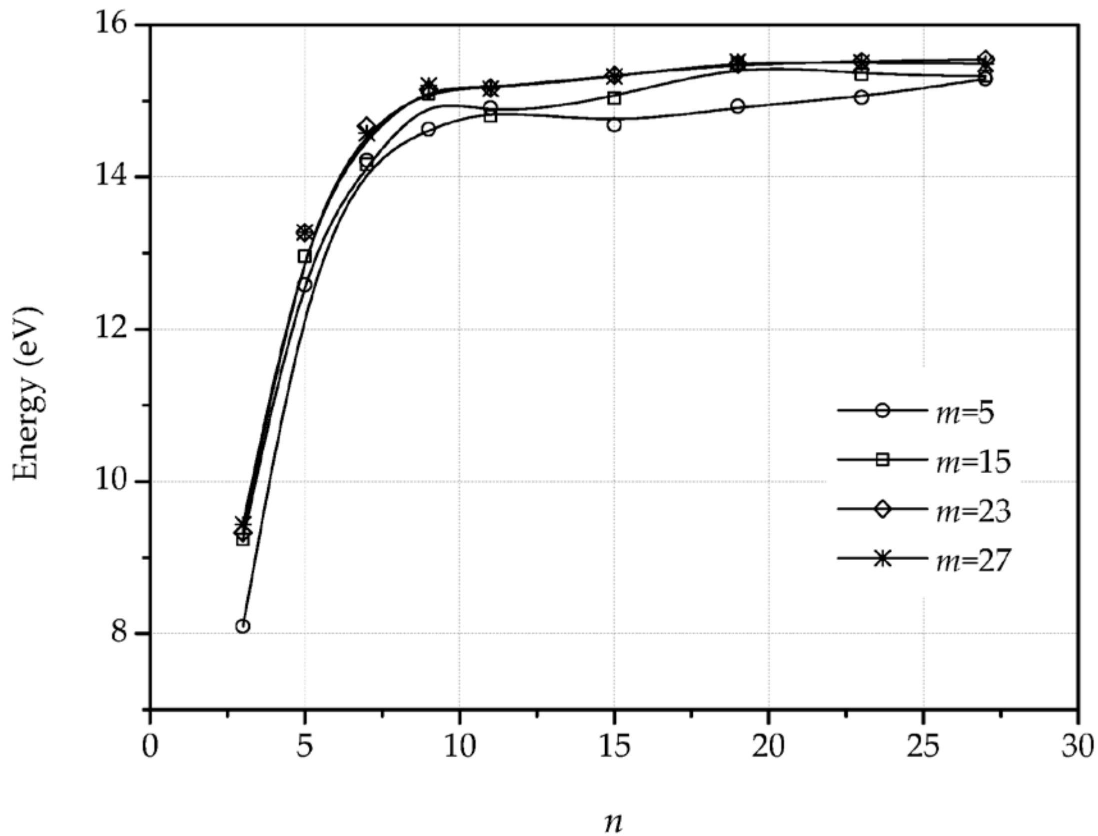
E = 7.94eV

Dislocation quadrupoles





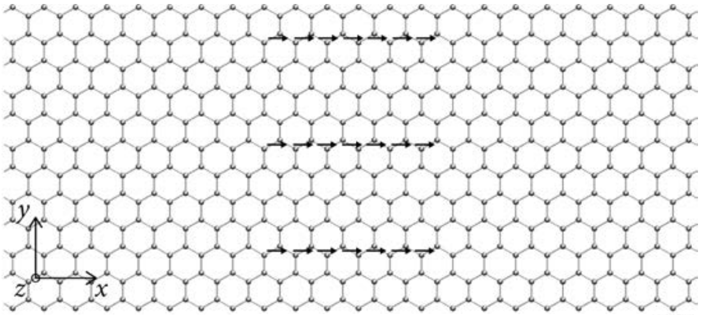




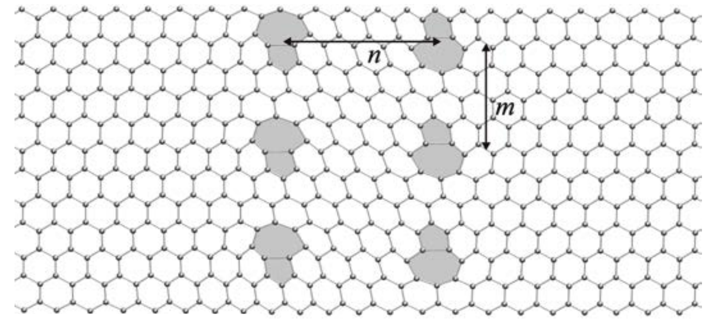
After relaxation

Arca et al. Nanomaterials **9** (2019) 1012

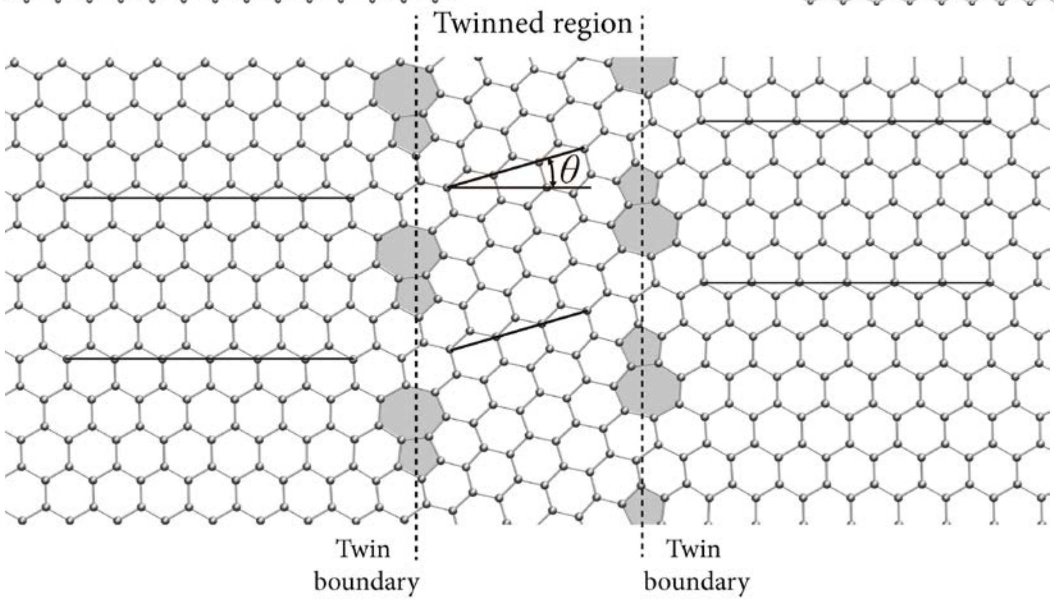
Arrays of dislocation dipoles



Pattern of defects

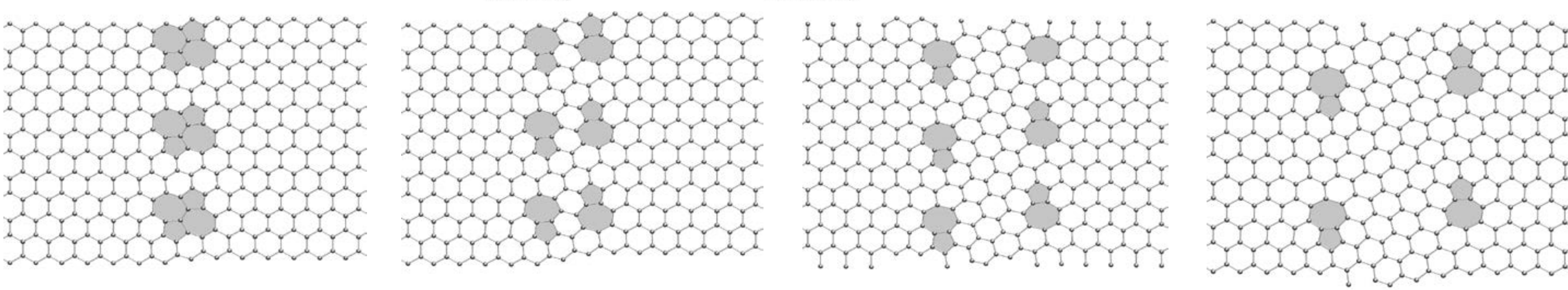


After relaxation



Spontaneous twining as an accommodation and relaxation mechanism

significant **reduction in energy**



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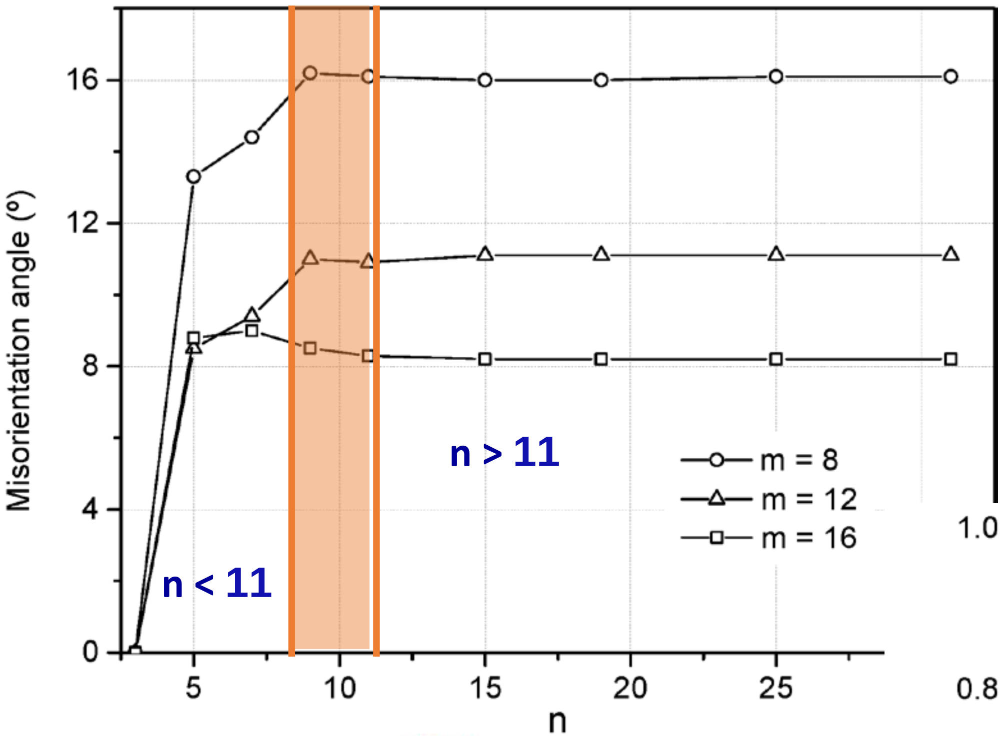
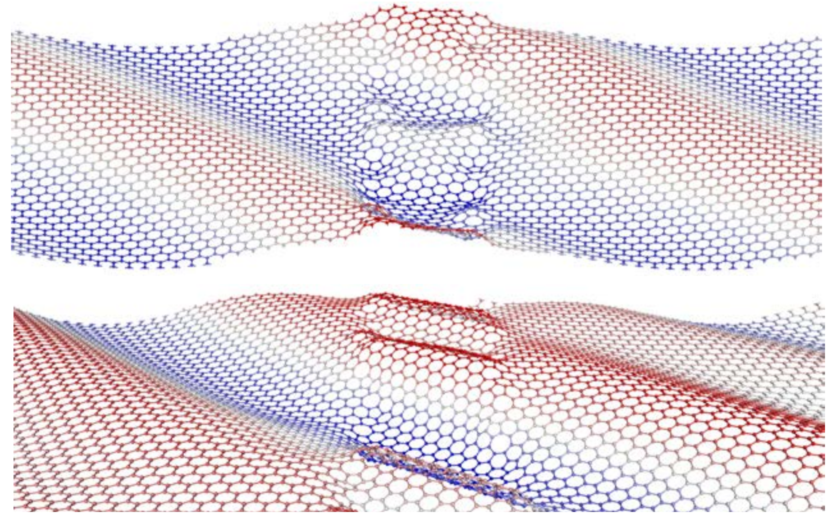
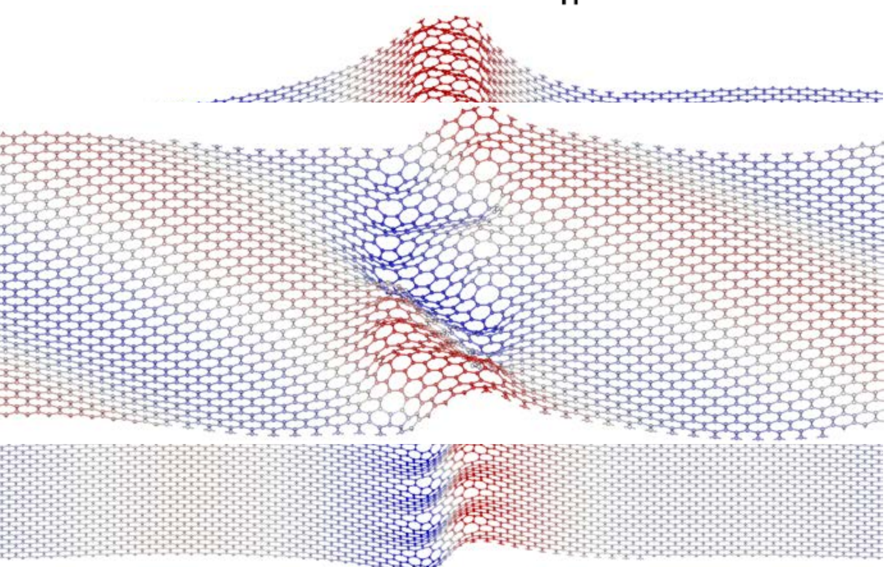
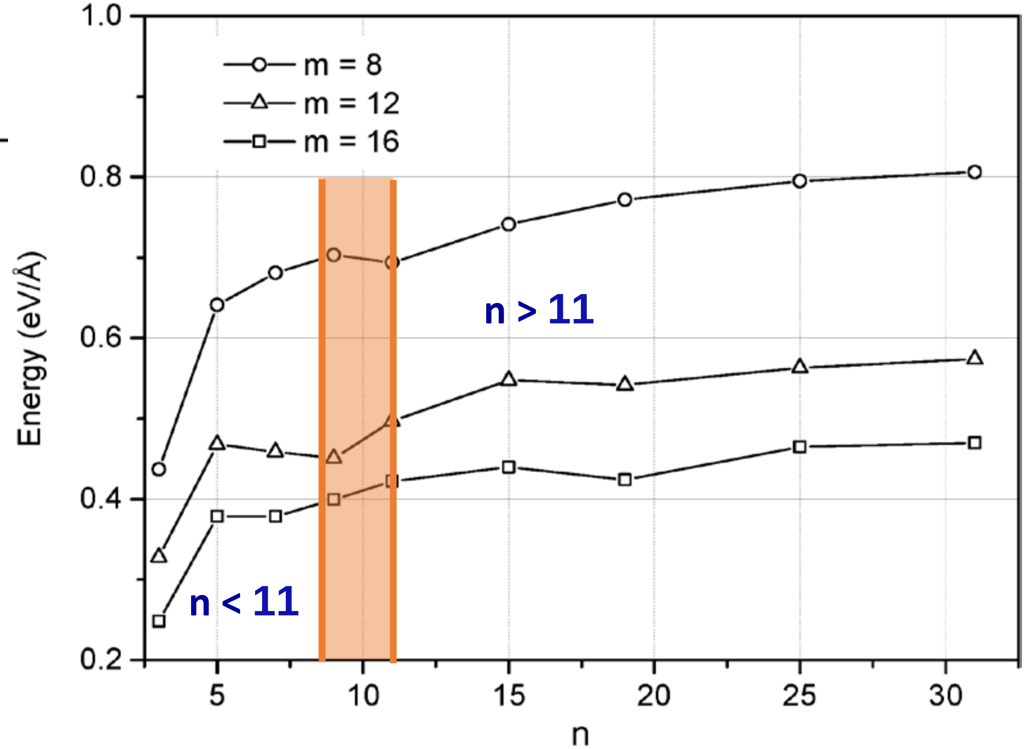
Arrays of dislocation dipoles









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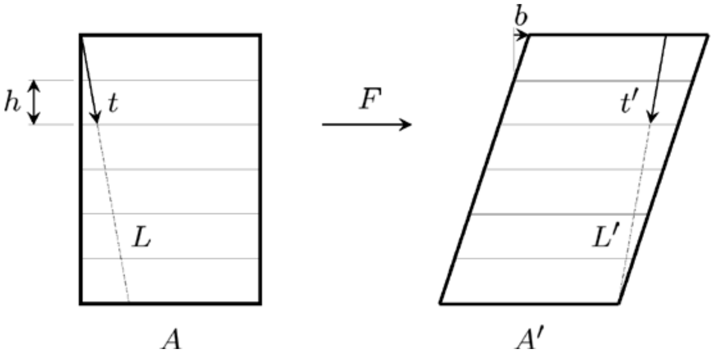
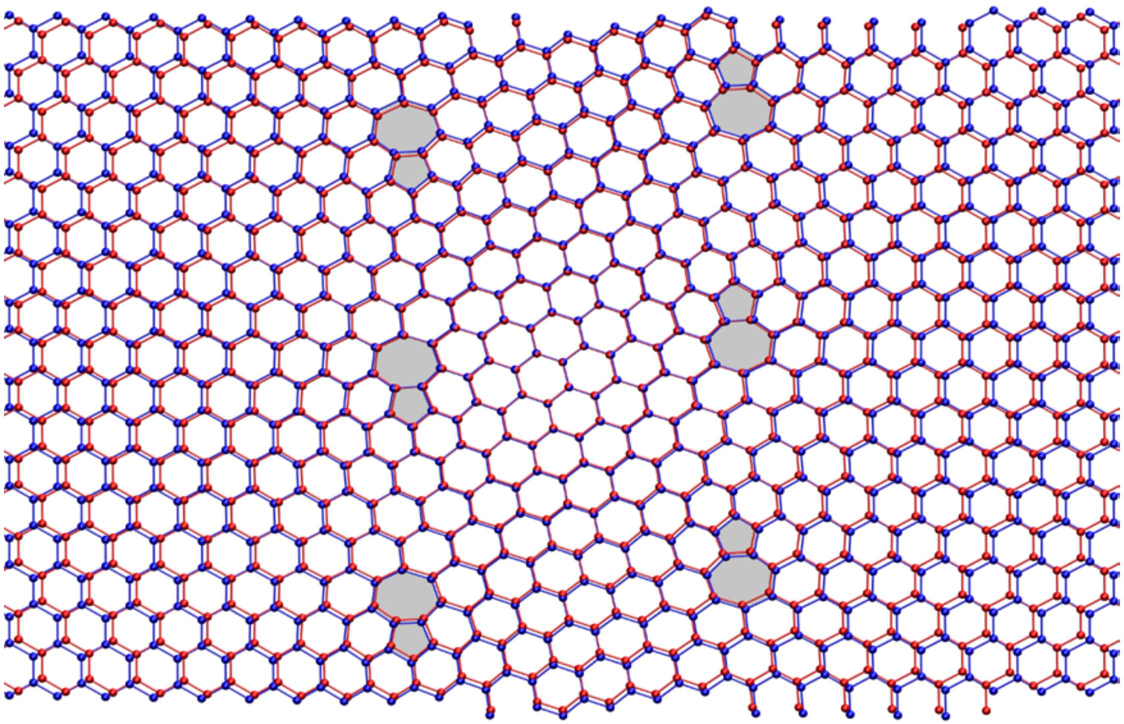
Dipolar arrays – Accommodation mechanism



m	Computed (°)	Twinning (°)
6	20.4	21.8
8	16.1	16.4
12	11.1	11.0
16	8.2	8.2
20	6.6	6.6
24	5.5	5.5

$$F = \begin{pmatrix} 1 & b/h \\ 0 & 1 \end{pmatrix}$$

Twinning : kinematical mode of deformation



red – AIREBO potential
blue – LCBOP potential

angle: 11.1 energies: 0.717 vs 0.548

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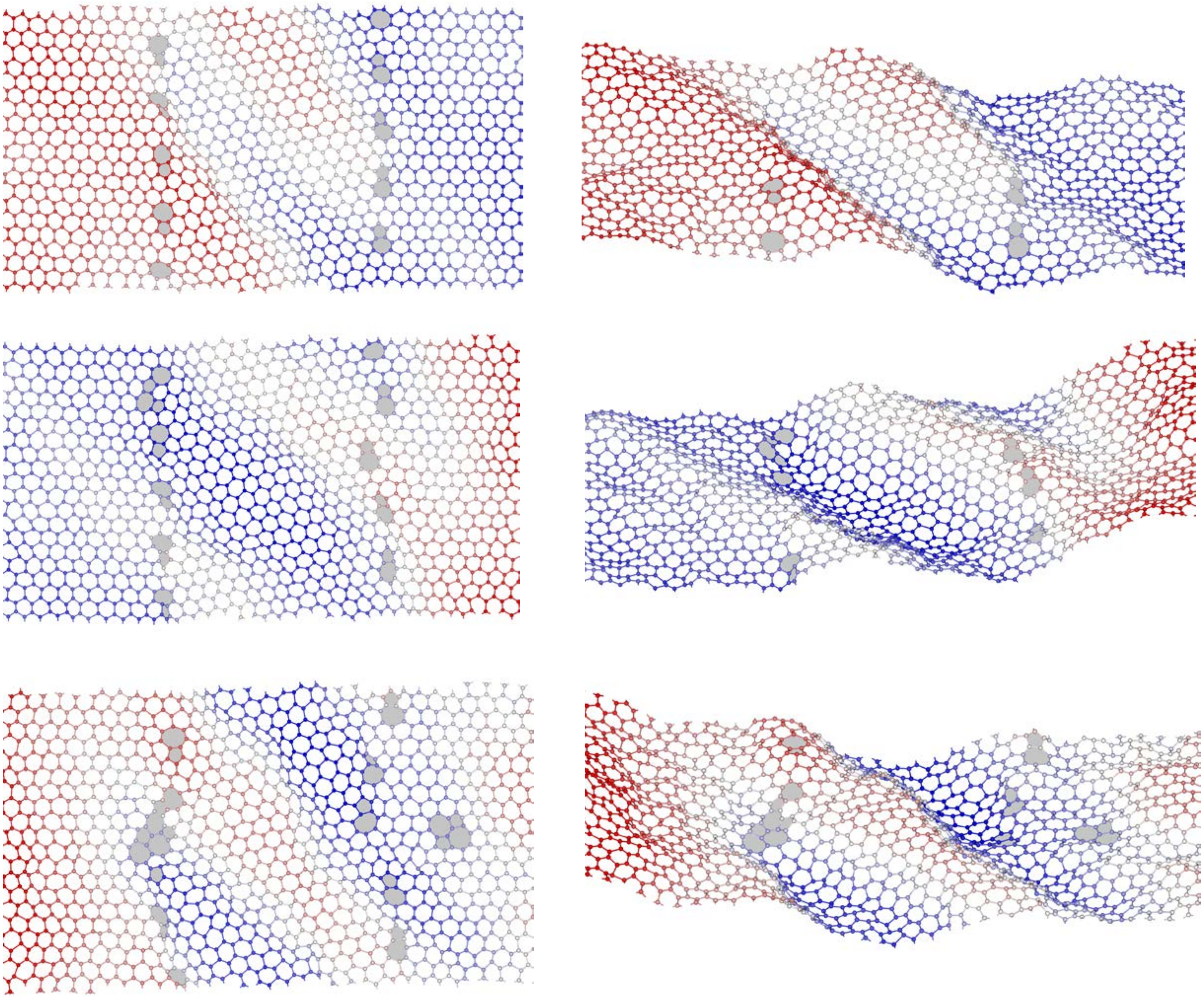
Arrays of dislocation dipoles

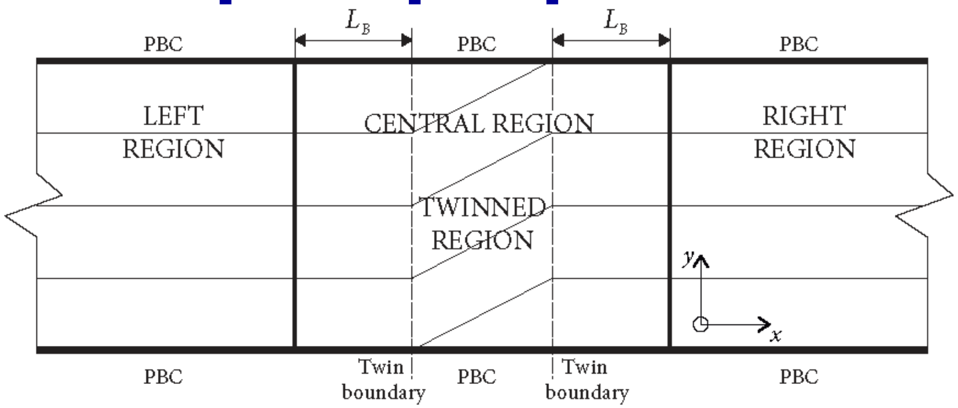


T = 3500K

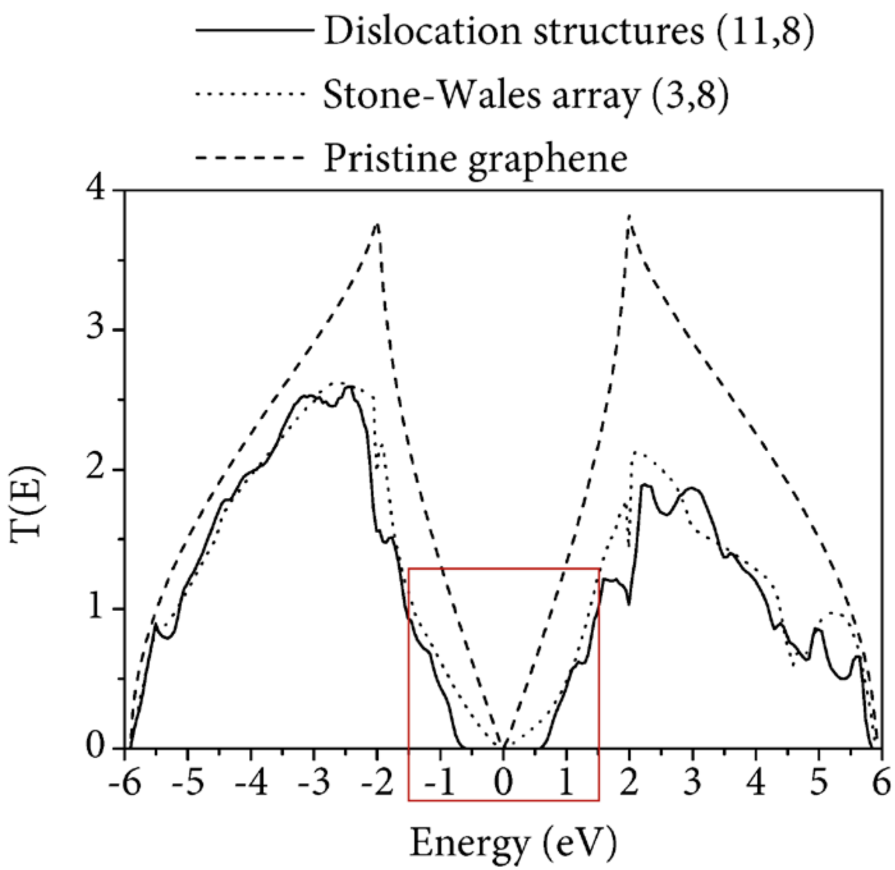
T = 4000K

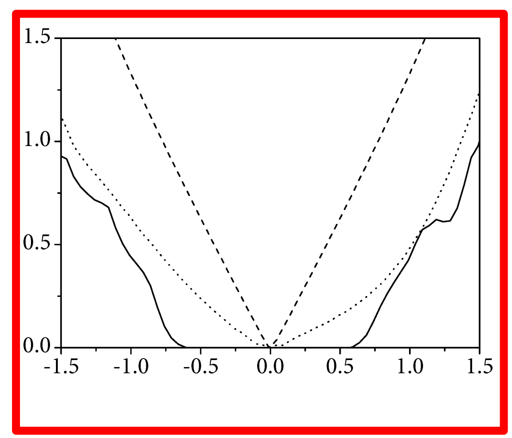
T = 4500K

Transport properties across twin boundaries

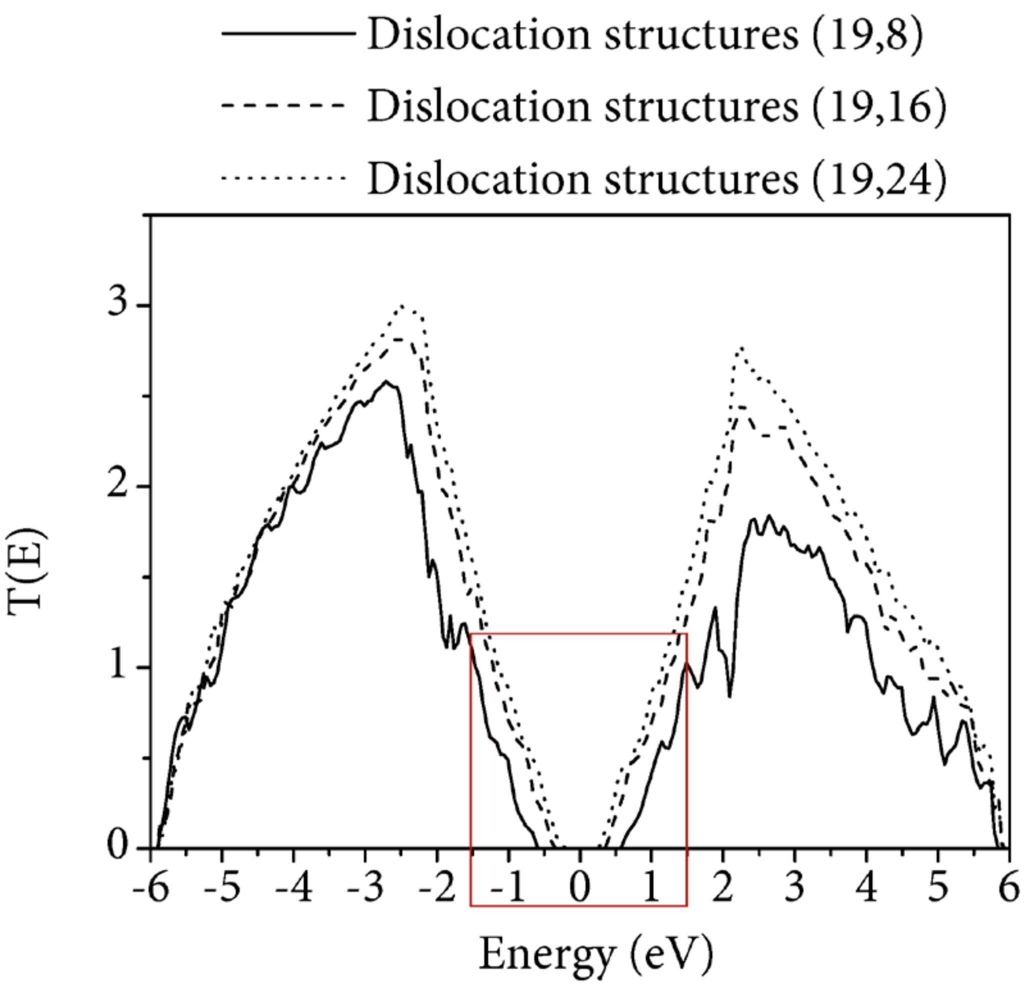


	$m = 8$		$m = 12$		$m = 16$	
	gap (eV)	θ (°)	gap (eV)	θ (°)	gap (eV)	θ (°)
$n = 3$	0.0	0.0	0.0	0.0	0.0	0.0
$n = 5$	0.35	13.3	0.0	8.5	0.0	8.8
$n = 7$	0.7	14.4	0.1	9.4	0.0	9.0
$n = 9$	1.05	16.2	0.2	11.0	0.25	8.5
$n = 11$	1.1	16.1	0.6	10.9	0.3	9.3
$n = 15$	1.05	16.1	0.8	11.1	0.55	8.2
$n = 19$	1.1	16.1	0.95	11.1	0.65	8.2
$n = 25$	1.05	16.1	0.8	11.1	0.6	8.2
$n = 31$	0.95	16.1	0.75	11.1	0.6	8.2





Transport properties across twin boundaries



	$m = 8$		$m = 12$		$m = 16$	
	gap (eV)	θ (°)	*gap* (eV)	θ (°)	*gap* (eV)	θ (°)
$n = 3$	0.0	0.0	0.0	0.0	0.0	0.0
$n = 5$	0.35	13.3	0.0	8.5	0.0	8.8
$n = 7$	0.7	14.4	0.1	9.4	0.0	9.0
$n = 9$	1.05	16.2	0.2	11.0	0.25	8.5
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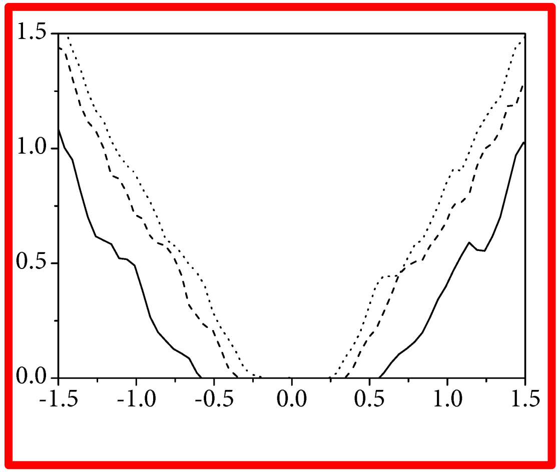
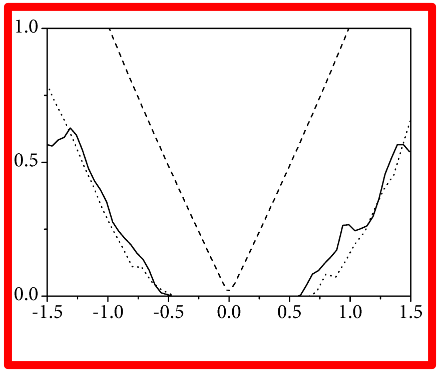
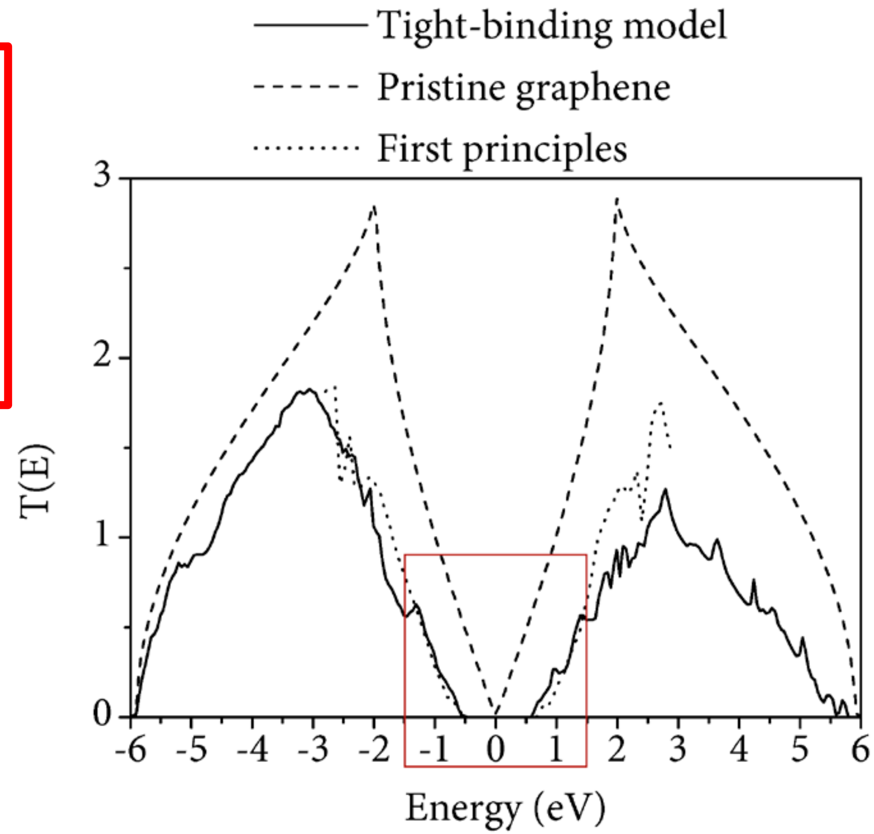
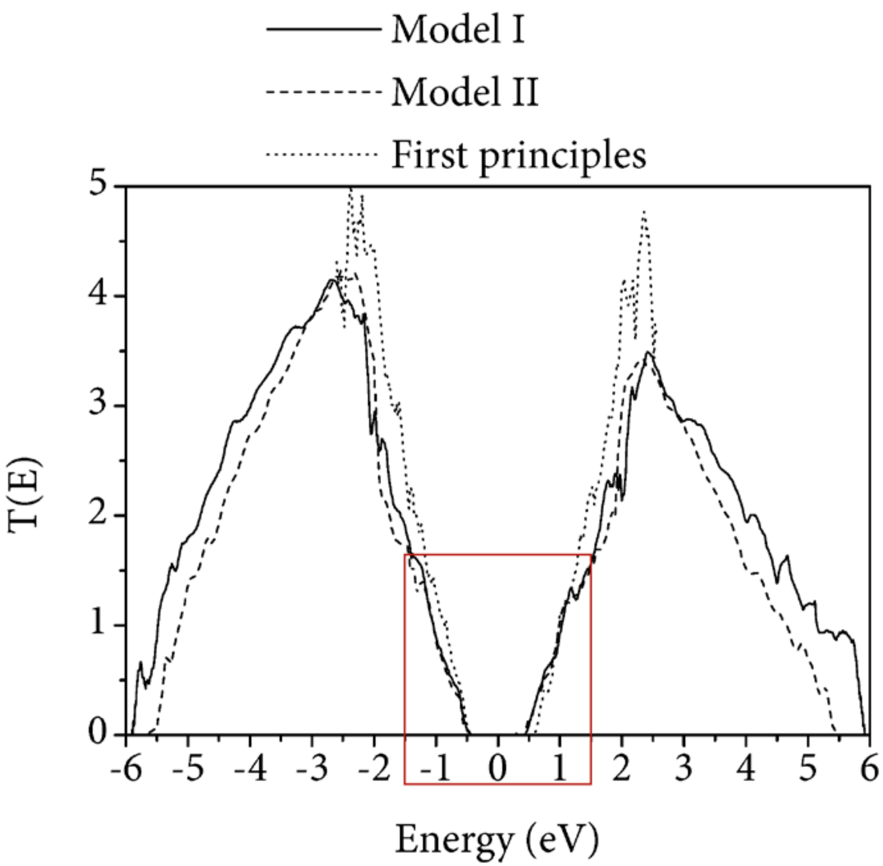


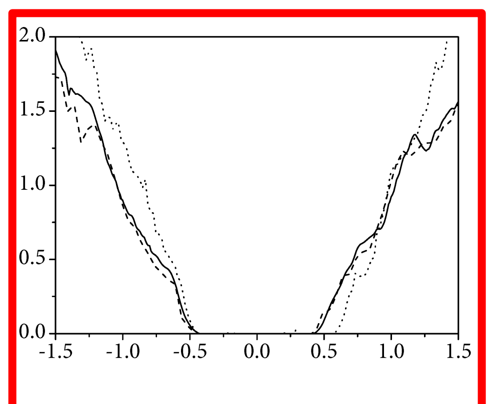
Charge carrier transmission coefficient per period across twin boundaries n=19

Transport properties across twin boundaries

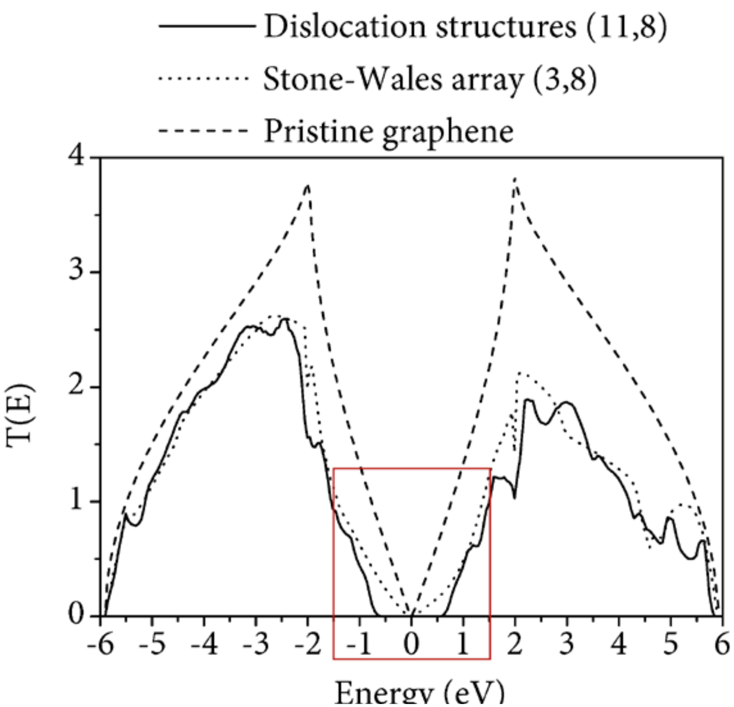


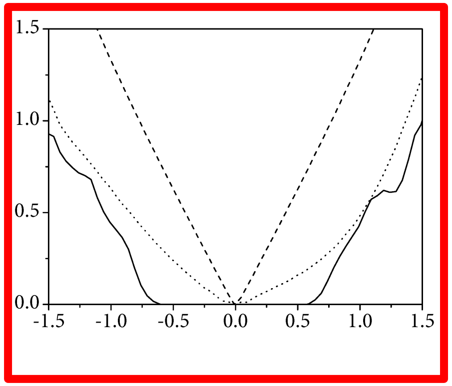


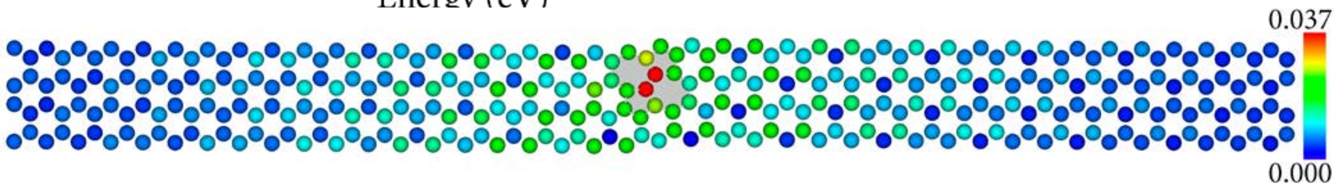




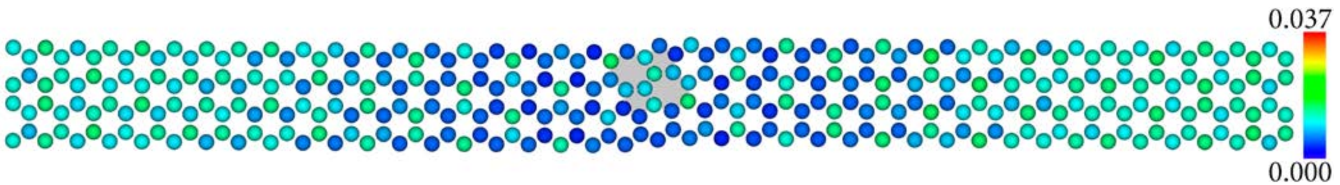
Transport properties across twin boundaries



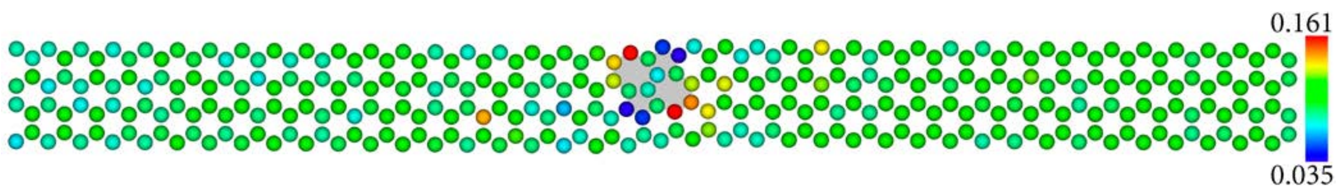




E=0 eV ≈
Fermi level

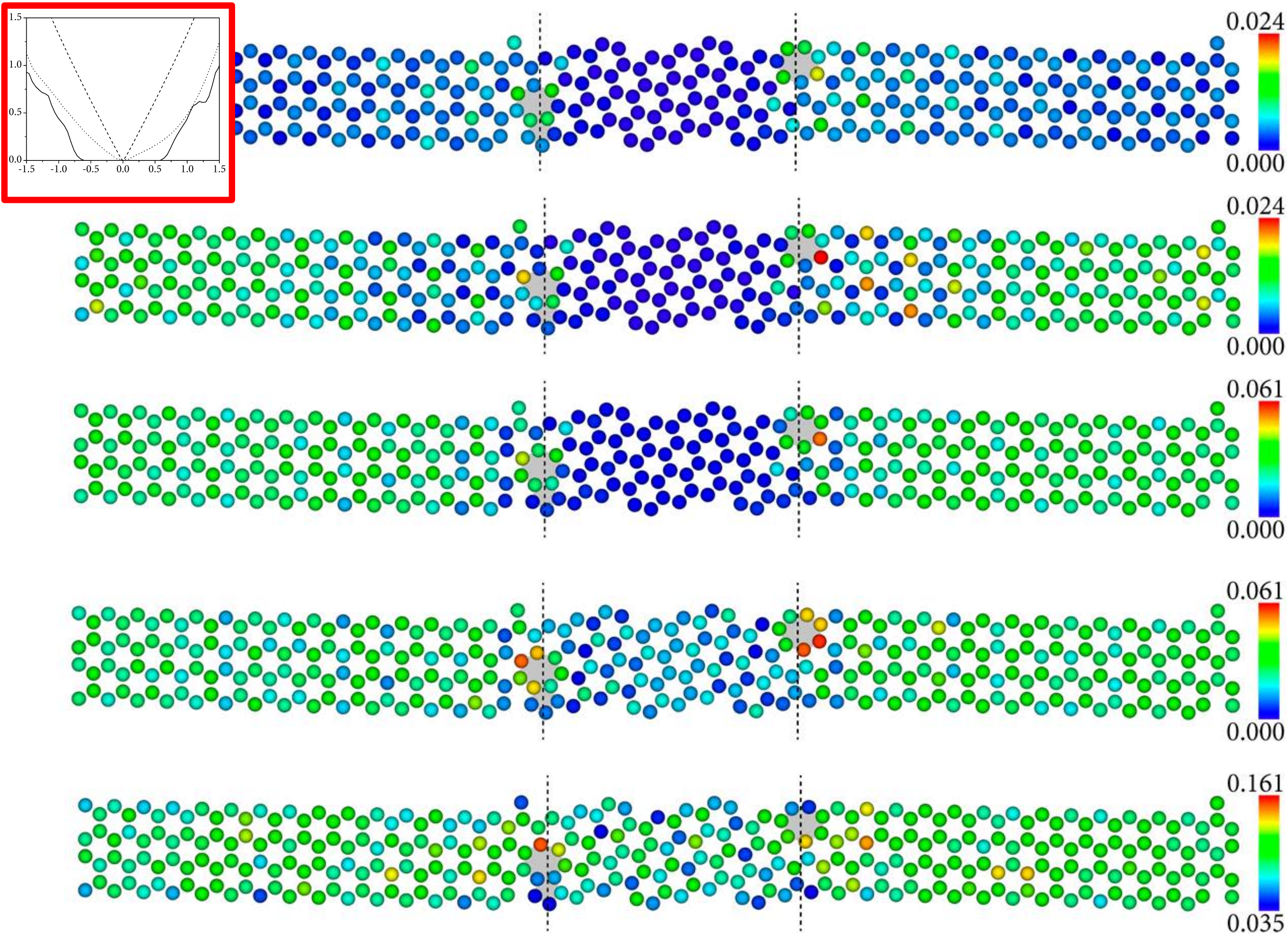


E=0.25eV



E=1.55eV

Transport properties across twin boundaries



E=0 eV ≈ Fermi level

E=0.25eV

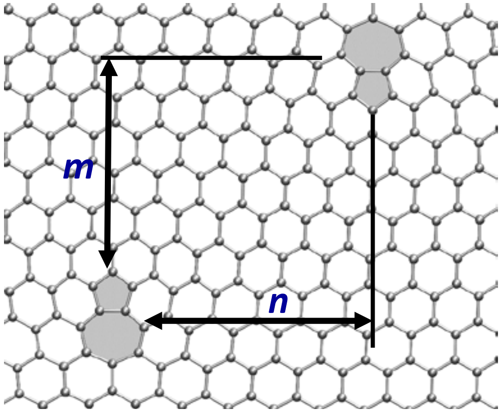
E=0.55eV

E=0.60eV

E=2.64eV

Isolated dislocation cores - Bilayers

Out-of-plane displacements → Steric interactions between layers

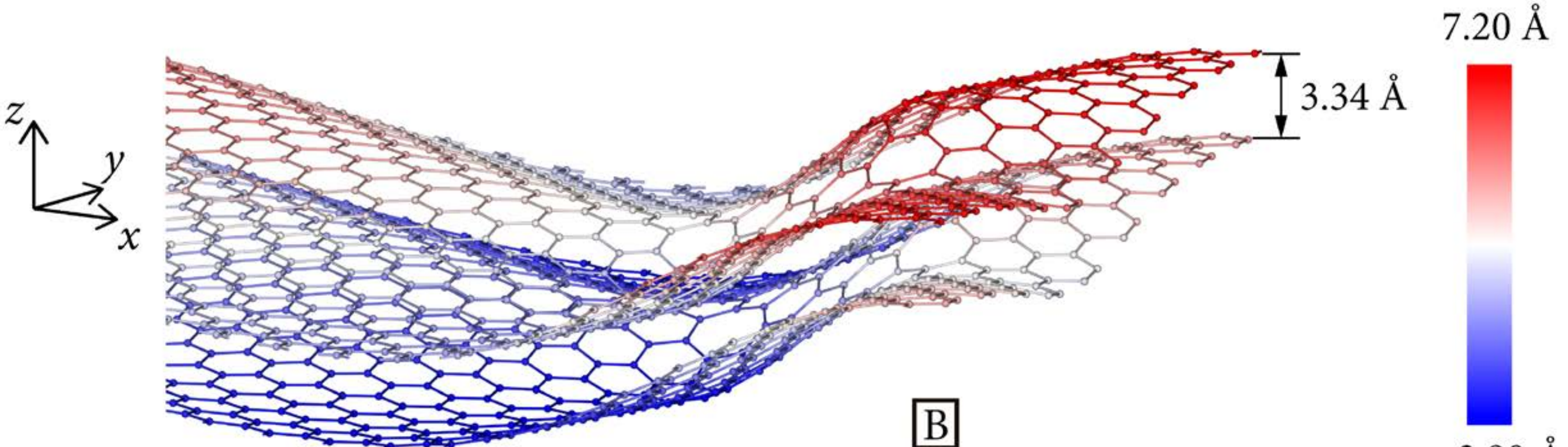


Two dipoles n = 9 **in registry**

Energy per layer: E = 7.96 eV

Bilayer energy: E = 15.70 eV

→ modest attractive interaction between the layers



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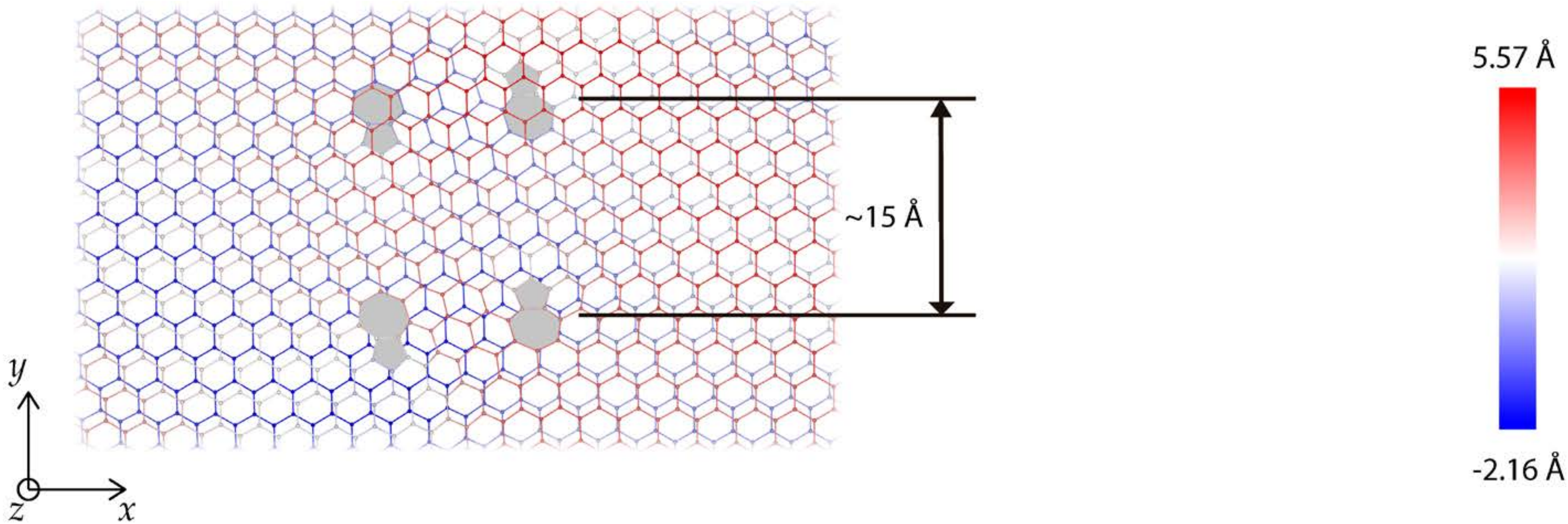
Isolated dislocation cores - Bilayers

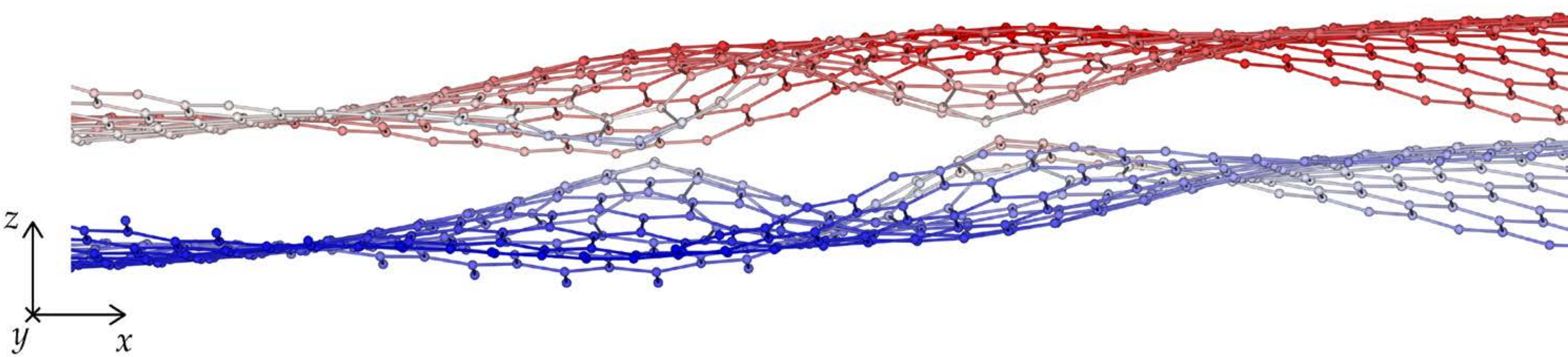
Two dipoles n = 9
separated 15Å

Energy per layer: E = 7.96 eV

Bilayer energy: E = 23.0 eV

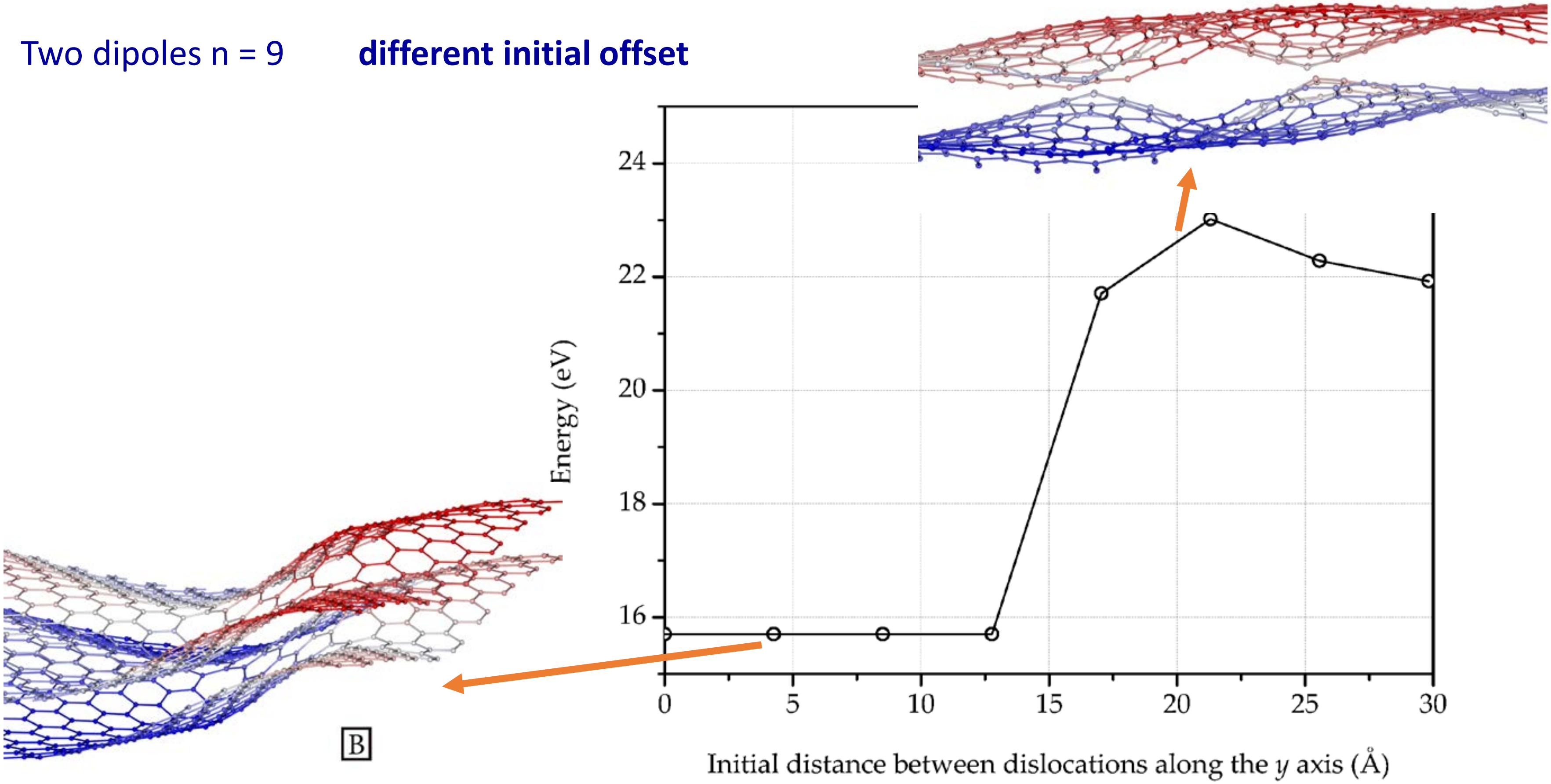
→ Strong steric interference between the layers





Isolated dislocation cores - Bilayers

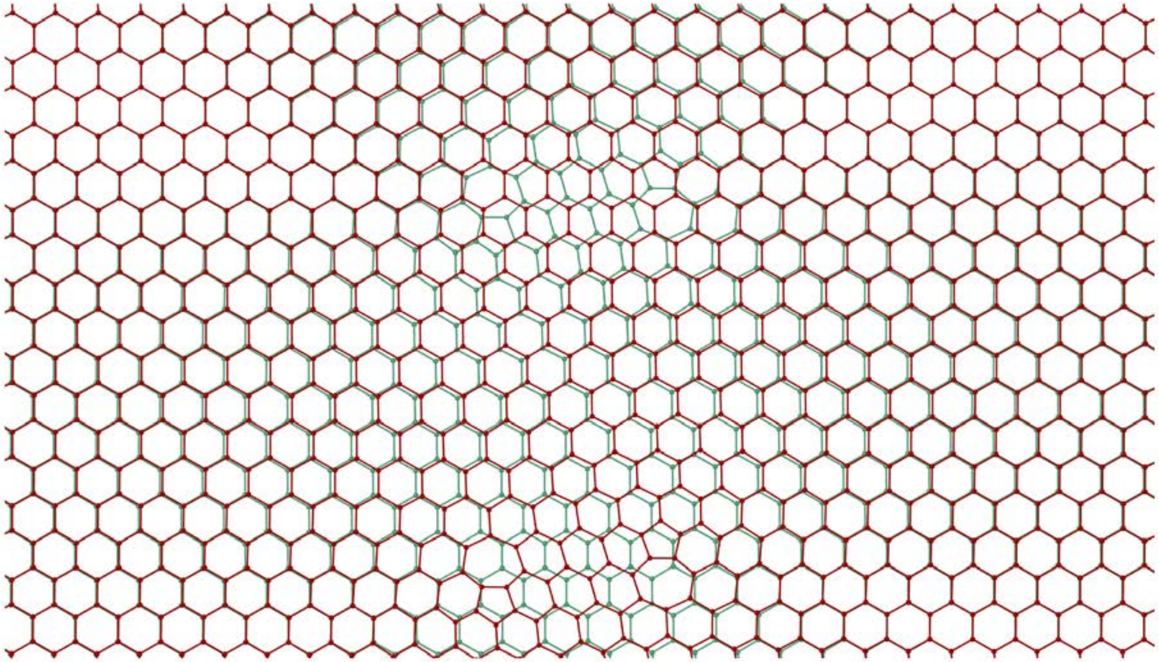
Two dipoles n = 9 **different initial offset**



The steric interference between the monolayers:

1. Strong attractive interaction between the dipoles, which relaxed to a zero-distance configuration of energy 15.7 eV.
2. The attractive interaction between dipoles is not strong enough and the dipoles remain offset to each other, resulting in comparatively larger energies.

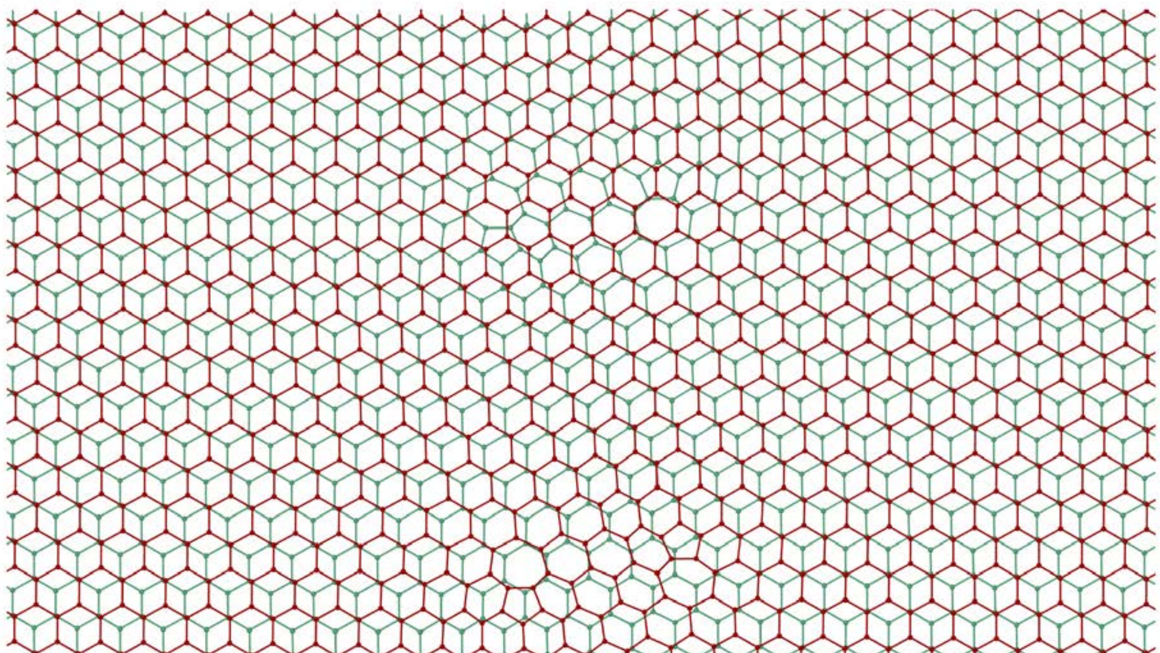
Isolated dislocation cores - Bilayers



Relaxation of a bilayer containing two unmatched dislocation dipoles

Initial condition
(stacking sequence AA)

Upon relaxation
(stacking sequence AB)



Dislocation accommodation mechanisms in monolayer and bilayer graphene

Thank you for your attention !!!

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JANUARY 13 - 17, 2020