Buckling, Folding and Rippling of Graphene Nanoribbon Edges

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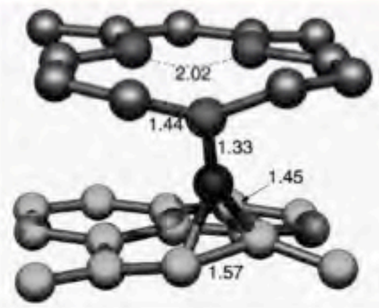
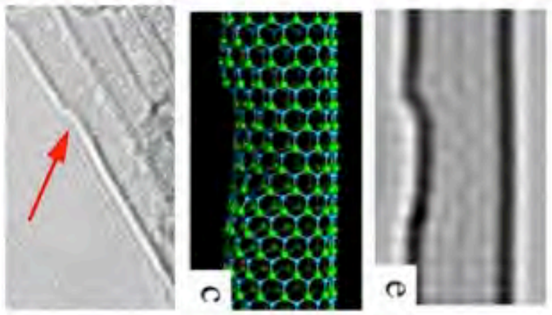
Carbon Modelling at the IMN Nantes

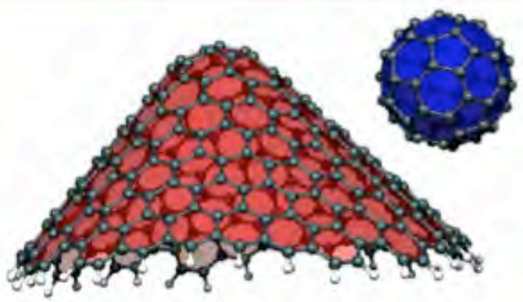
Structural Defects



Intrinsic Defects

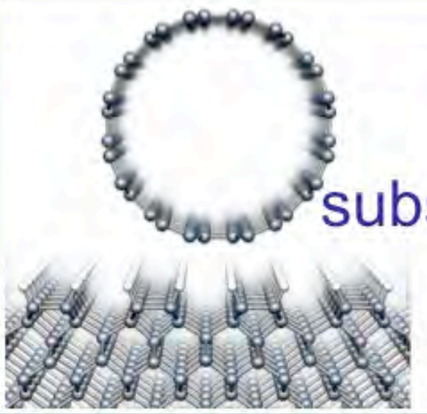


Irradiation Effects

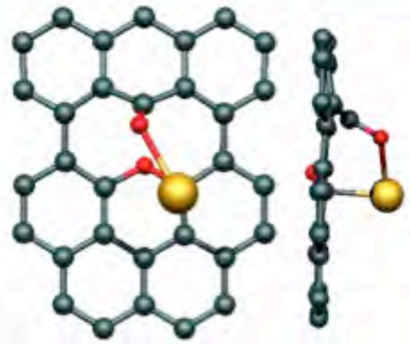


Other nanoobjects

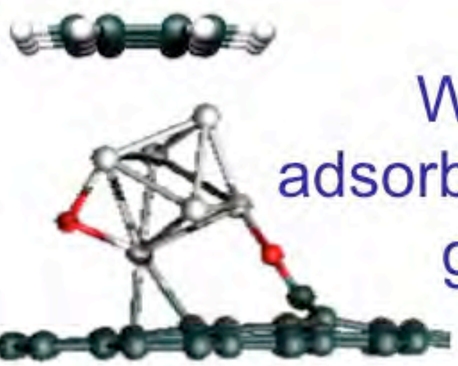
Graphene / CNT interactions



With substrates

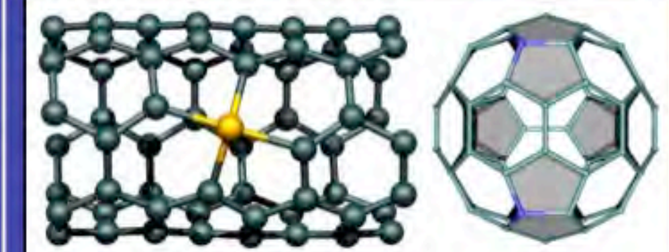


With metals

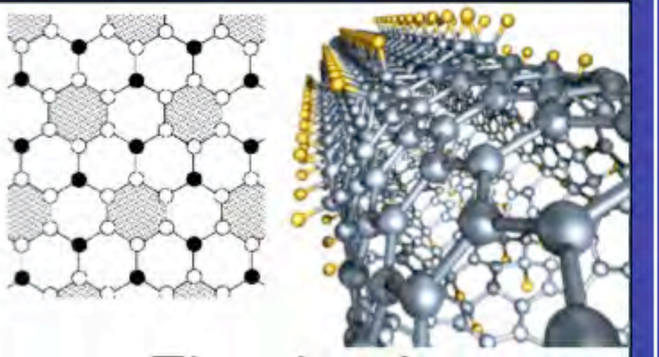


With adsorbed gas

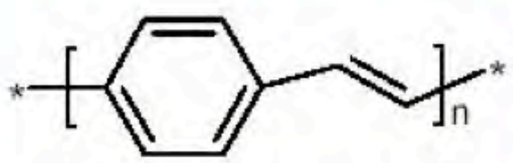
Doping and Functionalisation



N and P Doping



Fluorination

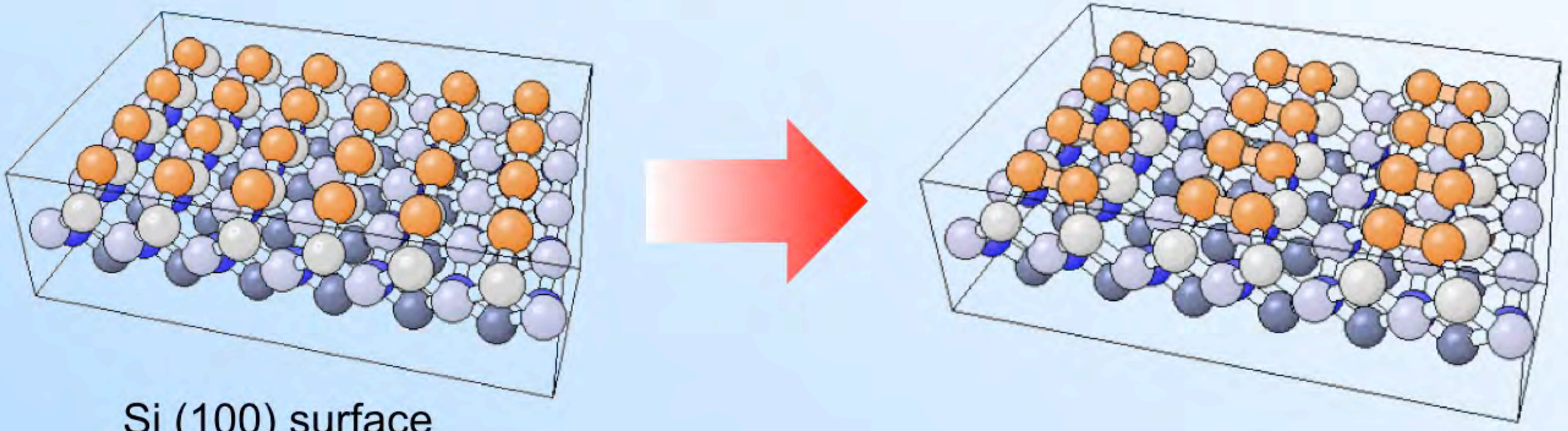


Hybrid Polymer (PPV) / CNT

« Face it, Fred - you're lost! »

« … atomically controlled **interfaces** play a key role in the performance of nanodevices … »

3D Solids → 2D Interfaces



Si (100) surface

- Dangling bonds
- Surface Reconstruction / Rehybridisation
- Surface Strain

Nanoribbons : 2D Graphene → 1D Edges?

http://www.chem.qmul.ac.uk/surfaces/scc/scat1_6a.htm

Graphene Interface Types

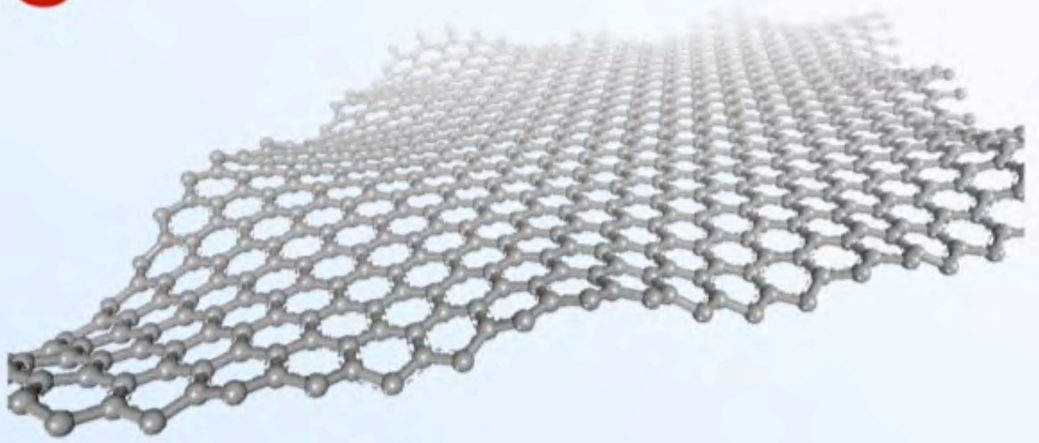
- Unfunctionalised edges
- Chemically functionalised edges

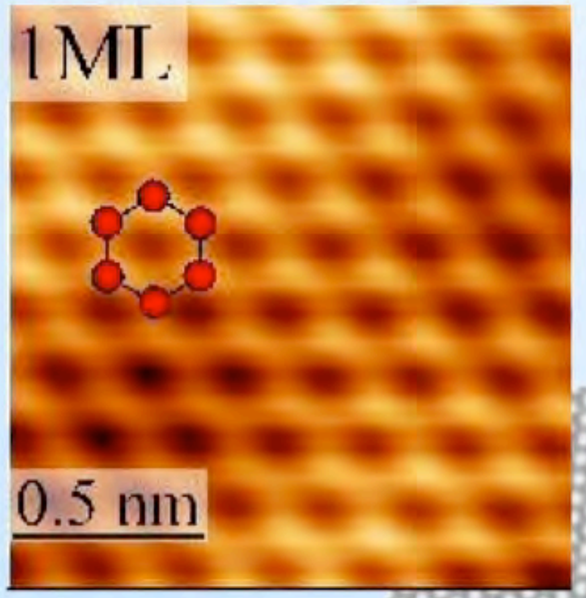
- AIMPRO : Density Functional Calculations
- Local spin density approximation
- Localised basis sets (large)!
- HGH Pseudopotentials

Graphene

Synthesis:

- mechanical exfoliation
- epytaxial growth
- chemical exfoliation→ self-suspended

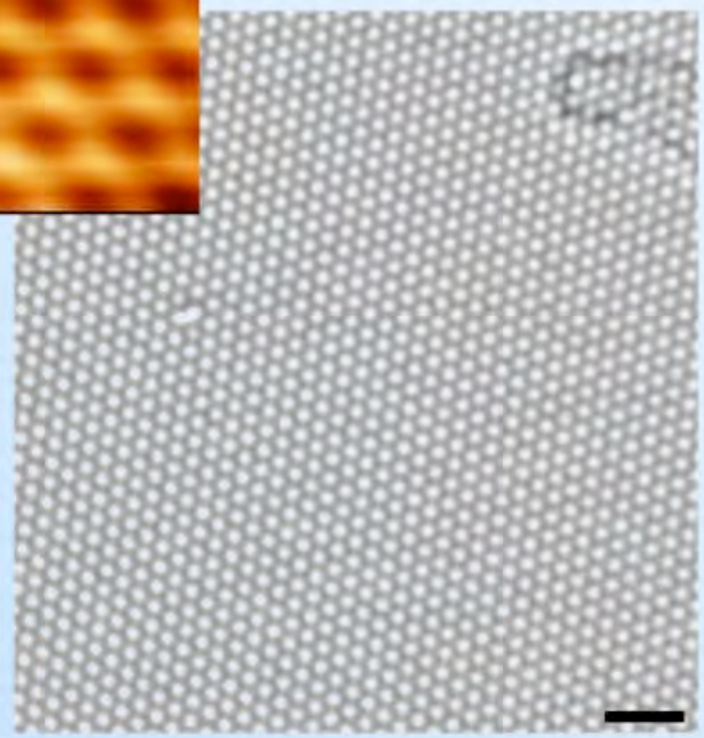




P. Lauffer et al Phys. Rev. B 77 (2008) 155426

Edge structure? Difficult to image:

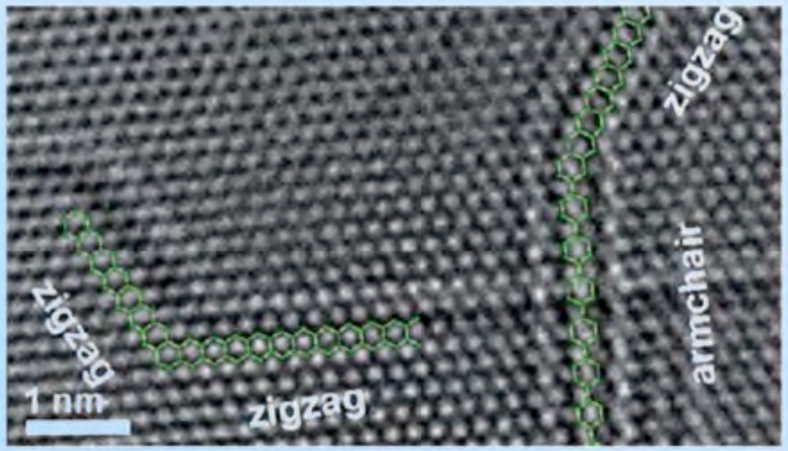
- AFM & STM narrow view field
- TEM: irradiation damages



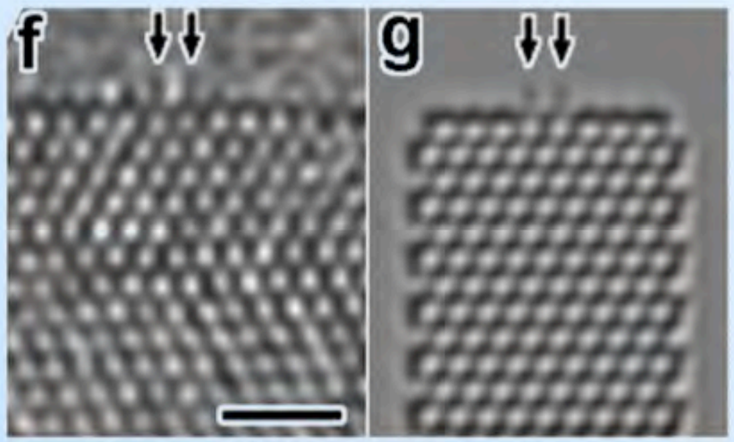
J.C. Meyer et al. Microscopy & Microanalysis 15 (2009) 126

Unfunctionalised Graphene Edges

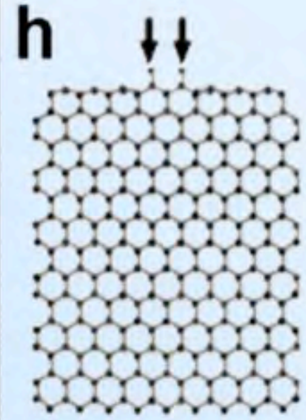
- Different types of edges: standard “zigzag” and “armchair”
- More “exotic” Kleine edges & reconstructed edges also possible
- Chemically stabilized might exist. Possible to see in TEM?

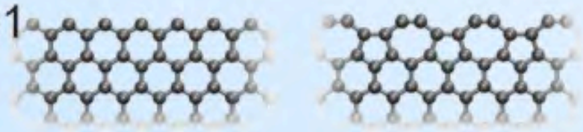


X. T. Jia et al. Science, 323 (2009) 1701

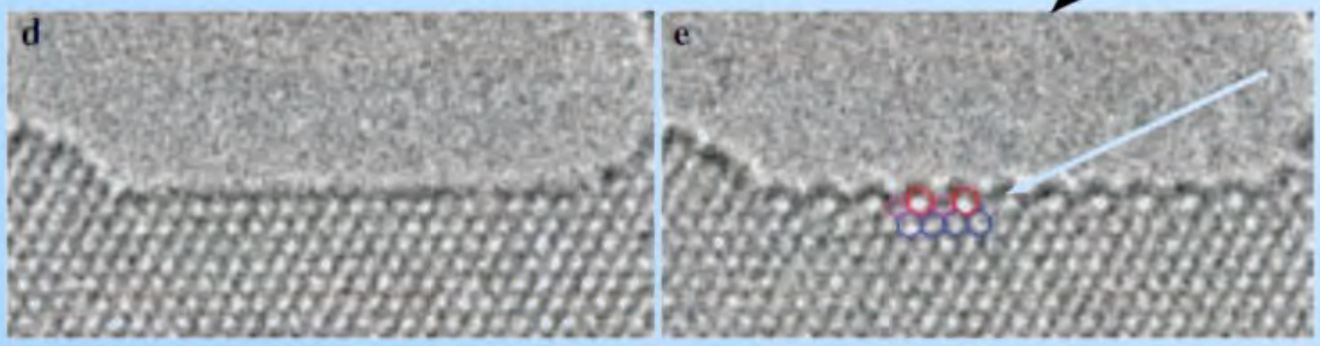


Z.Liu et al. PRL 102 (2009) 015501

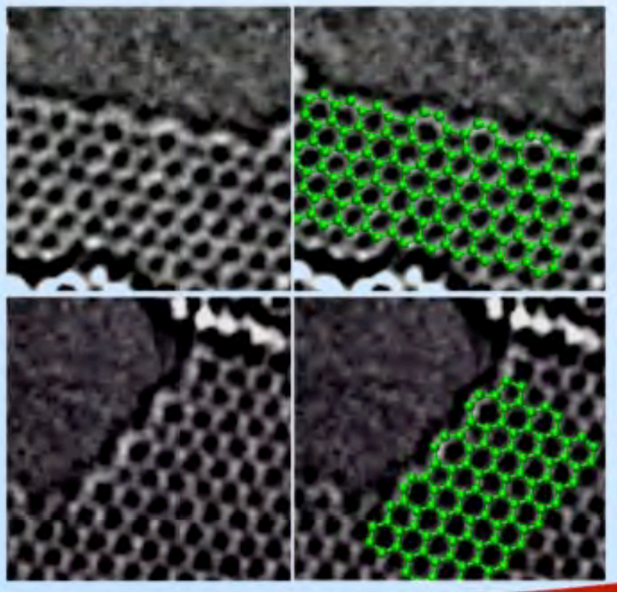




57 reconstruction

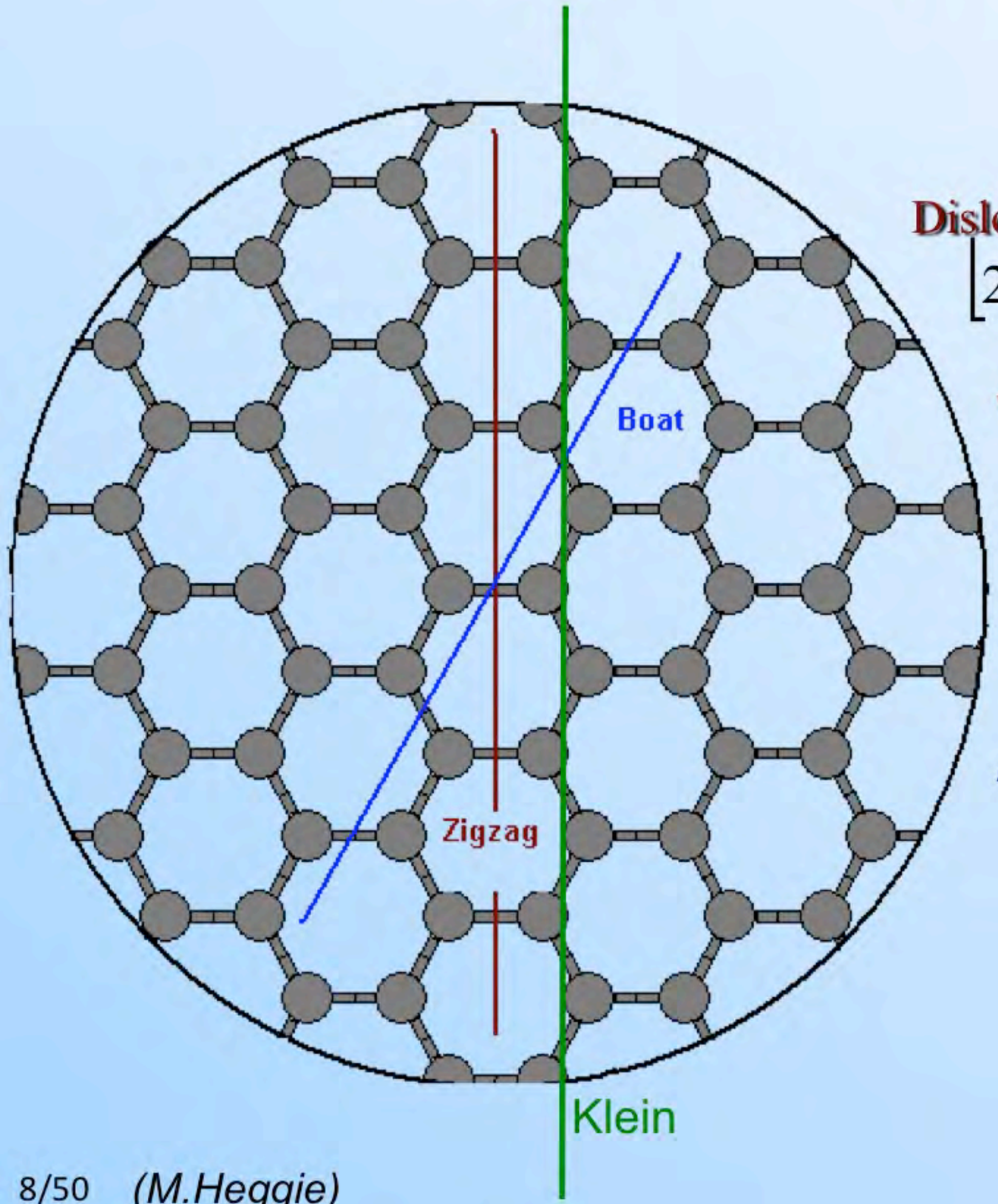


A. Chuvilin et al New Journal of Physics 11 (2009) 083019

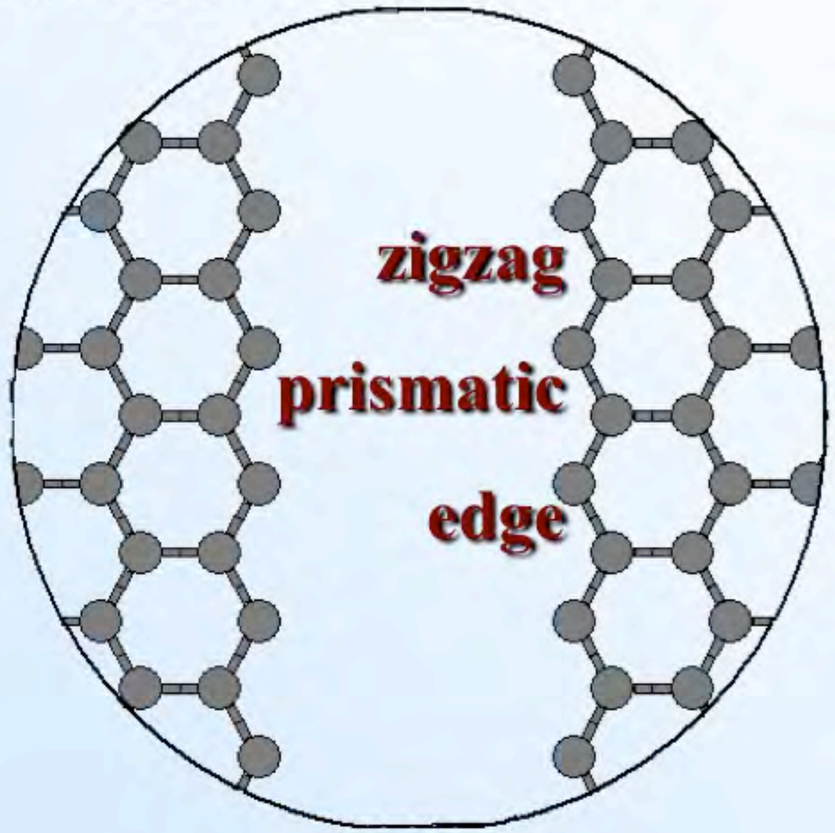


P. Koskinen et al PRB 80 (2009) 073401

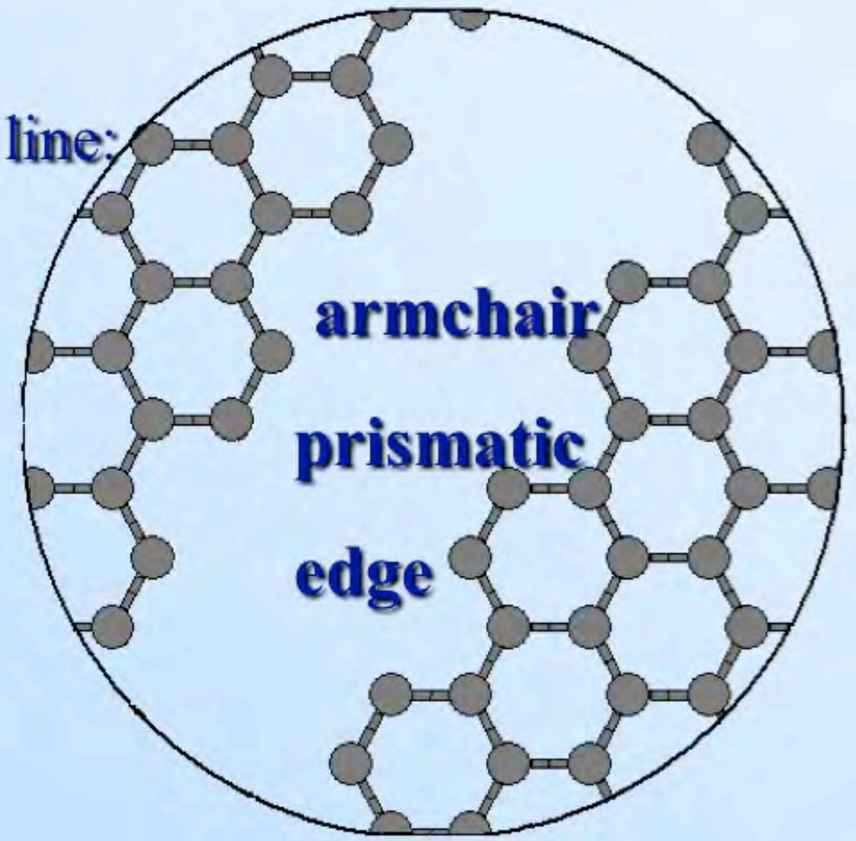
Prismatic Edges in Graphite



Dislocation line: $[2\bar{1}\bar{1}0]$



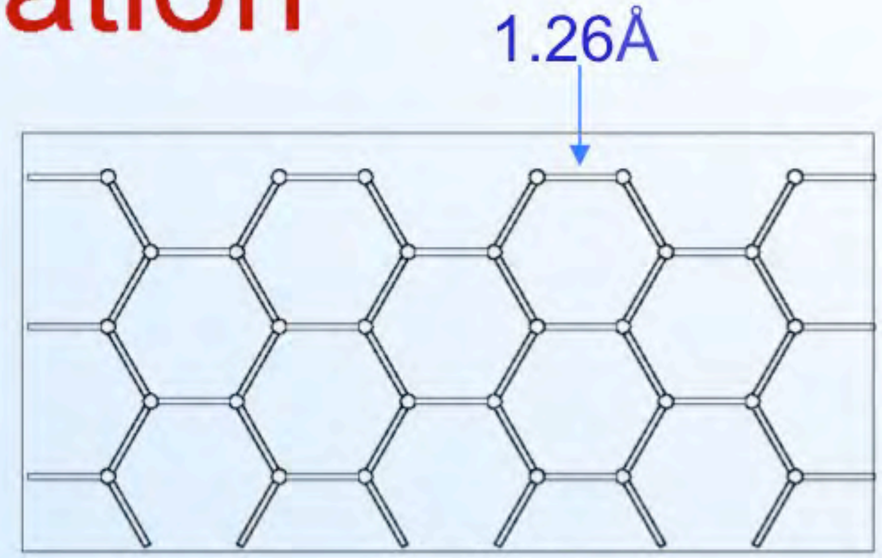
Dislocation line: $[10\bar{1}0]$



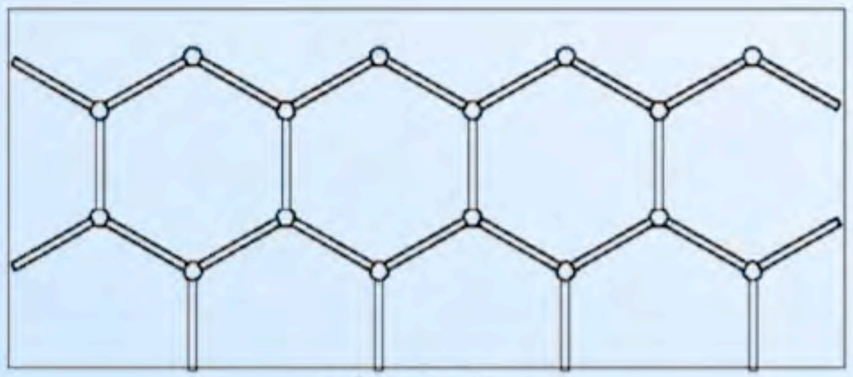
 (M.Heggie)

Edge stabilization

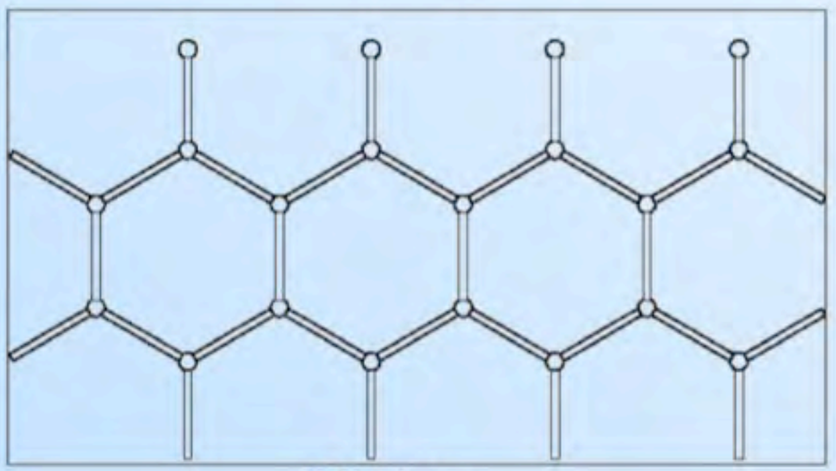
Edge type	Eform (eV/atom)	Eform (eV/Angst)
Armchair	2.35	1.10
Zigzag	3.29	1.34
Kleine	5.43	2.21



armchair



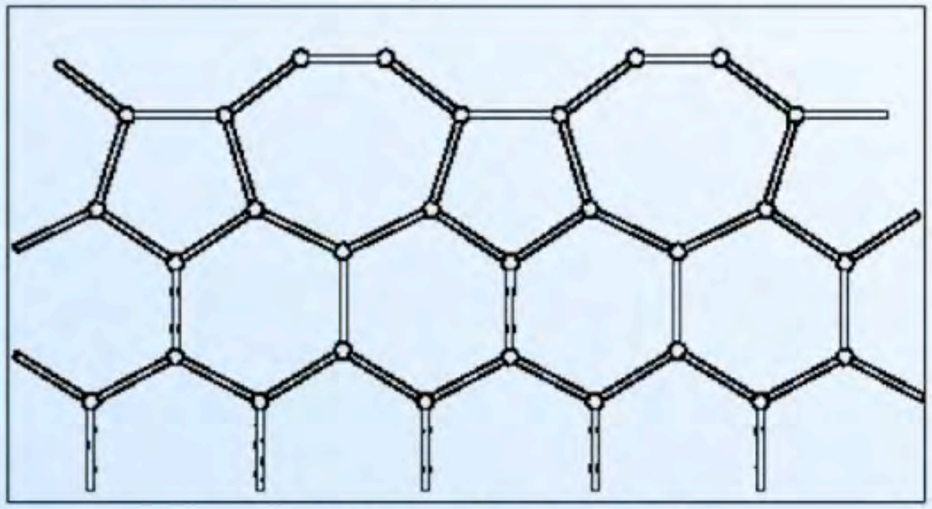
zigzag



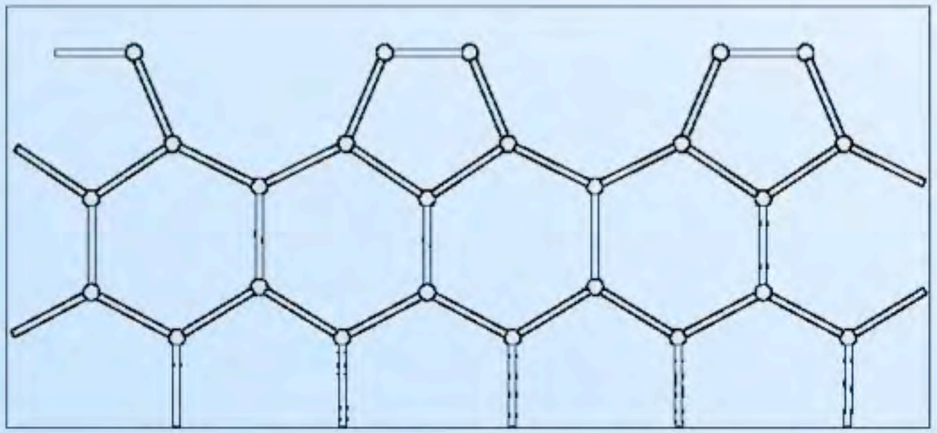
Kleine

Edge stabilization

Edge type	Eform (eV/atom)	Eform (eV/Angst)
Armchair	2.35	1.10
Zigzag	3.29	1.34
Kleine	5.43	2.21
Reconst. zigzag	2.70	1.09
Reconst. Kleine	3.68	1.50



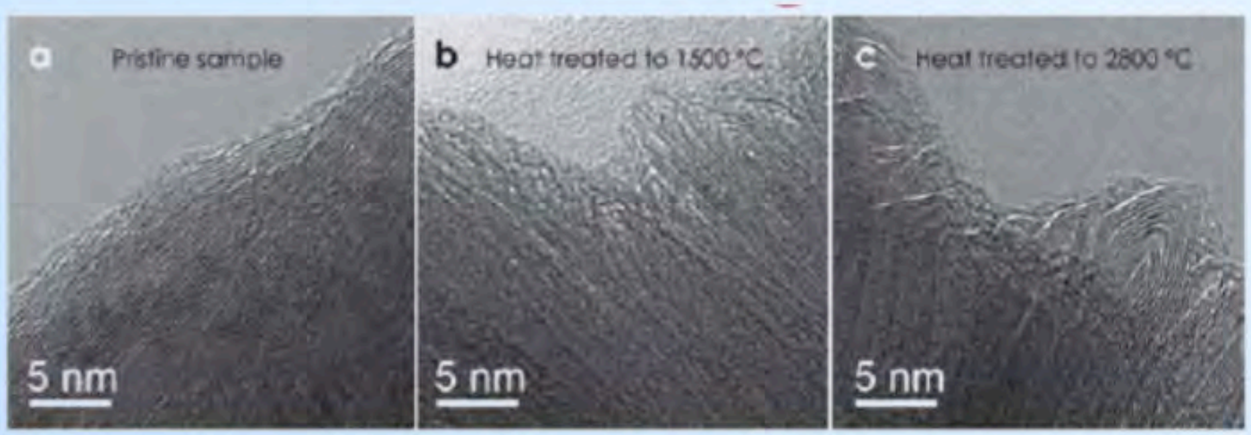
Reconst. zigzag

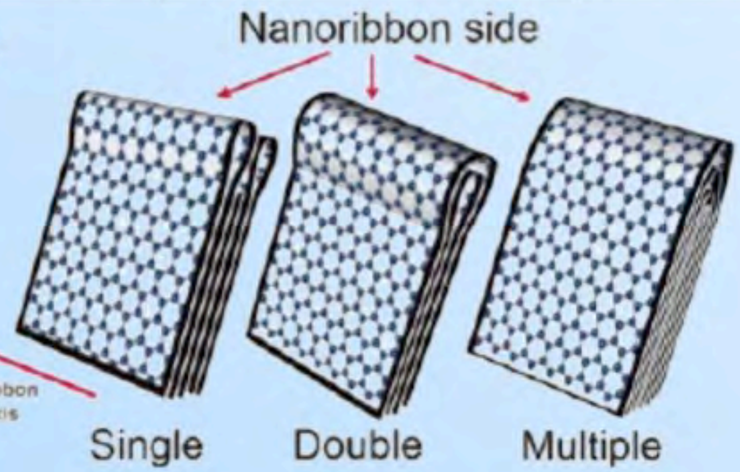


Reconst. Kleine

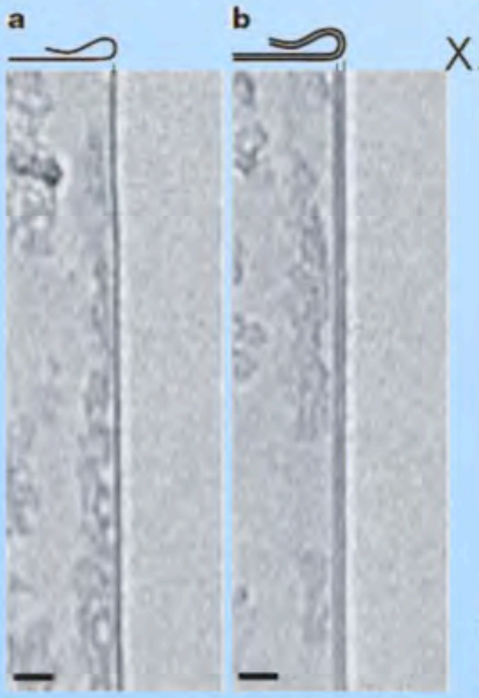
(2x1) reconstruction

Unique 2D Edge stabilisation mechanisms

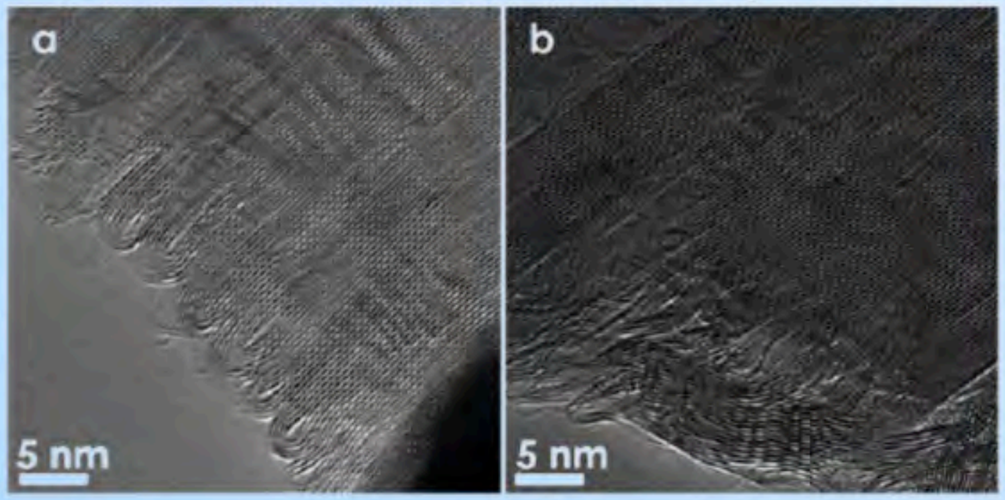


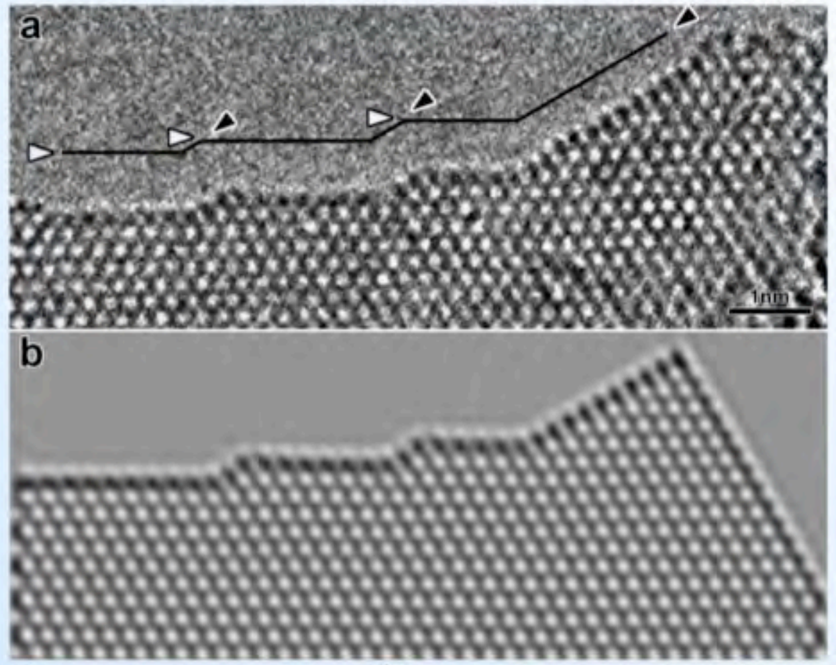


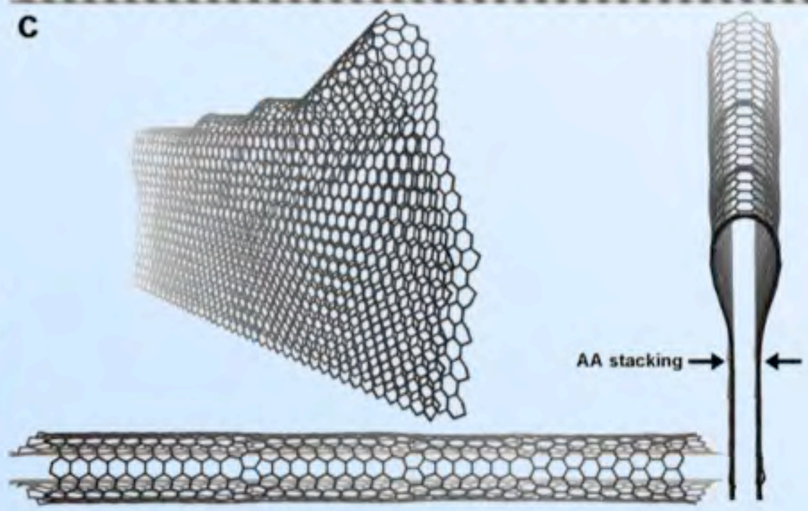
J. C. Meyer et al Nature 446 (2007) 60



X. T. Jia et al J. Vac. Sci. Technol., B 27 (2009) 1996





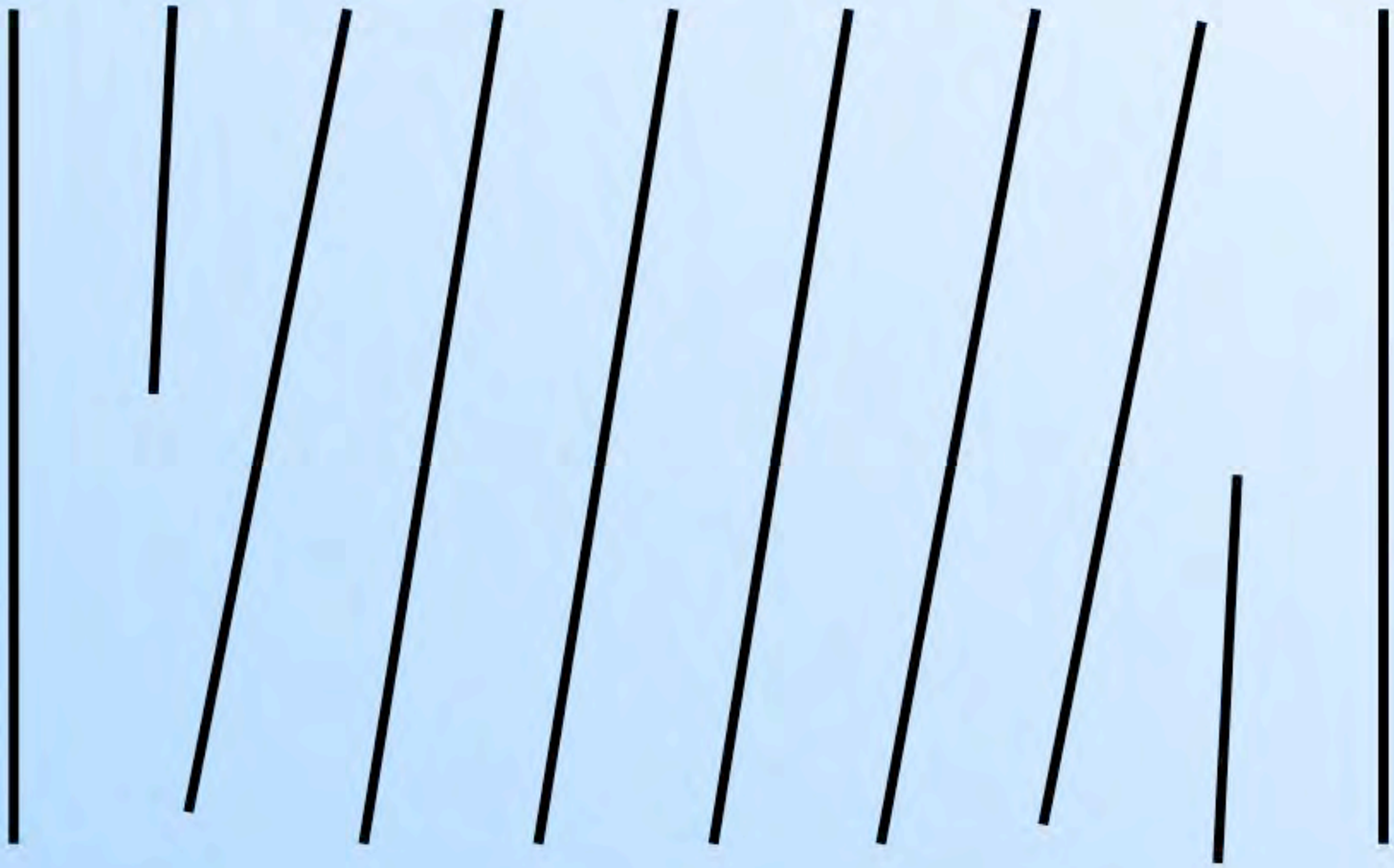


Z.Liu et al. PRL 102 (2009) 015501

Way of edge stabilization without adsorption? Rolling up!

Zigzag Prismatic Edge in Graphite

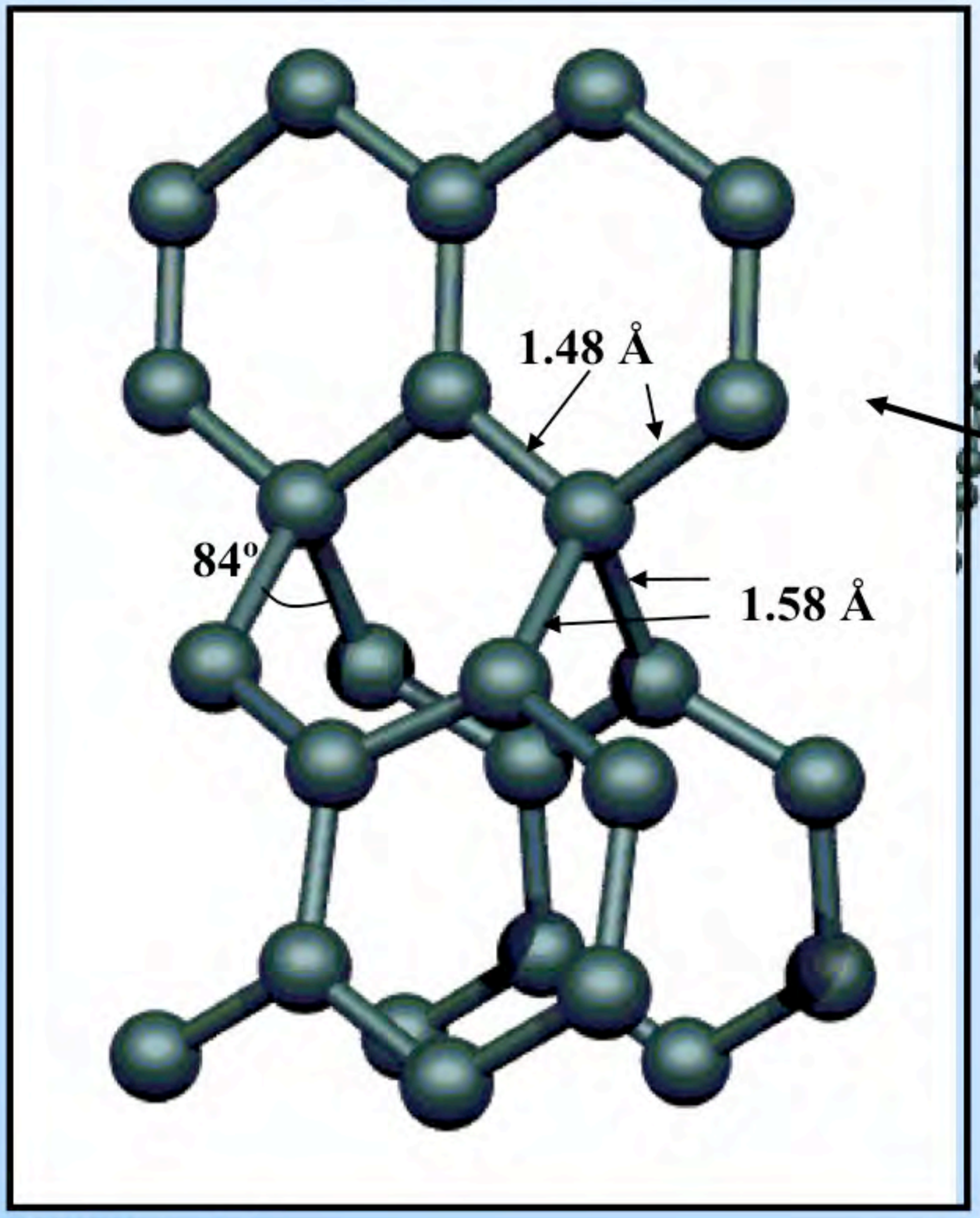
Zigzag Prismatic Edge in Graphite



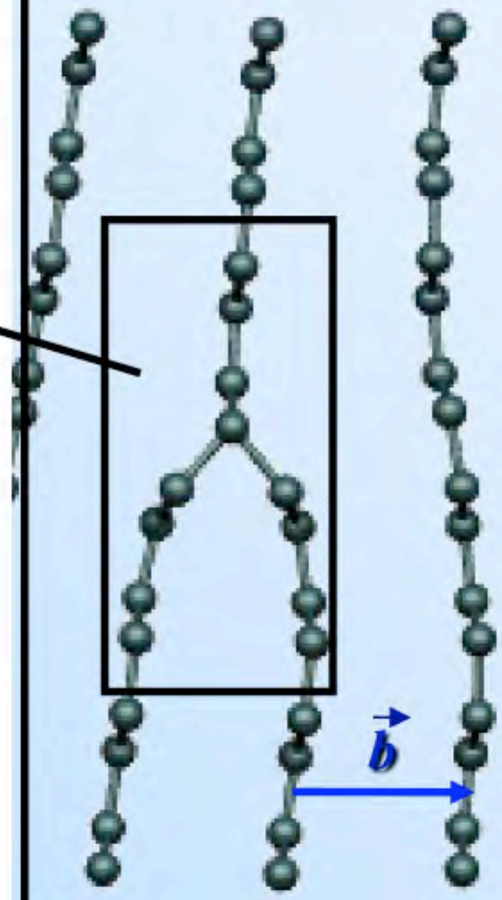
Prismatic edge dislocation dipole

- **Dislocation line lies in the direction:** $\lfloor 2\bar{1}\bar{1}0 \rfloor$

Zigzag Prismatic Edge in Graphite



(M.Heggie)

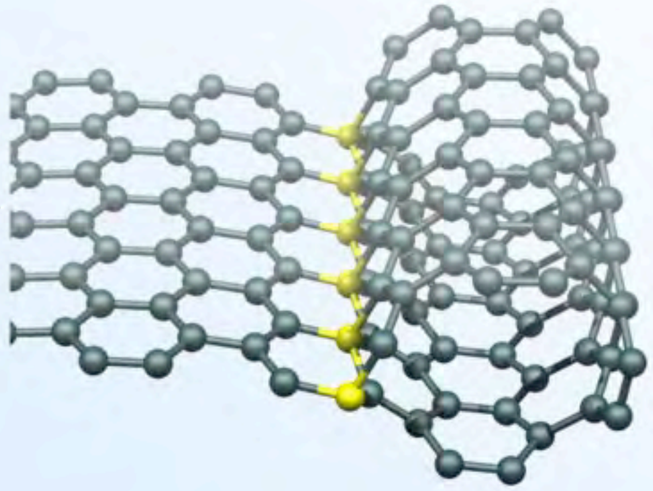


- **Dislocation line lies in the direction:** $\lfloor 2\bar{1}\bar{1}0 \rfloor$
- **Rebonding to the neighbouring layer**
- **Dangling bonds replaced with line of sp^3-C atoms.**

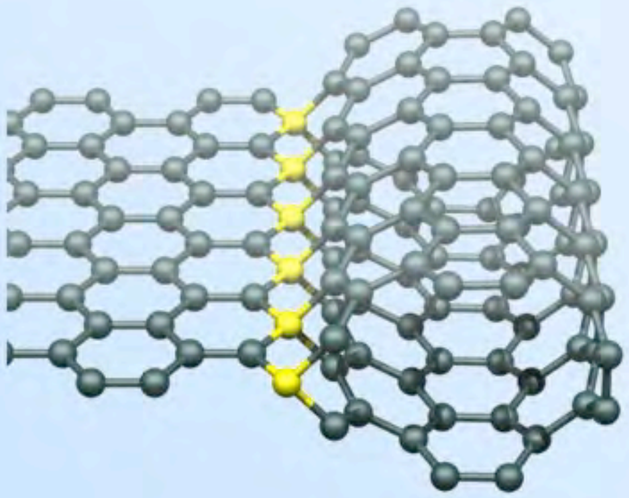
G. Savini, G. Haffenden, J-M. Campanera and M.I. Heggie, Phys. Stat. Sol. (c) 4 (8) 2958-2962 (2007).

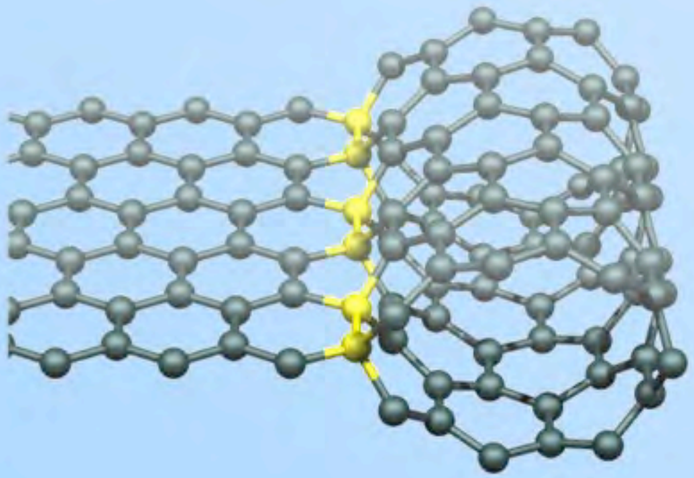
Tubes-on-edges

Folded Kleine edge →



Folded zigzag edge →



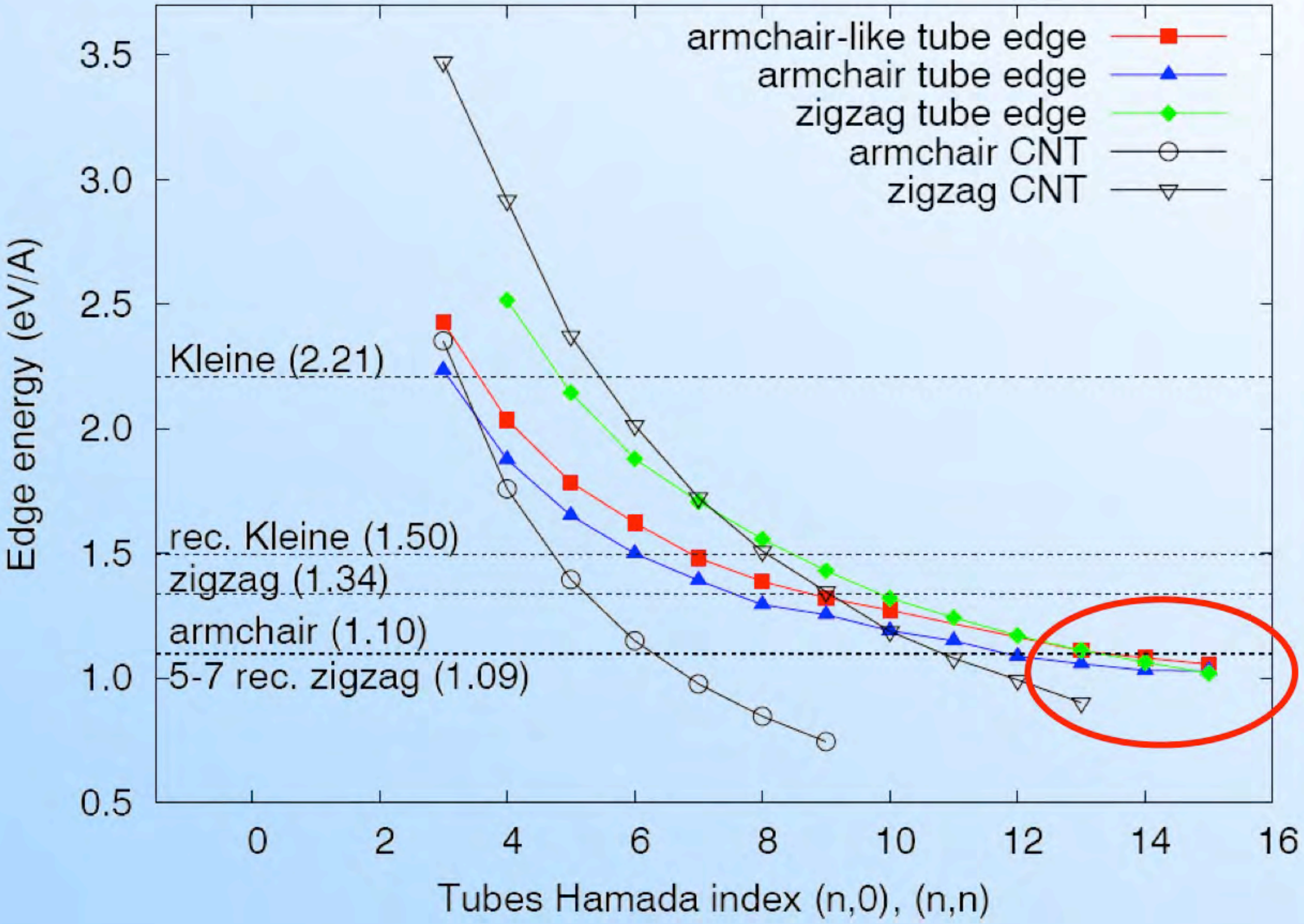


← Folded armchair edge

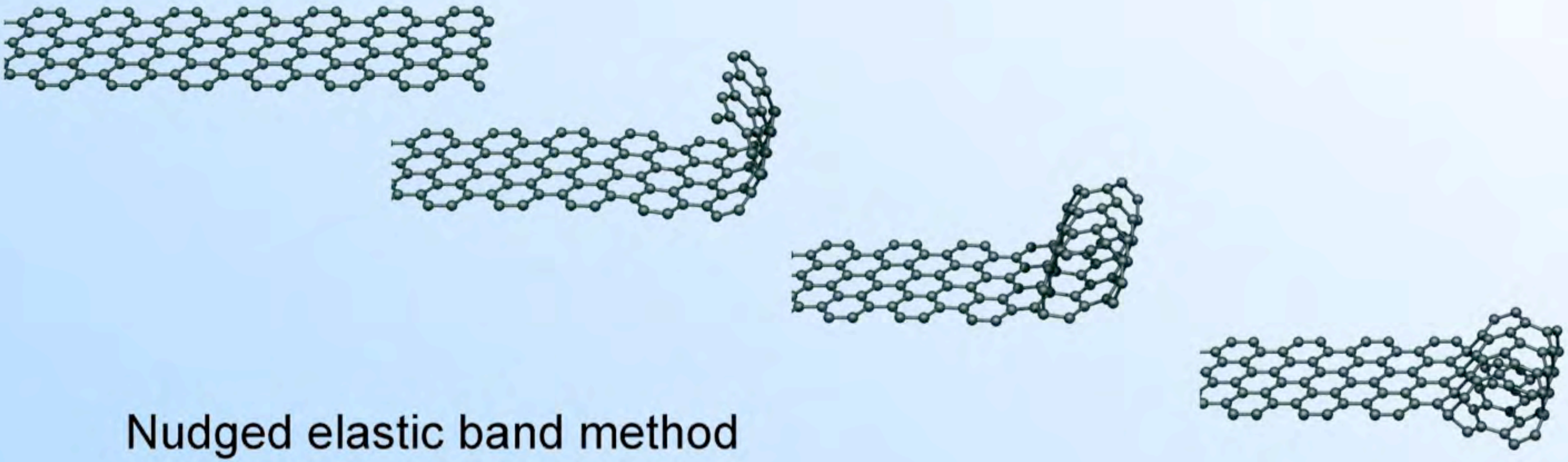
Each “new” edge has sp^3 bonded C-atoms!

V. Ivanovskaya, C. P. Ewels *et al*, submitted (2011)

Energetic stability



Rolling barriers



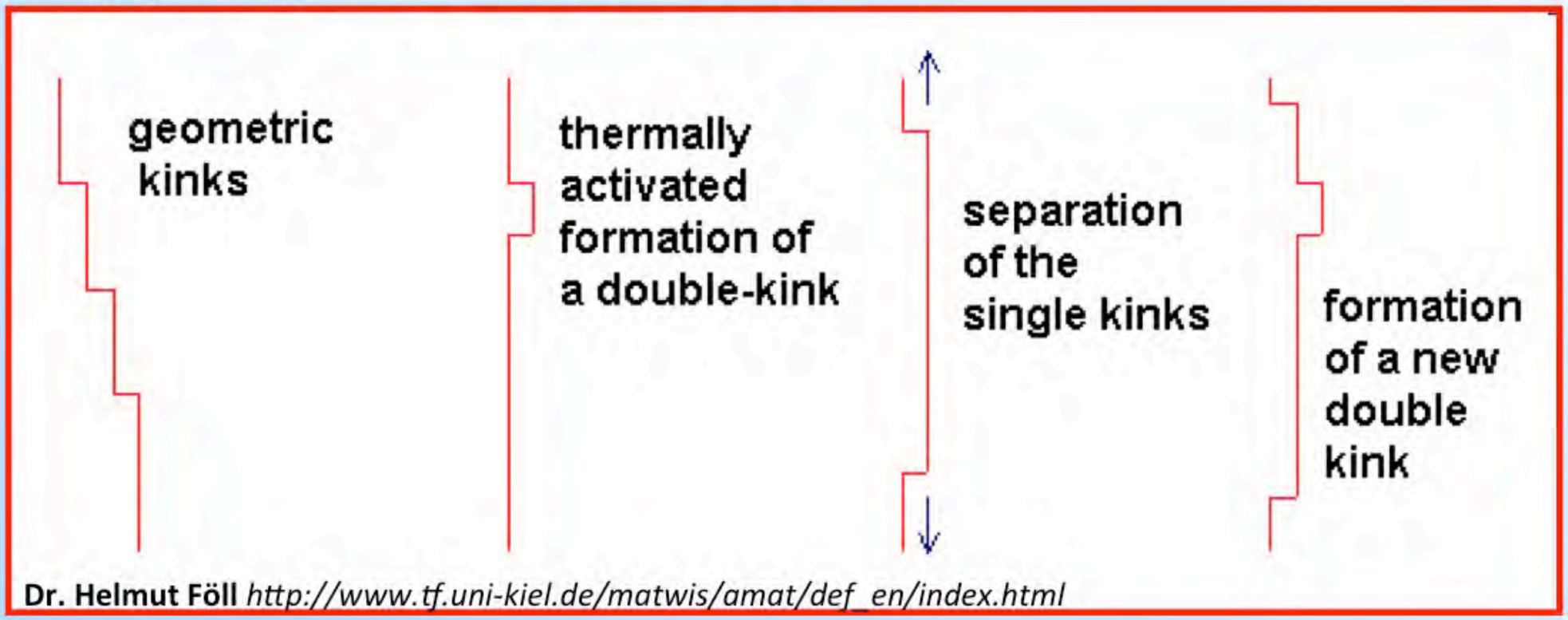
Nudged elastic band method

Rolling barriers:
~4.9 eV for narrow (4.4) tube and ~ 3.2 for bigger (8.8) tube

Derolling barriers:
~2.2 eV for (4.4) tube and ~ 4.0 for (8.8) tube

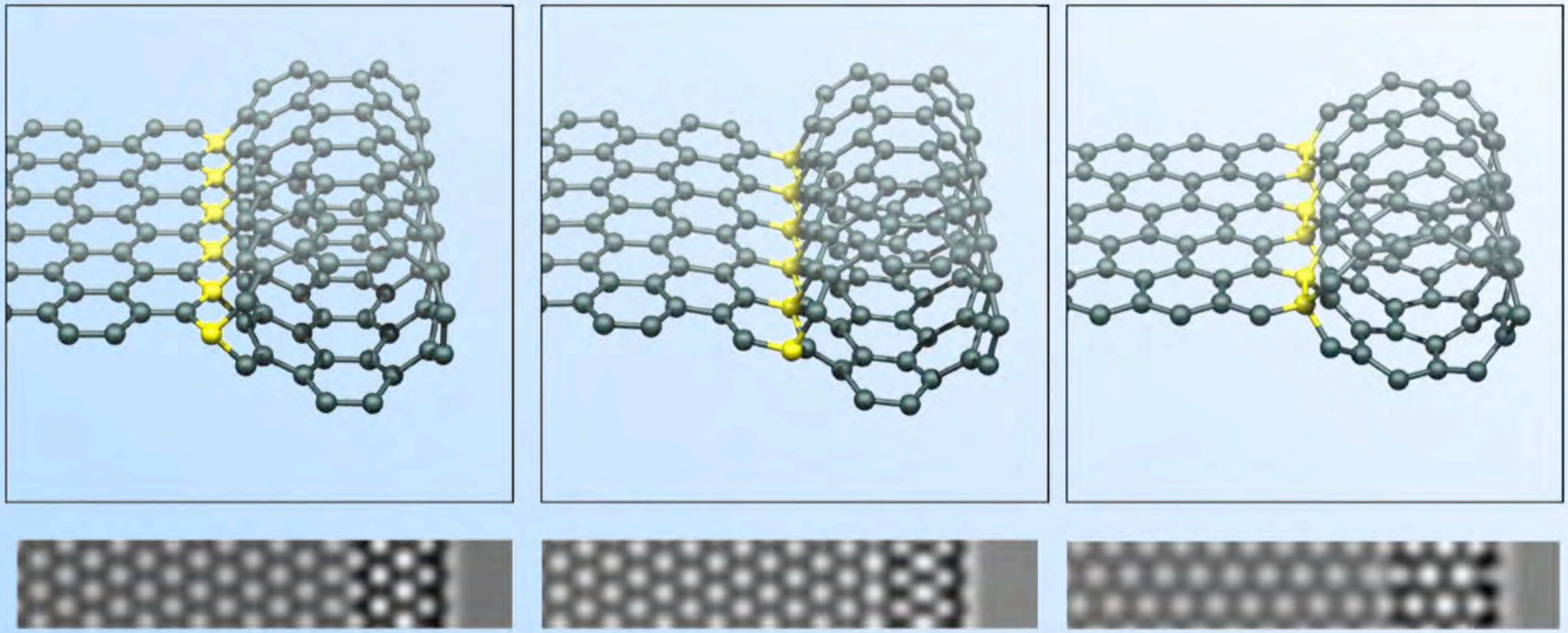
Reducing the barrier

- « Zipping » Mechanism



- Kinetic Energy

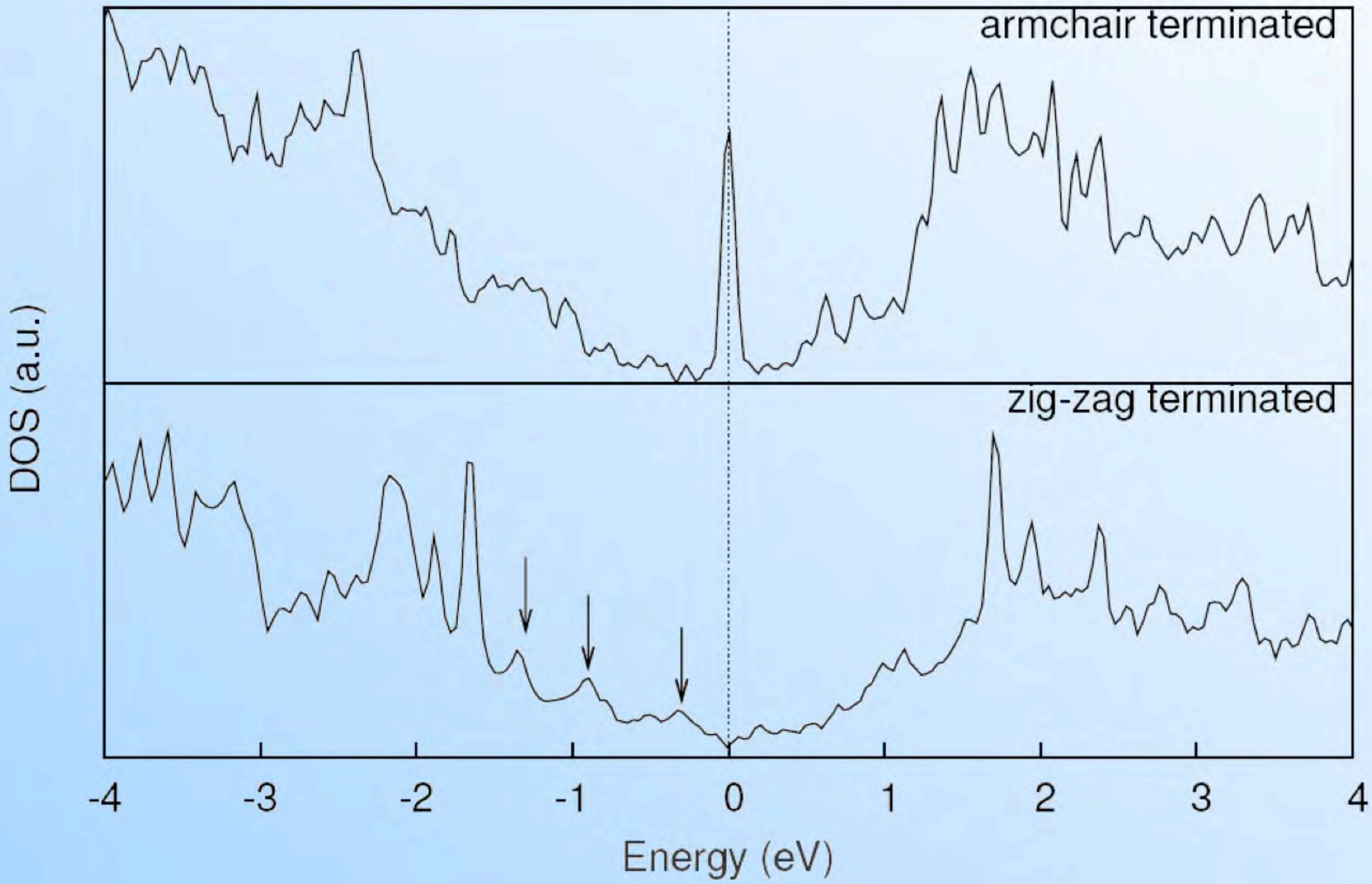
TEM image simulations

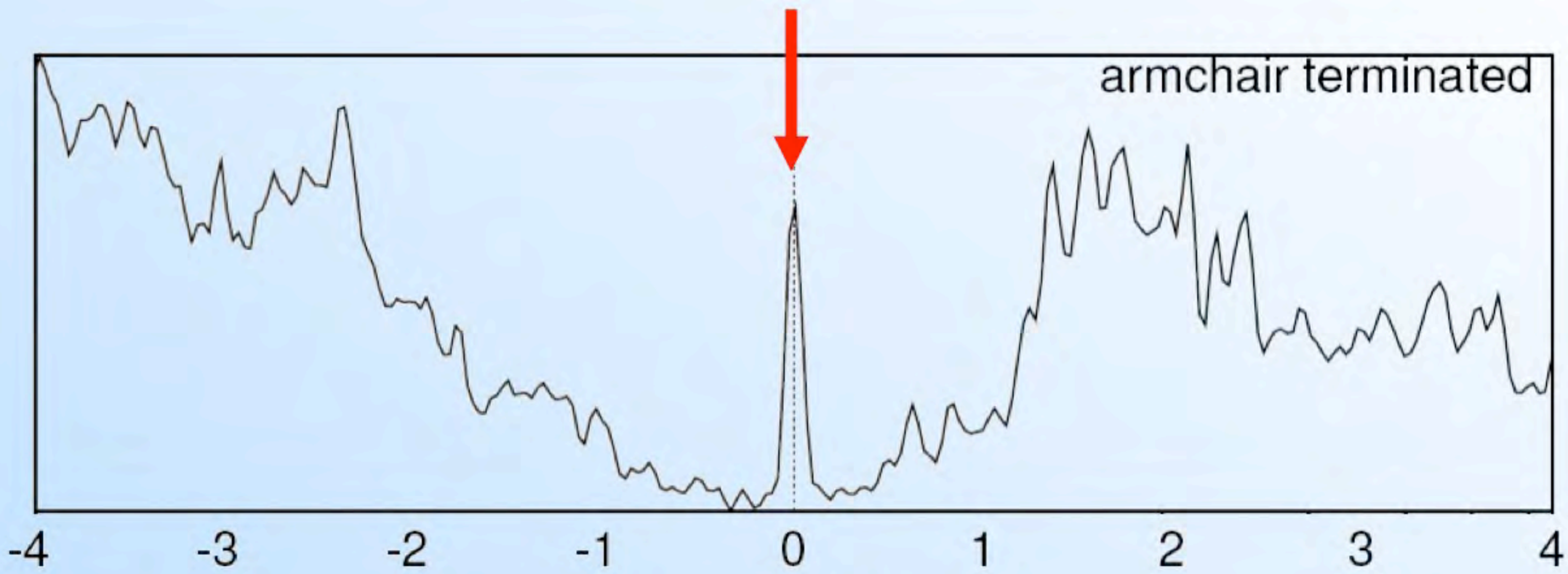


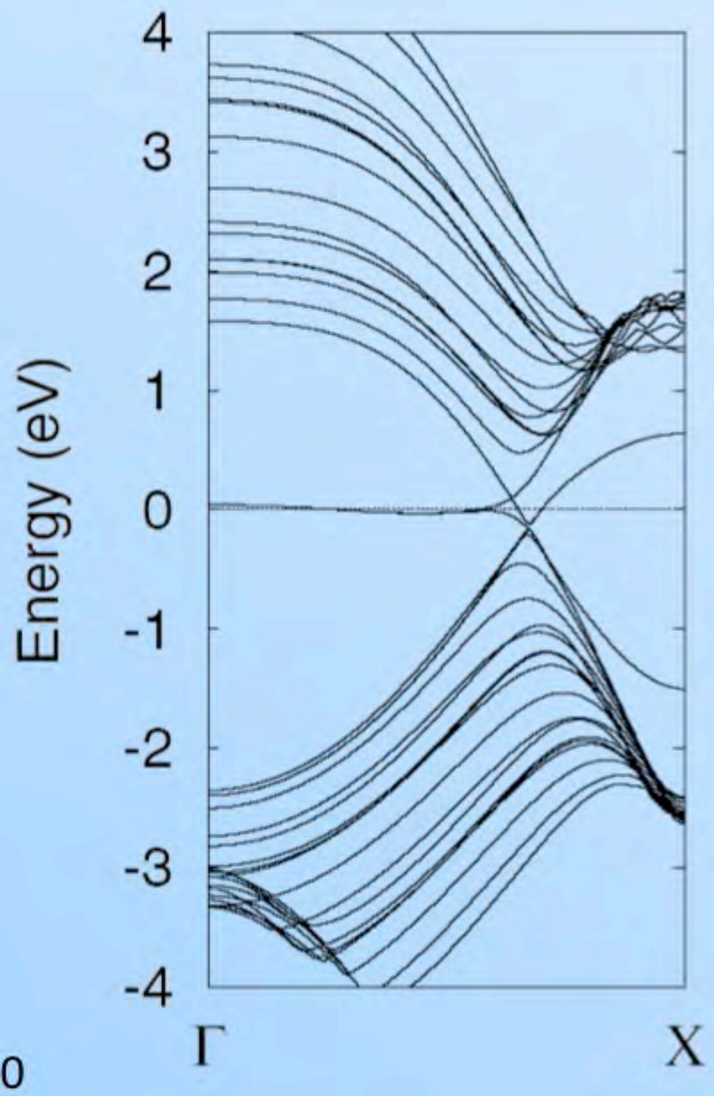
rolled zigzag edge | rolled Kleine edge | rolled armchair edge

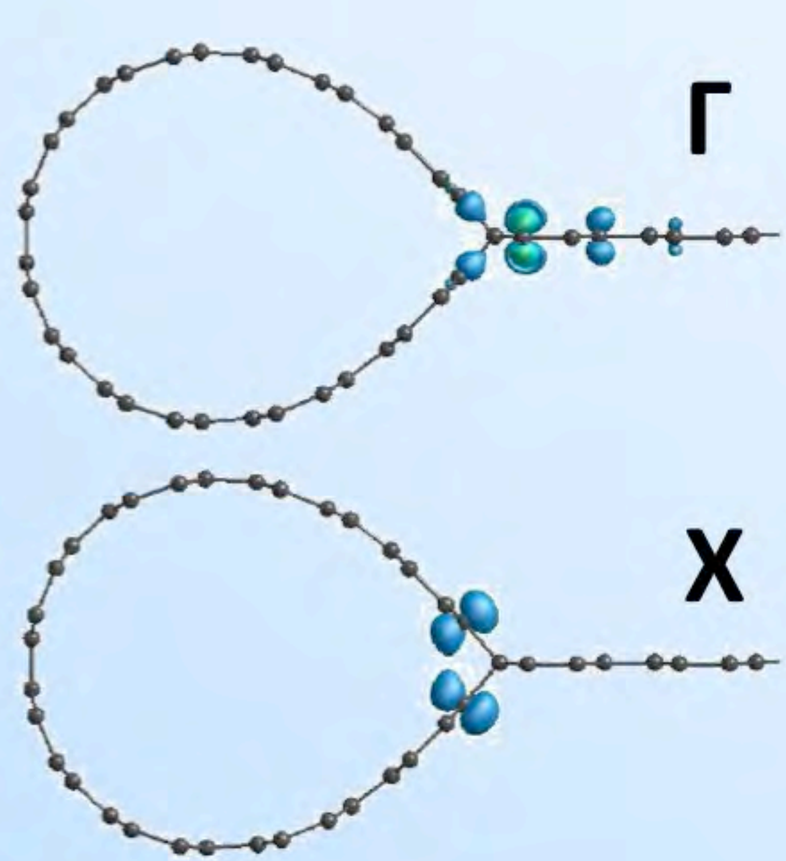
TEM images simulations of tubes-on-edges: high similarity to "clean" edges

Electronic Properties









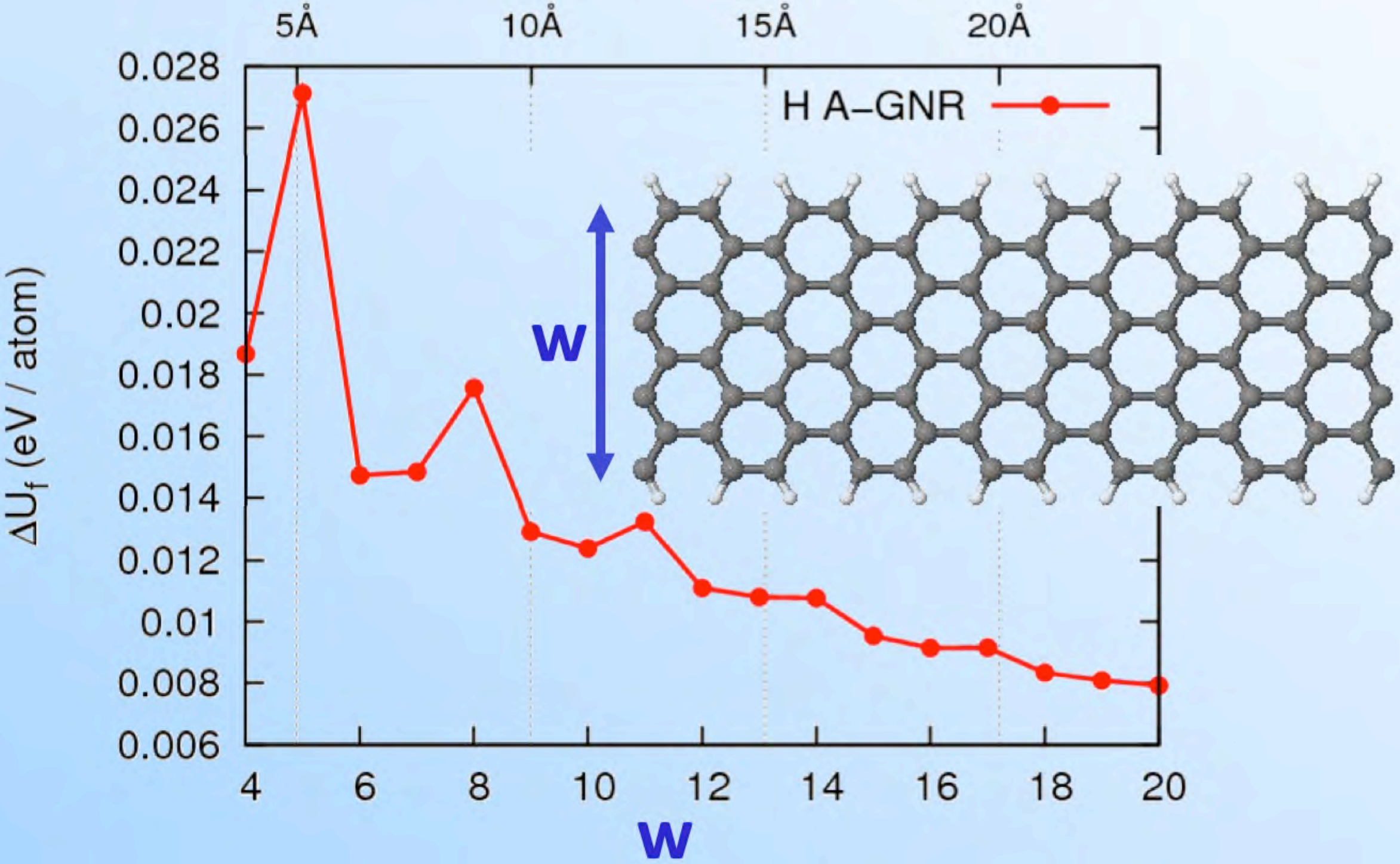
V. Ivanovskaya, C. P. Ewels *et al*, submitted (2011)

That’s non-functionalised…

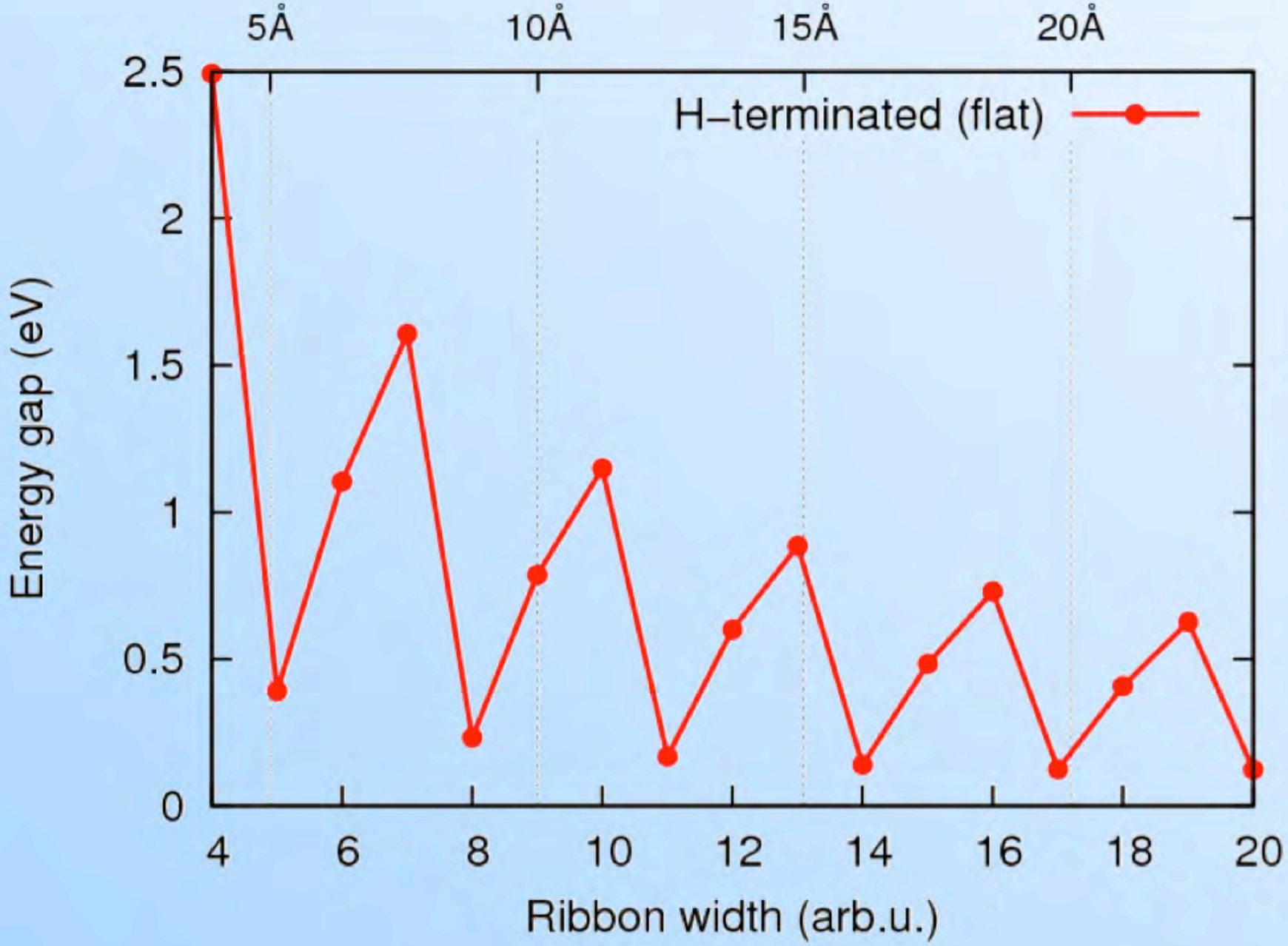
What about adding some chemistry?

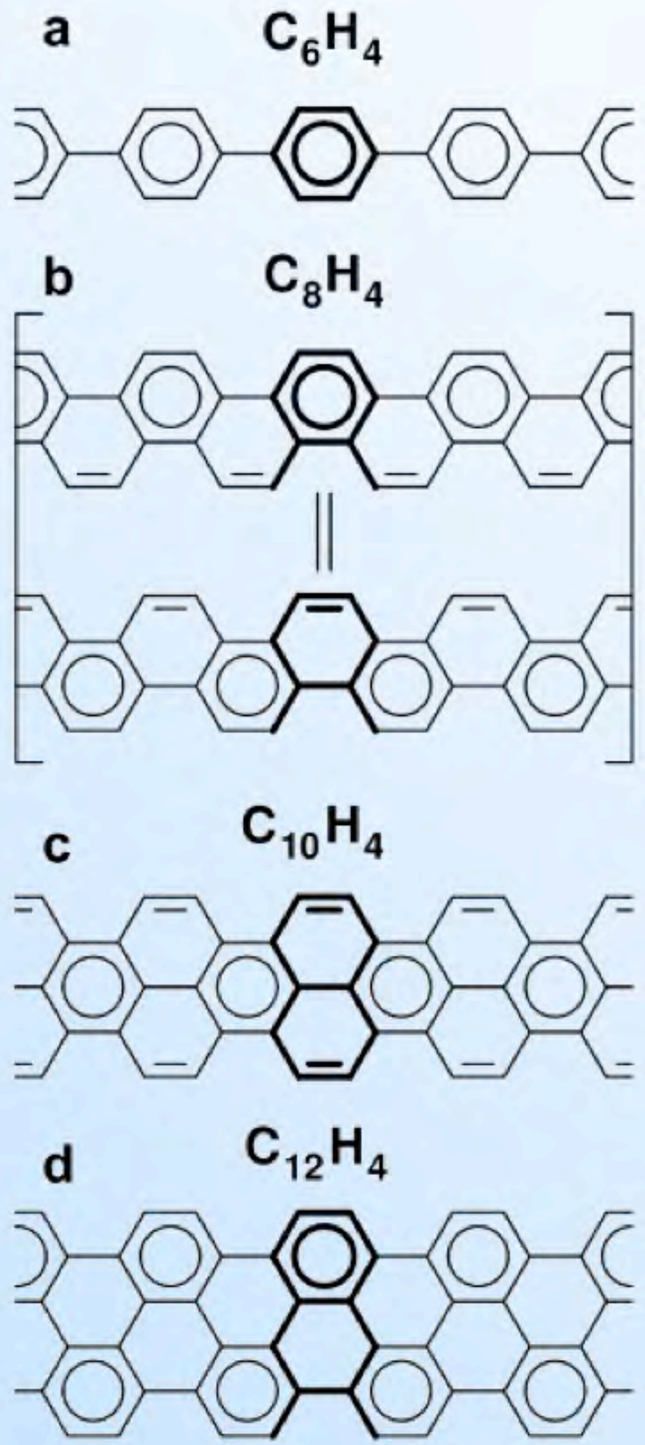
-H, -OH, -NH_2, -COOH, -SH, …

H- terminated edges



H terminated edges



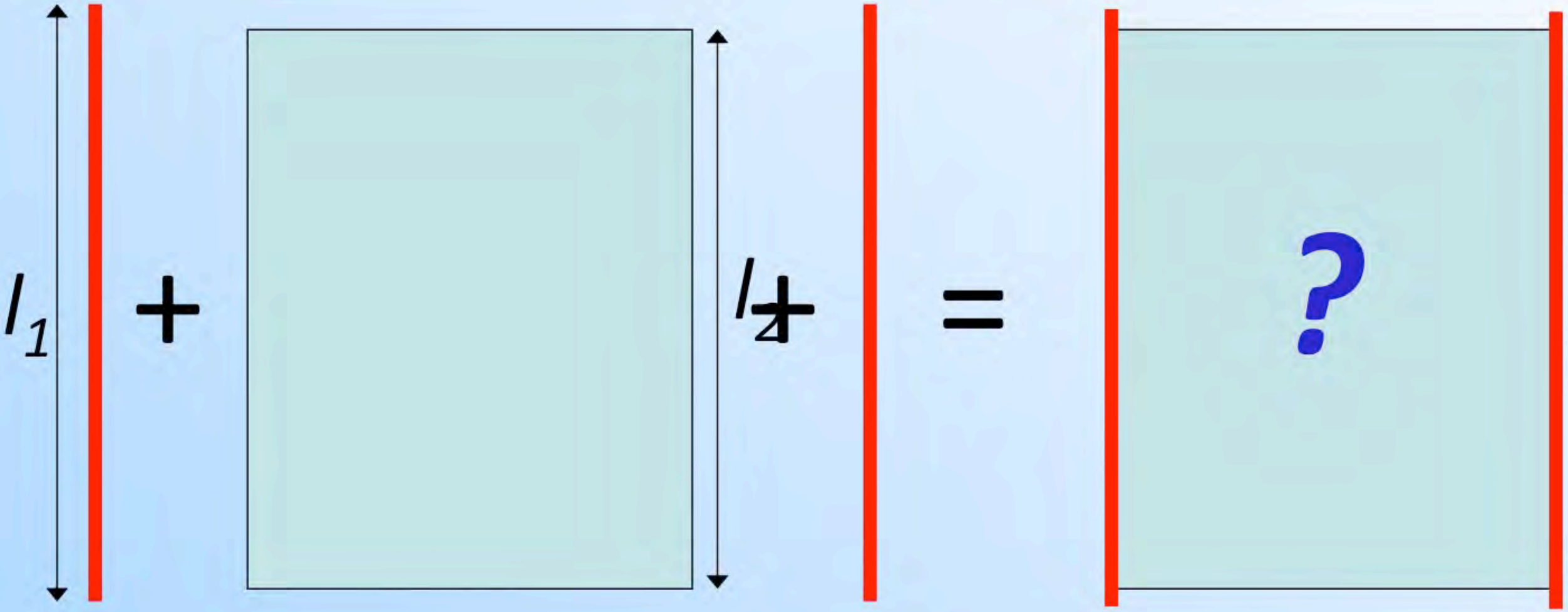


*M. Baldoni, A. Sgamellotti, F. Mercuri, Chem. Phys. Lett. (2008), **464**, 202*

Functionalised Edges

- Many functional groups possible
  -H, -OH, -NH_2, -COOH, -SH, …
- Interaction between groups
  - Coulombic Repulsion ?
  - Hydrogen bonding ?
  - Steric Hindrance ?
- **Edge strain**

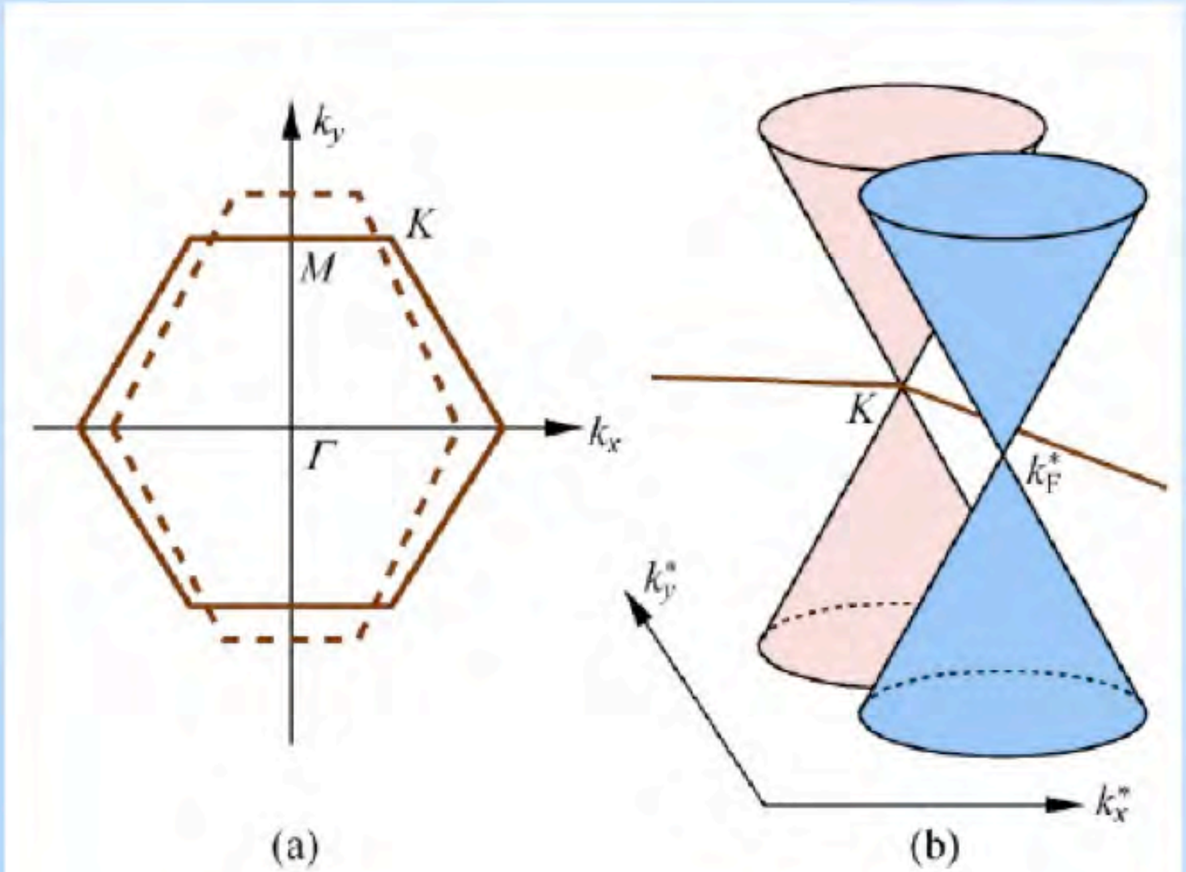
Edge Strain

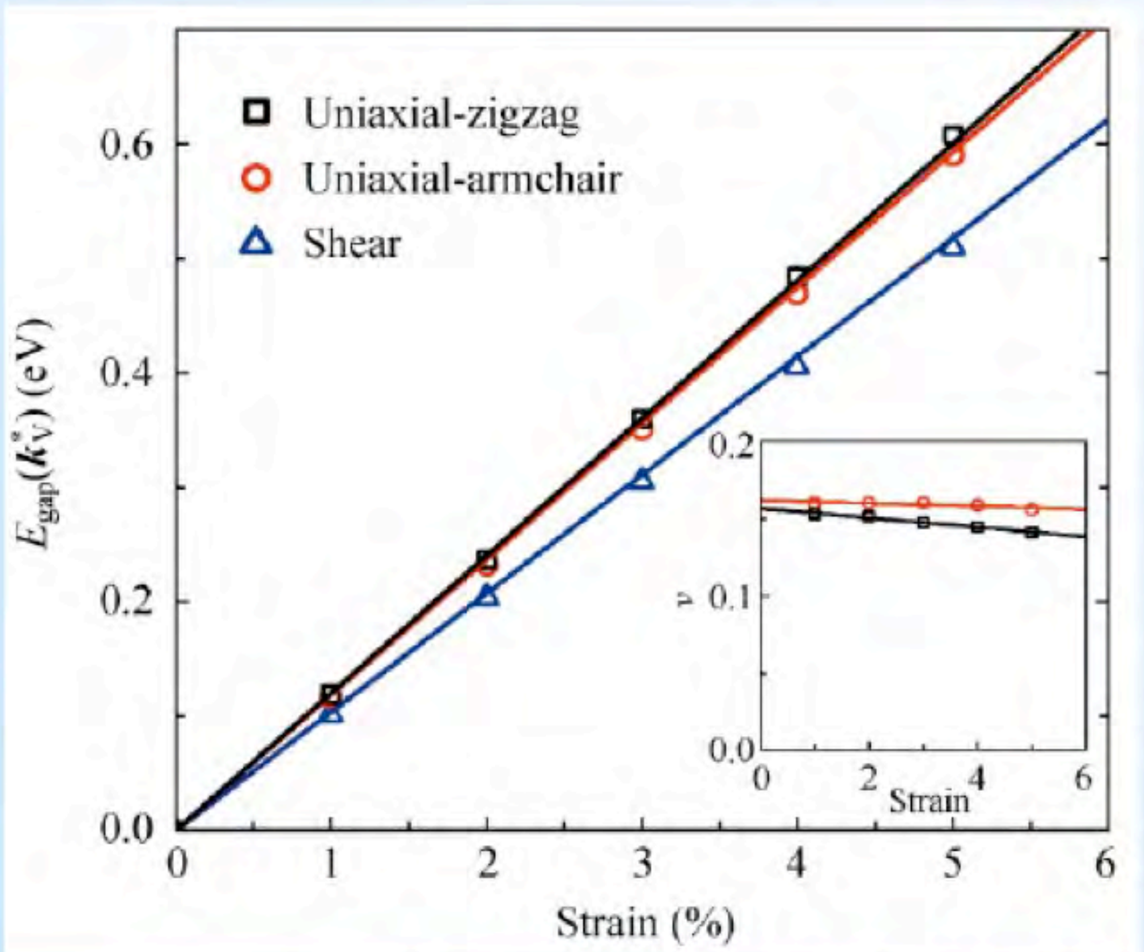


Edge Sheet

Effects of strain in graphene

- Modify the gap, shift Dirac cones ?



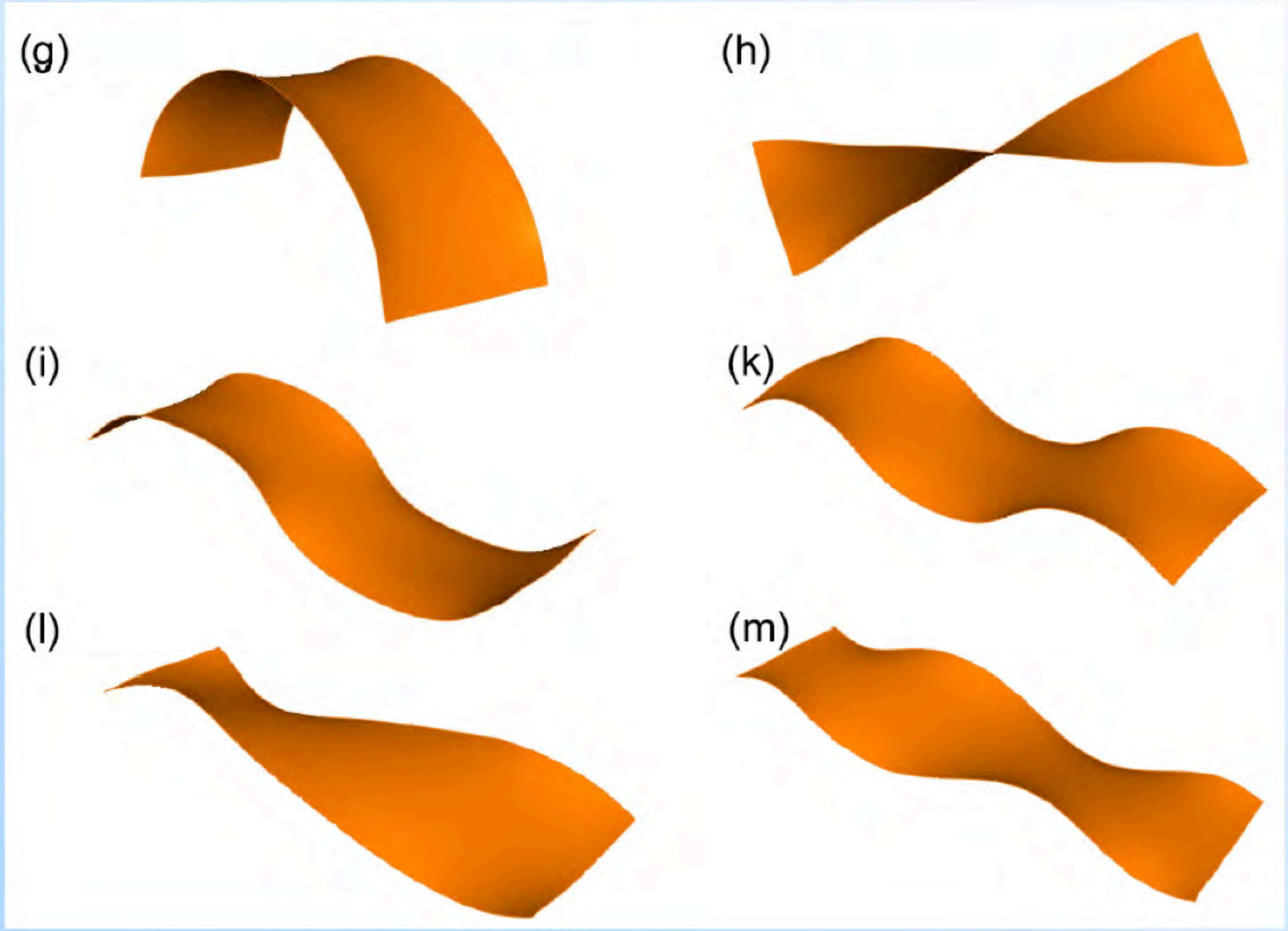


(e.g. Nano Res. 3, 545, 2010)

Functionalised Edges

- Young's Modulus of graphene = 1.08TPa
  - very strain resistant!
- New edge deformation modes available for 2D materials –
  out of plane (buckling, rippling, twisting, …)

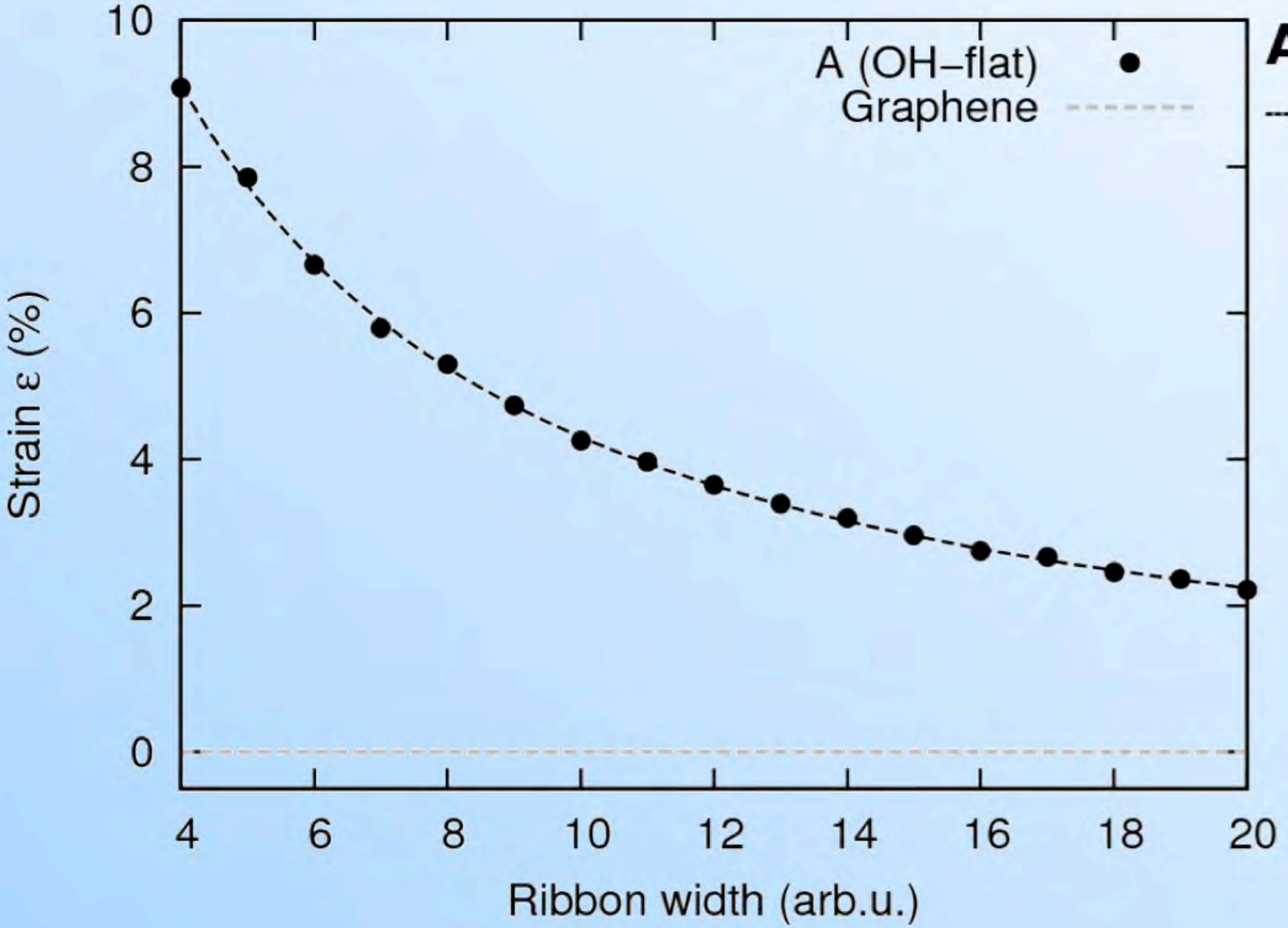
Some deformation modes $l_1 \neq l_2$

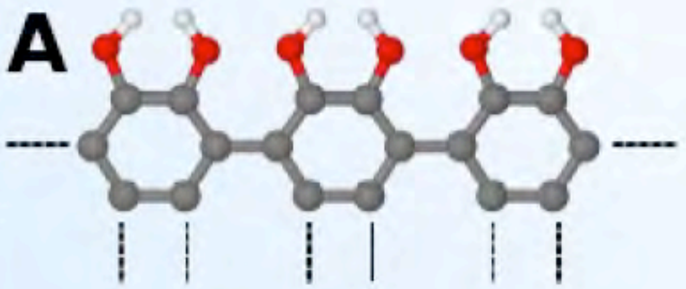


PRL 101, 245501 (2008)

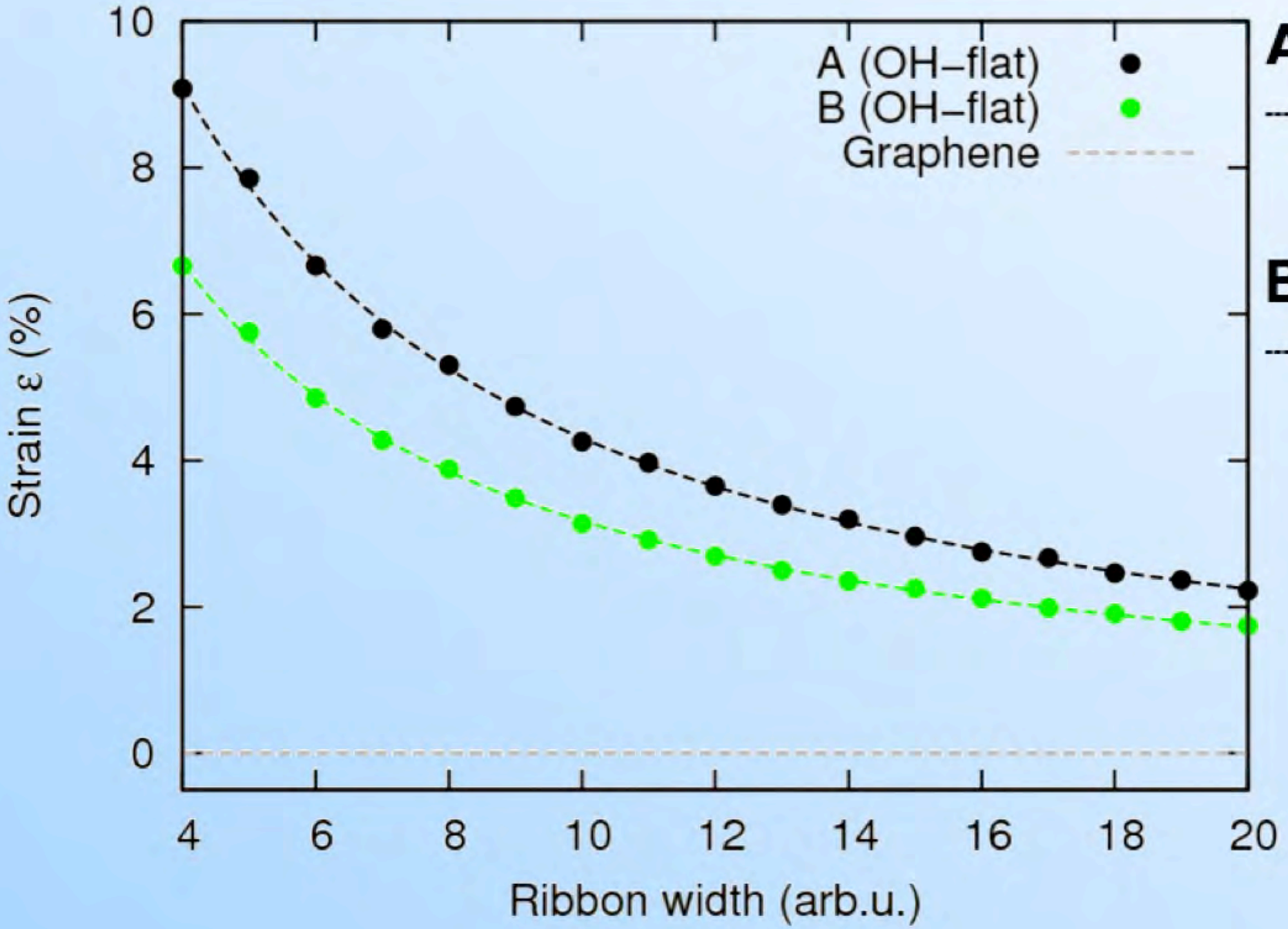
Edge Rippling

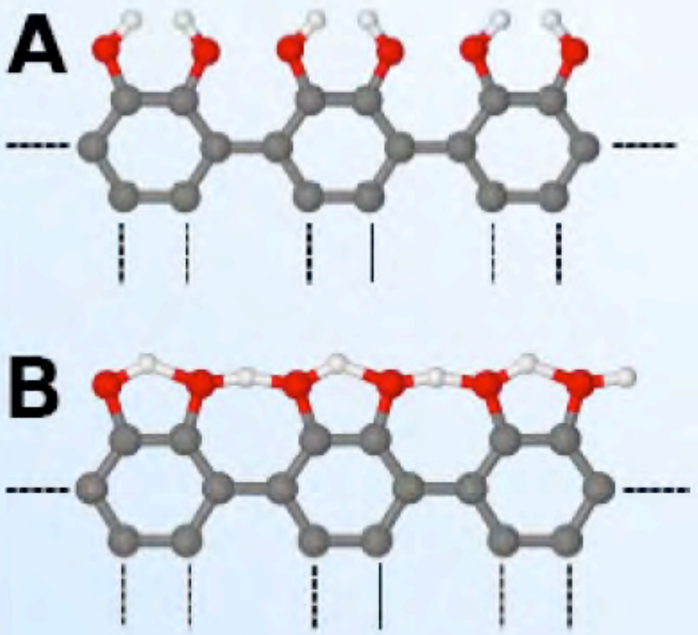
-OH terminated armchair ribbons



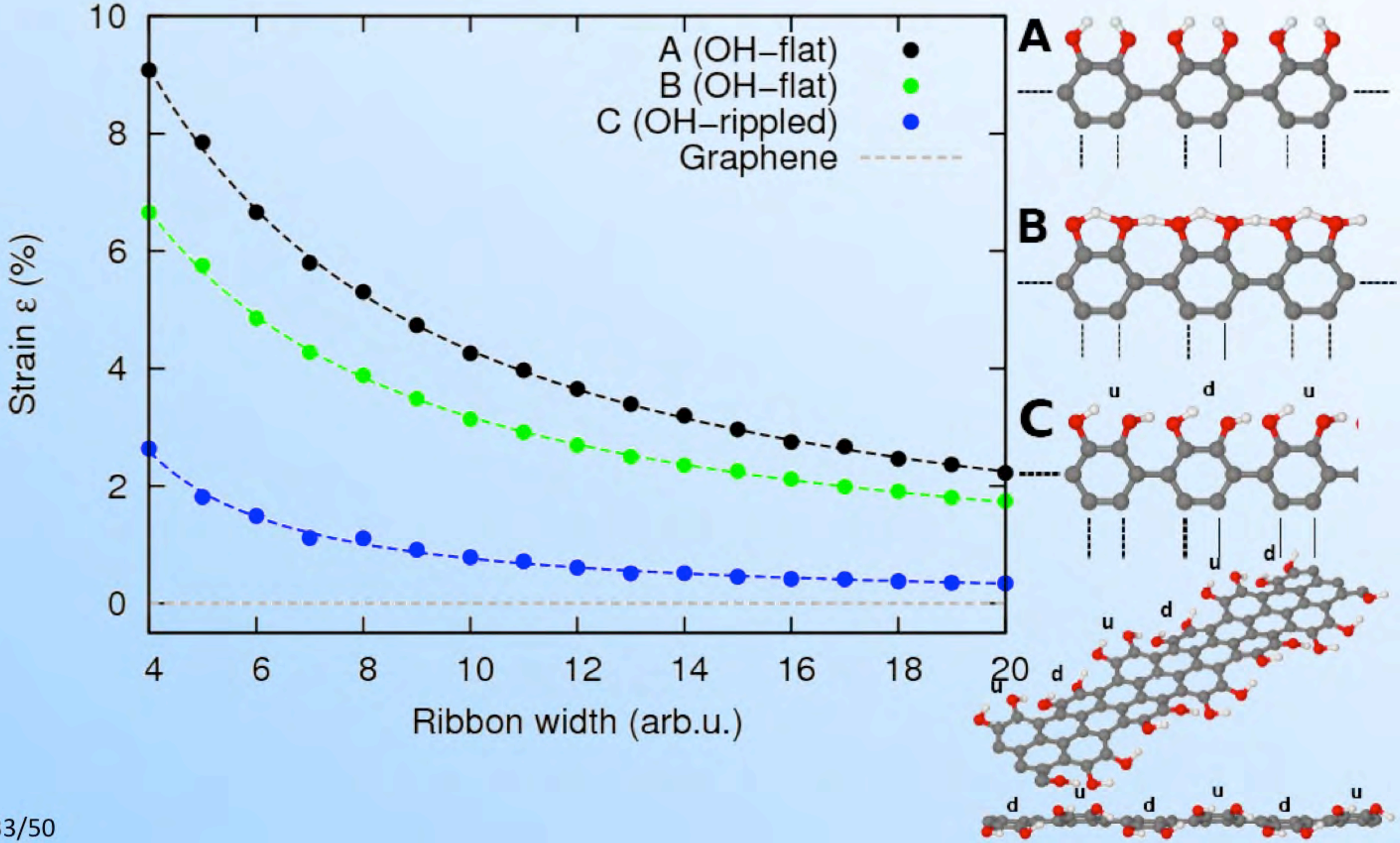


-OH terminated armchair ribbons

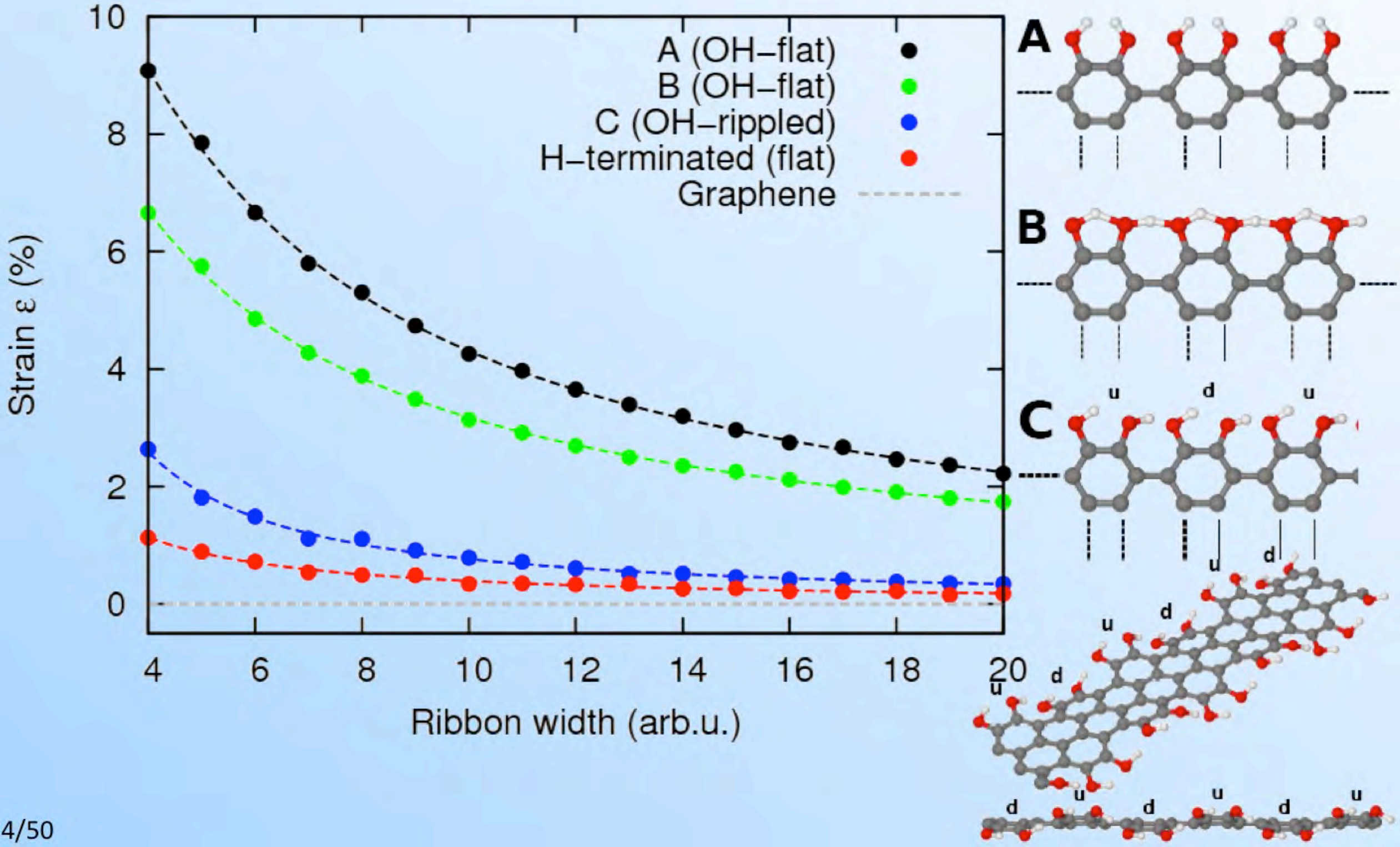




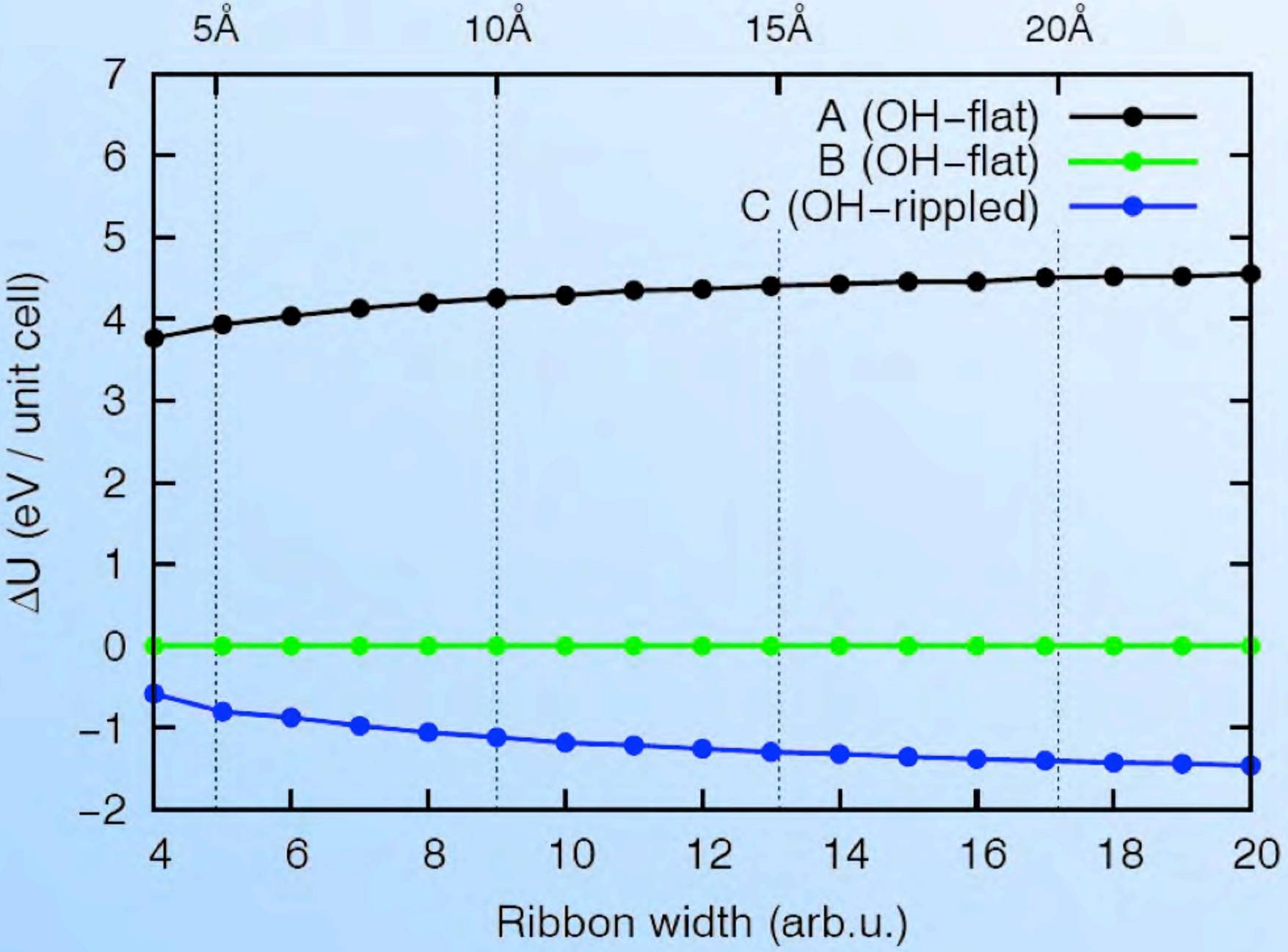
-OH terminated armchair ribbons

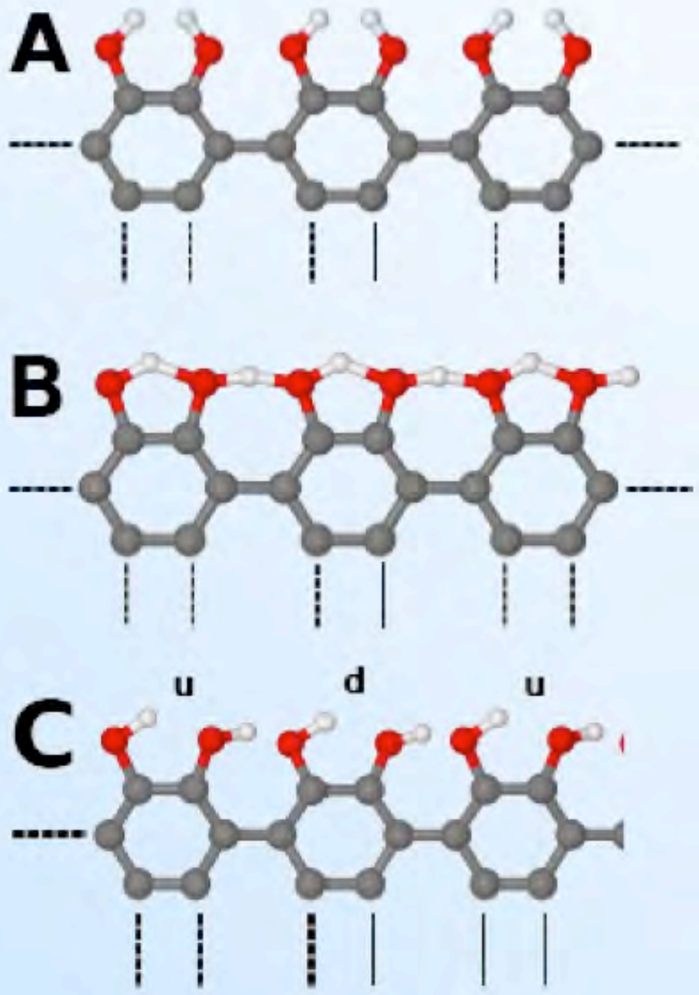


-OH terminated armchair ribbons

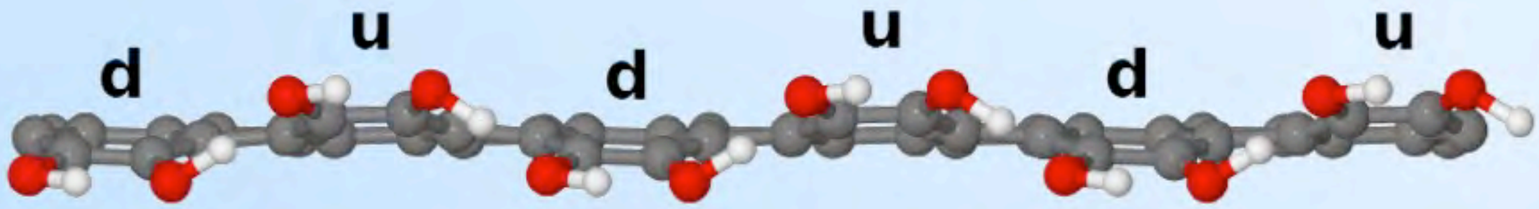


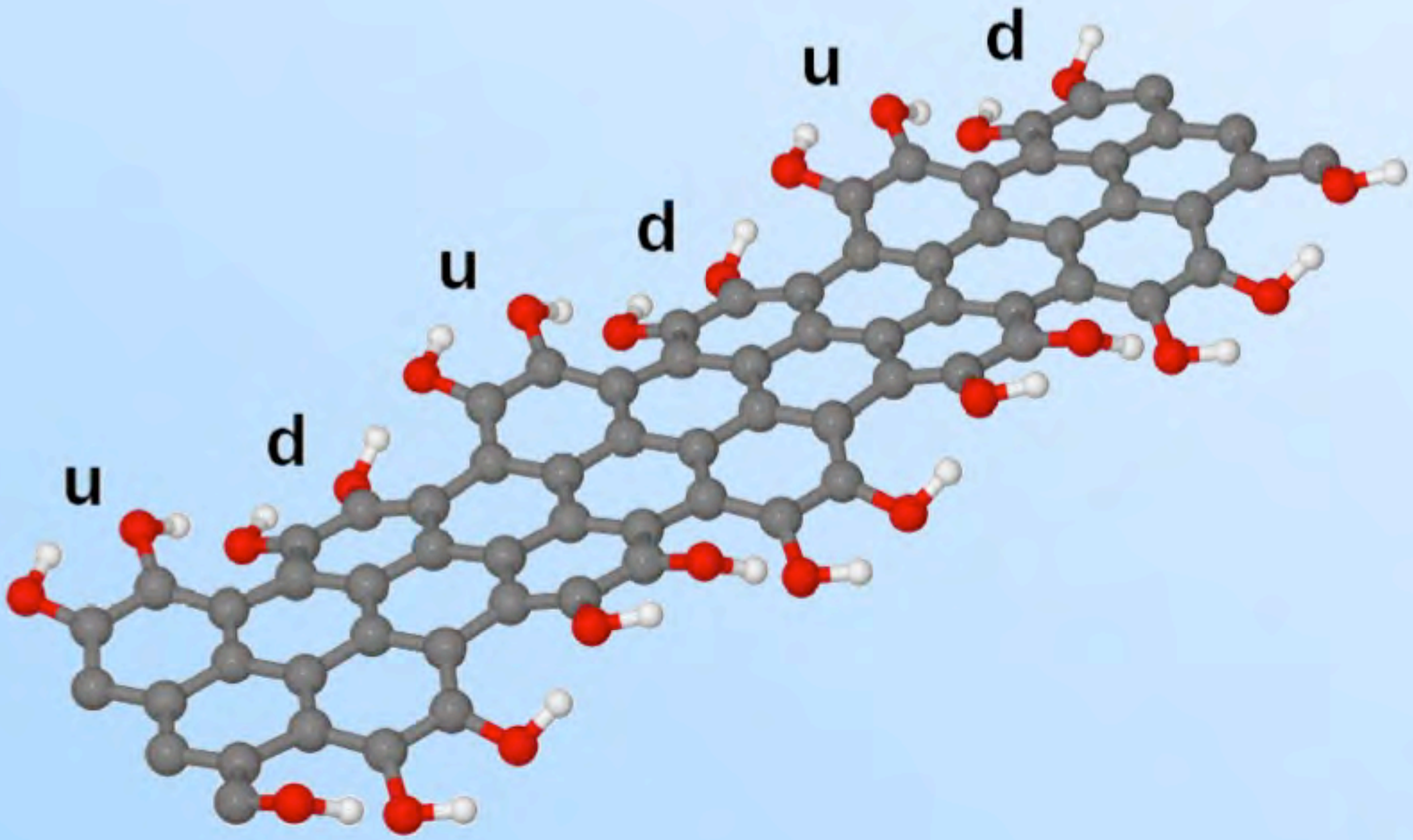
Relative formation energies

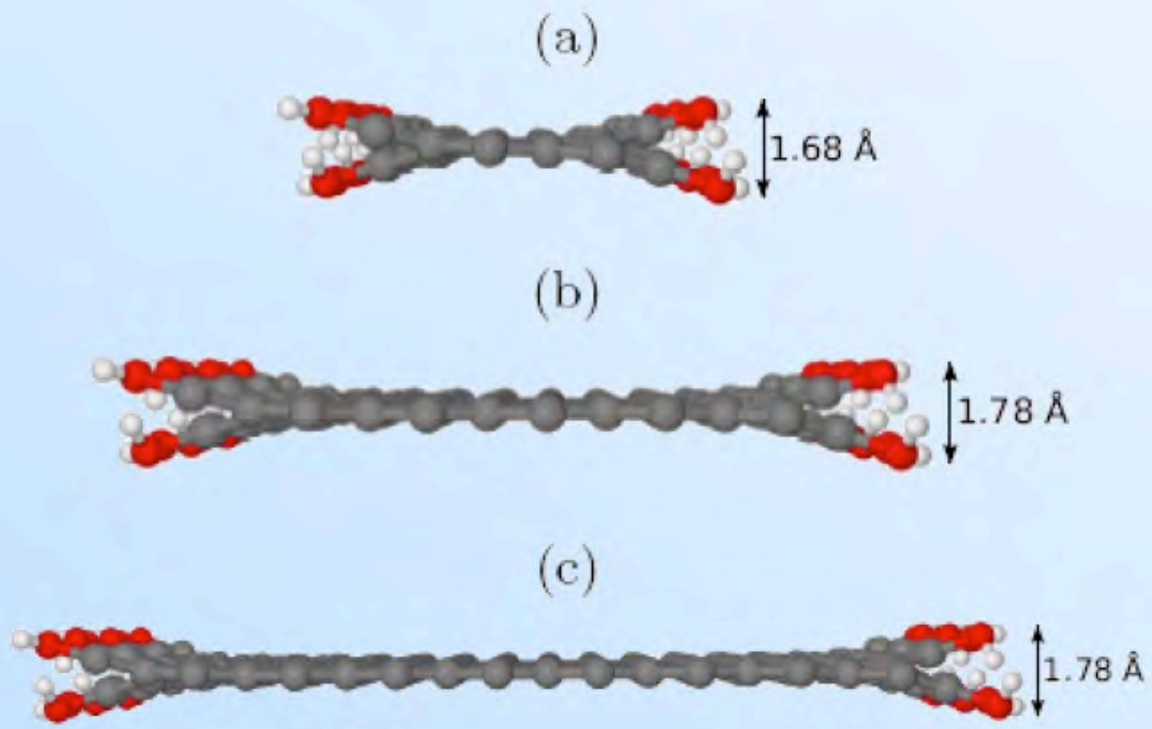




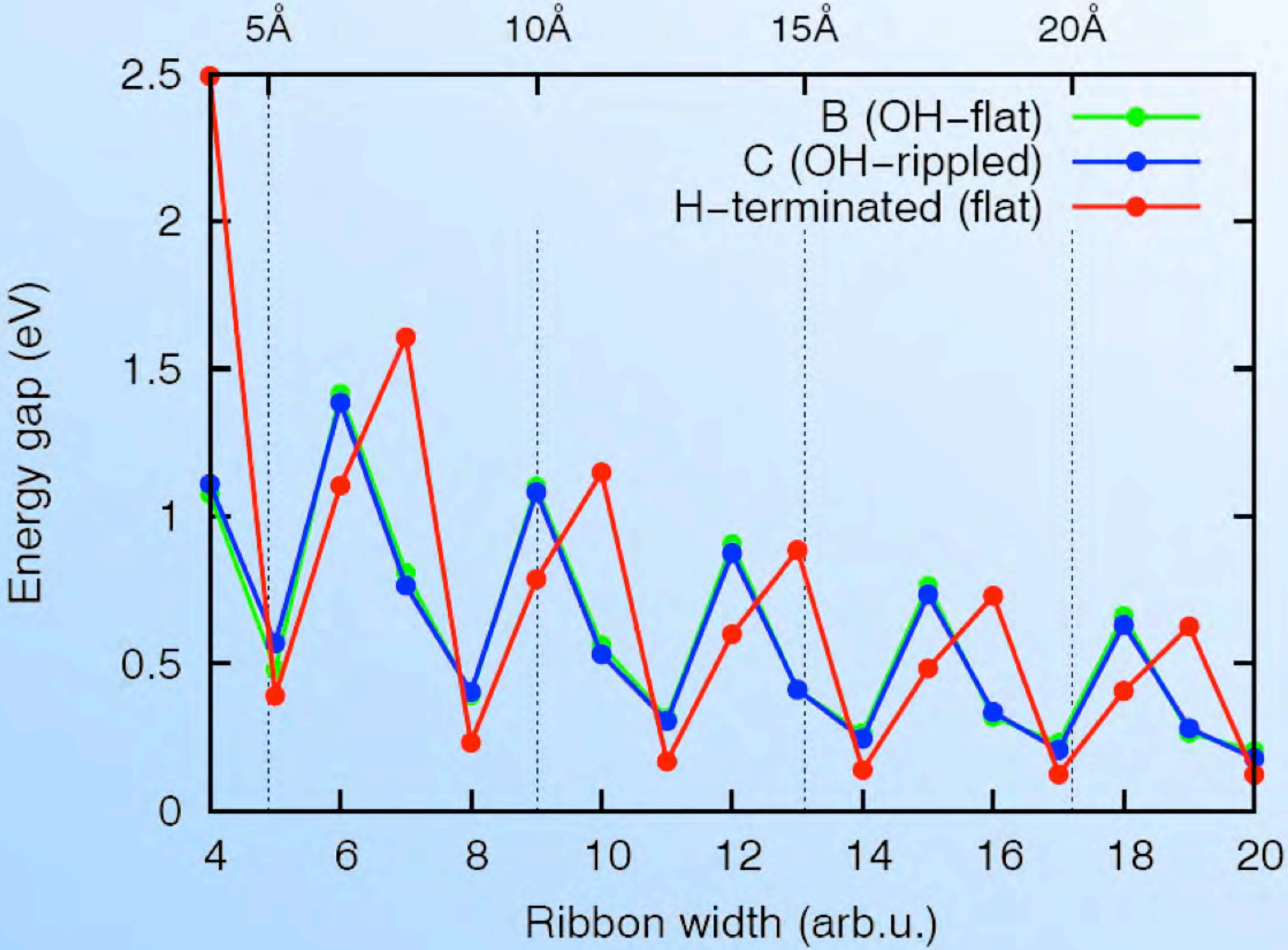
-OH edge structure



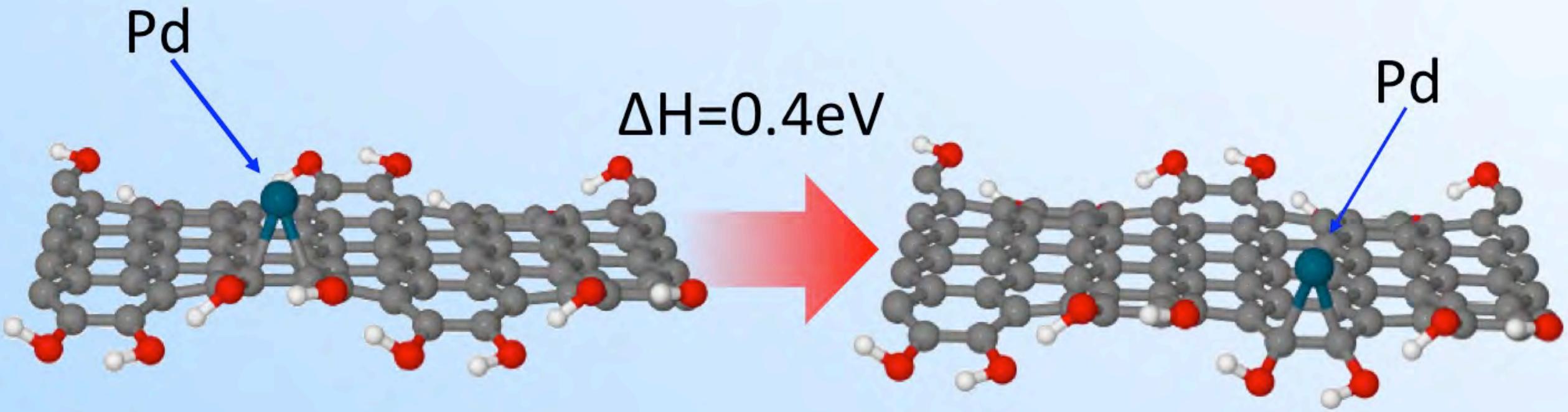




Edge Rippling : Band Gap

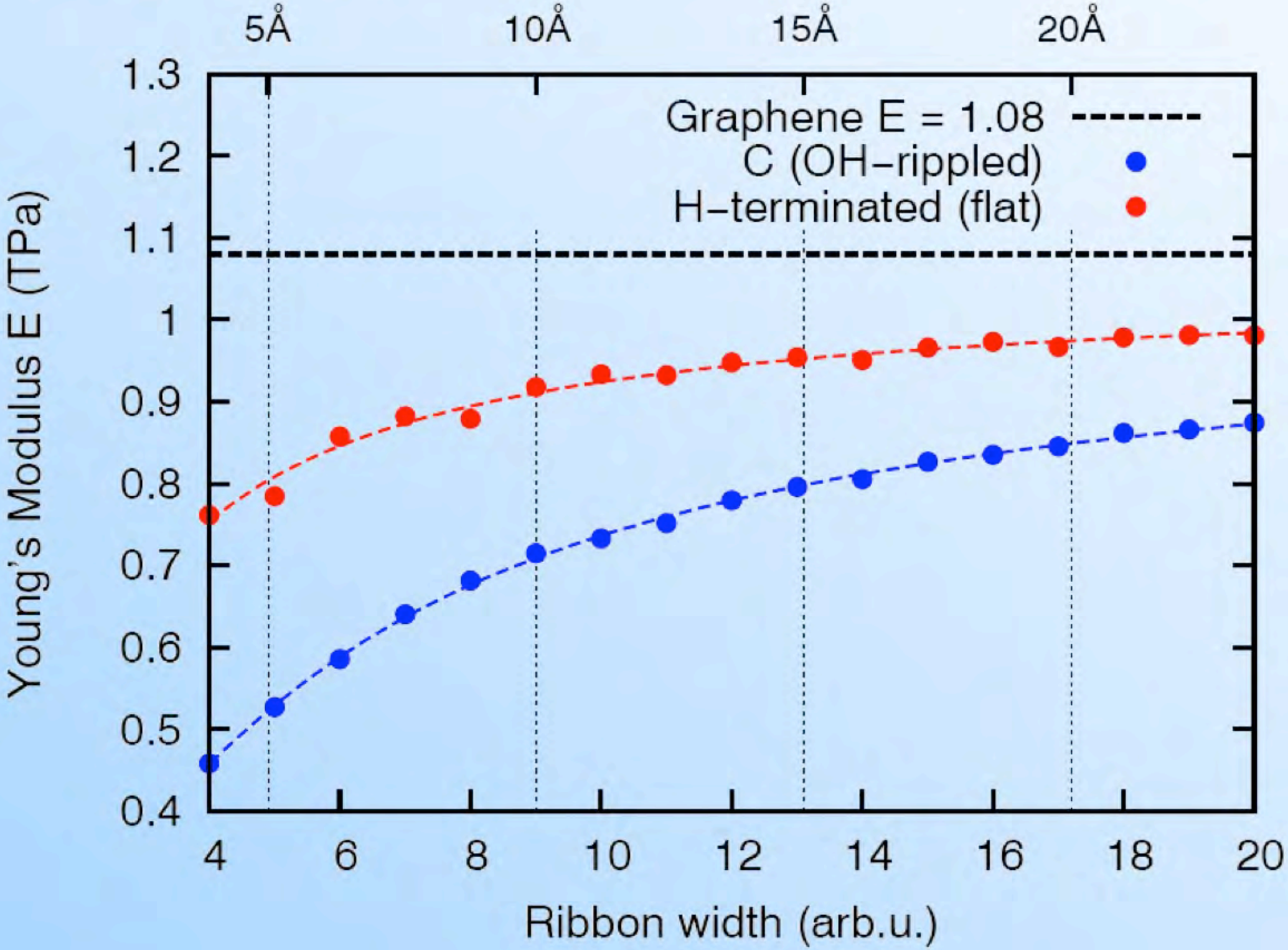


Edge Rippling : Chemical Reactivity



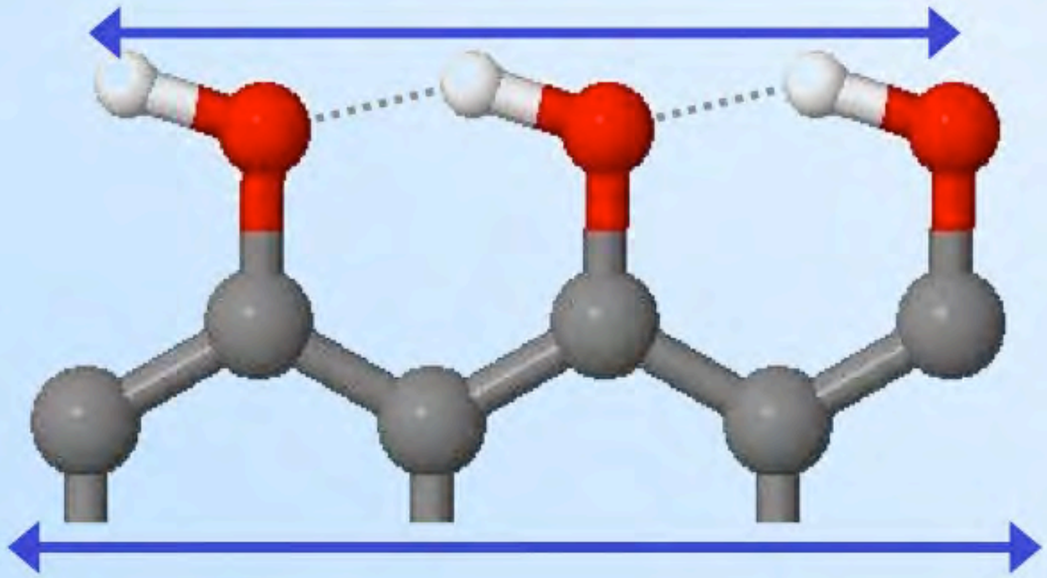
- Also surface functionalisation
- Gas phase absorbates?
- …

Edge Rippling : Young's Modulus



Other edge types

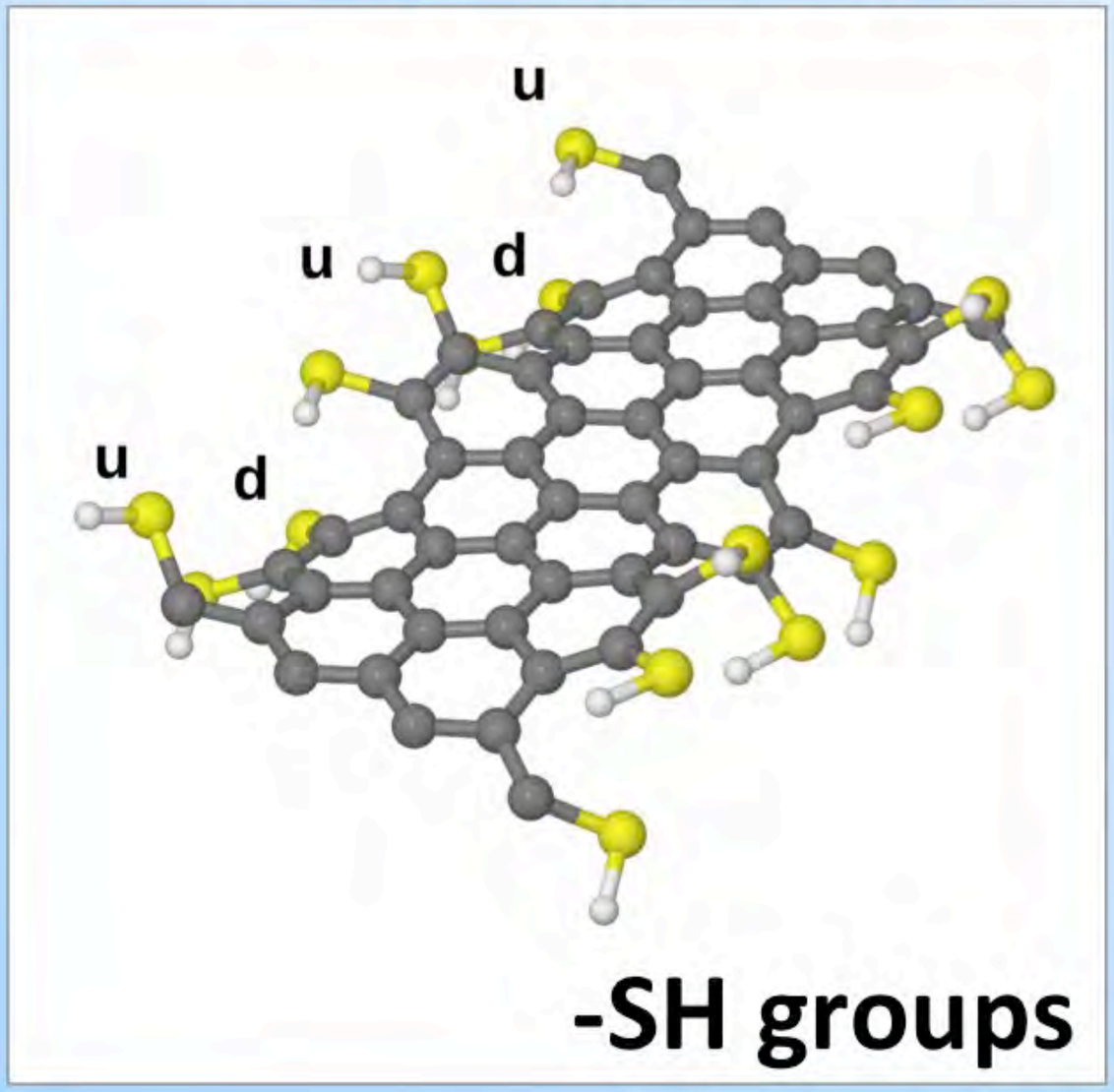
- Edge buckling not seen for zigzag edge



- Buckling looks to occur on **chiral edges** (scattering?)

Other functional groups

- We also see it for –SH, –COOH, -Cl, …
- **Flat** edges (H-) appear to be **the exception**



-SH groups

-Cl groups

Ph. Wagner, C. P. Ewels *et al*, submitted (2011)

Summary : Non-functionalised edges

- Non-functionalised graphene sheet edges can curl back reconstructing as nanotubes.
- Lower formation energies than any free edge structure reported to date in the literature.
- Simulated high resolution electron microscopy images show why rolled edges may be difficult to detect.
- High electron density at E_F localised along the rebonding line.
- High chemical stability.

Summary : Functionalised Edges

- Majority of nanoribbons may **not be flat**, but will have **static edge ripples**.
- True for armchair (and chiral) edges, and most functional groups (except –H) we have tested
- Strongly affects **mechanical** and **chemical** properties of the ribbon
- May cause scattering in chiral ribbons.

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www.cnrs-imn.fr

www.nanotp.org

www.vega.org.uk

www.nanosimgraphene.org

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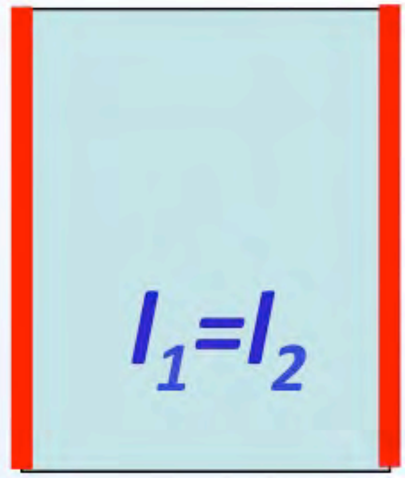
Nantes, France

30th August – 2nd Sept 2011

www.britishcarbon.org/nanotec

In conjunction with WG1 and WG2 meeting MP0901, « NanoTP »

The British Carbon Group


$I_1=I_2$