Atomistic Modeling of Graphene Nanostructures

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NSF

Outline

- Introduction/Motivation
  - » Why graphene is important
  - » Challenges for graphene applications
  - » Graphene nanostructures
- Model Details
  - » Nearest neighbor tight-binding model in graphene
  - » Need for P/D model
- Modeling of Graphene Nanomeshes (GNM)
  - » Circular hole GNM: Bandgap & edge states
  - » Rectangular hole GNM: Anisotropic conductance
- Conclusion and Future Work

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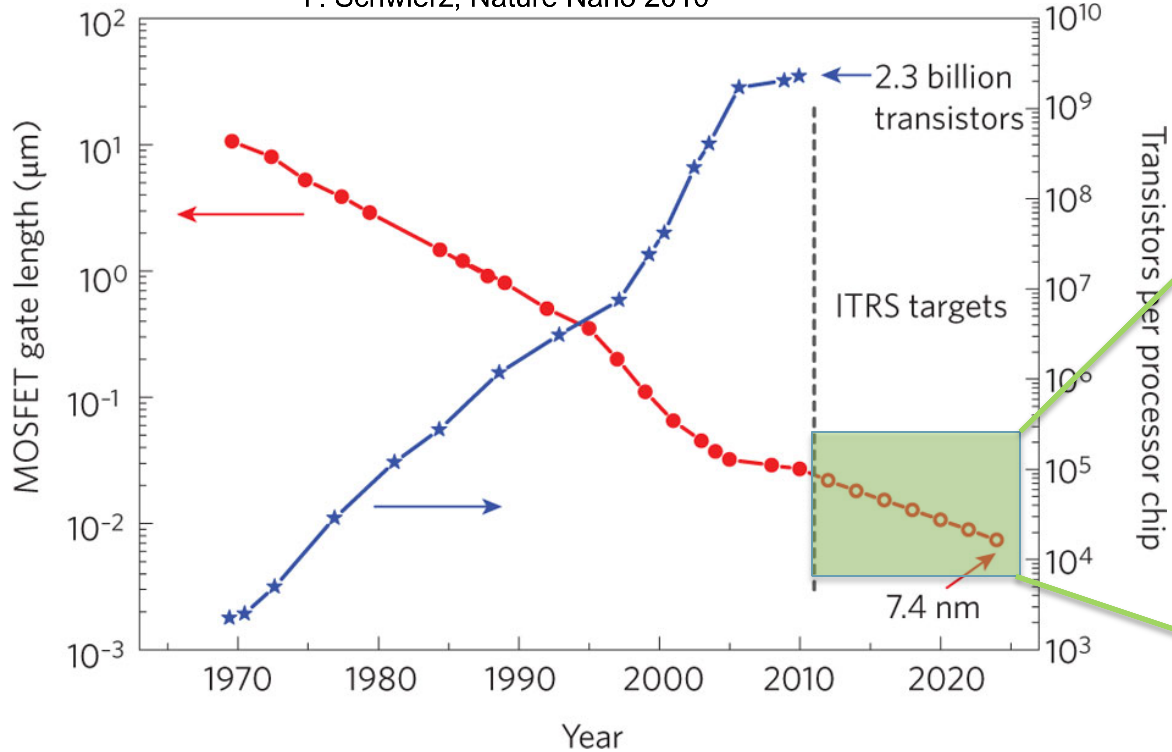
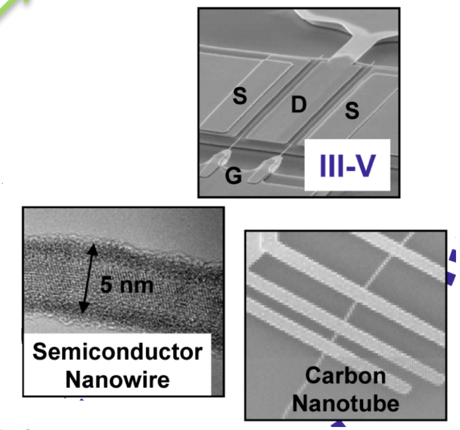
CMOS Scaling Challenges

F. Schwierz, Nature Nano 2010



Emerging Nanoelectronic Devices



Drain-Induced Barrier Lowering (DIBL)

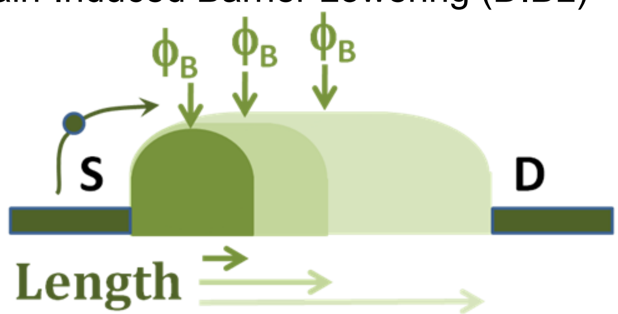


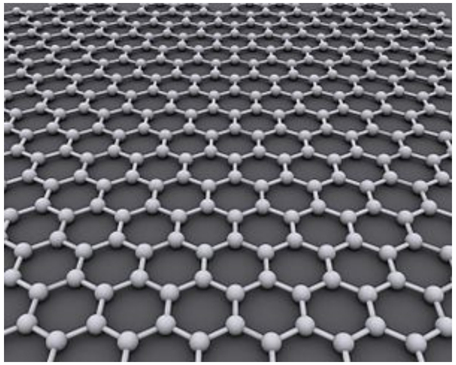
Image from wikipedia

- Device performance enhancement has mainly come from CMOS downscaling in the past few decades
- CMOS scaling is fundamentally limited by several technological issues, such as short channel effects
- Channel length of today's CMOS is close to such scaling limit of sub-10 nm

"Sitting on a Graphene Mine"

----- A. K. Geim, *Science* 2009

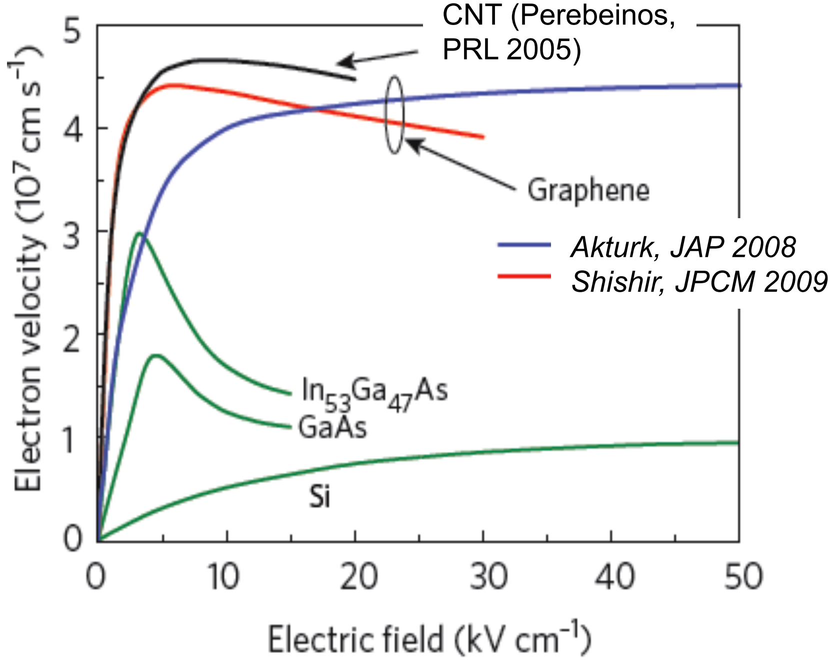
Graphene



- Giant intrinsic mobility
  - Over 15,000 $cm^2/V\text{-}s$ measured, upper limit predicted to be over 100,000 $cm^2/V\text{-}s$
  - Weak dependence on temperature and charge density
- Support high current density
- High thermal conductivity
- Outstanding Mechanical properties: strength, stiffness, etc.

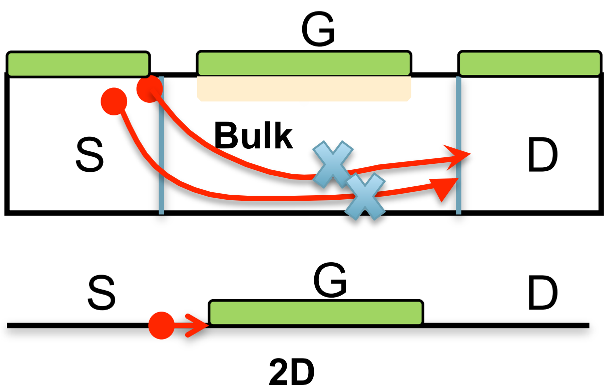
Electronics

Why Graphene Electronics?



Good high-field transport

- Device performance at small gate length is measured by high-field transport characteristics
- Graphene has much higher electron velocity compared to other semiconductor materials
- The electron velocity in graphene doesn't decrease much in the high field
- Graphene is ideal for high-speed applications, such as RF devices



The 2D nature

- Graphene makes extremely thin channel, which prevents off current
- Single atomic layer channel represents the ultimate limit of channel thickness

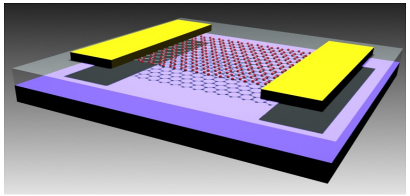


Image from: University of Maryland

Graphene progress

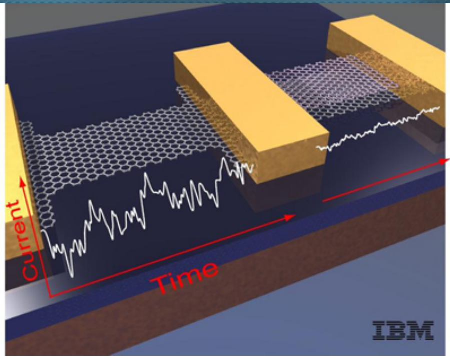


Image credit: IBM

First fabrication of graphene
Oct. 2004 (Novoselov et al. Science)

2.5 years

First graphene FET
April 2007 (Lemme et al. IEEE EDL)

< 2 years

First gigahertz graphene FET
Dec. 2008 (Meric et al. IEDM)

First experimental CNT paper
Nov. 1991 (Iijima et al. Nature)

6.5 years

First CNT FET, May 1998
(Tans et al. Nature)

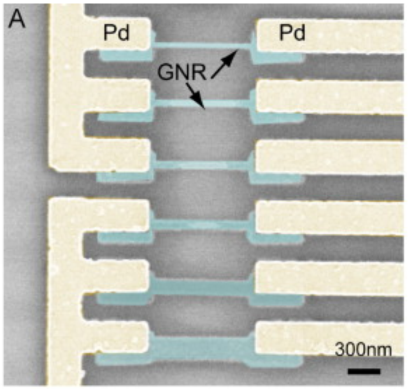
6 years

First gigahertz CNT FET
April 2004 (Li et al. Nano Lett)

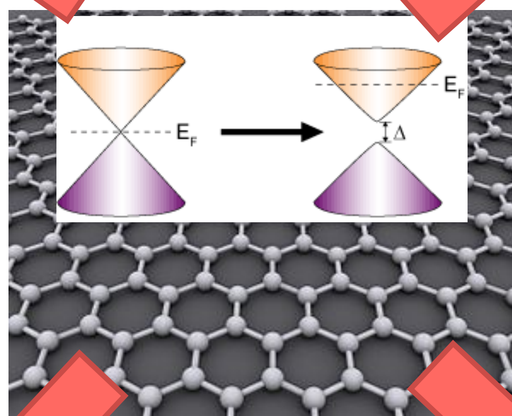
- Although graphene applications has seen rapid progresses, they are still limited mostly to radiofrequency devices
- Large area graphene sheet has zero banggap → Devices cannot be fully turned off → large leakage power
- The biggest challenge in graphene applications is opening up a bandgap !

Bandgap opening techniques

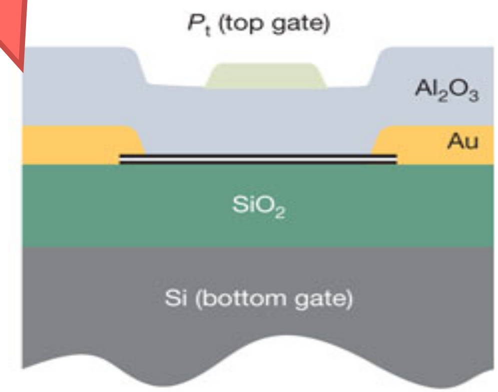
Nanoribbon



Z.Chen, *et al.* Physica **40**, 228-232 (2007)

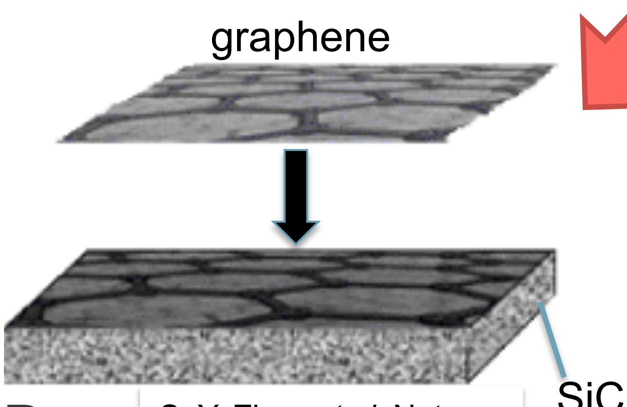


Biasing Bi-layer Graphene



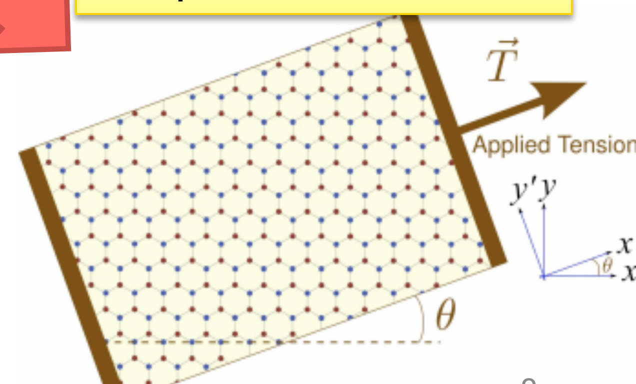
YB Zhang *et al. Nature* **459**, 820-823 (2009)

Epitaxial graphene on SiC



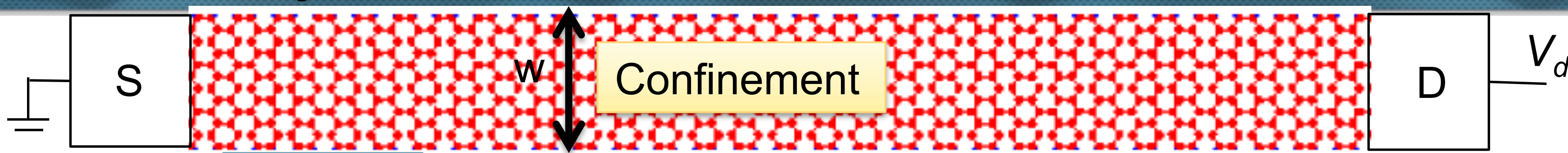
S. Y. Zhou *et al.* Nature Materials 6, 916 (2007)

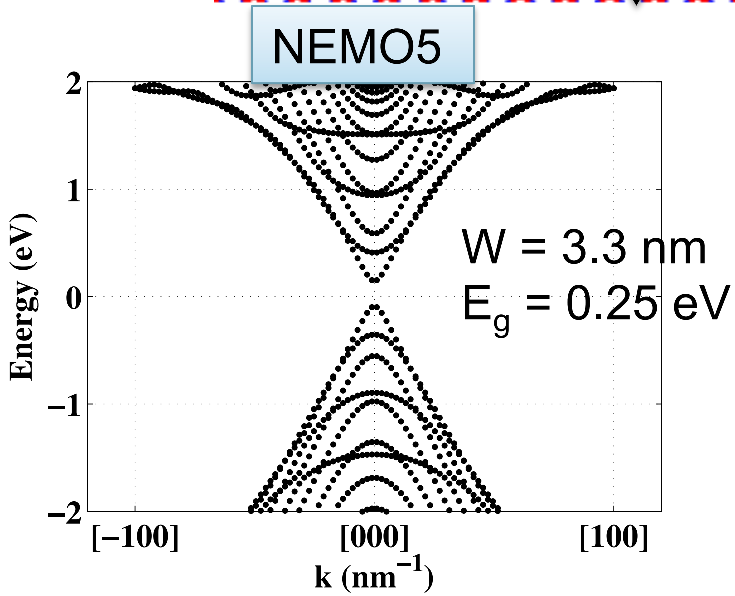
Apply strain in Graphene

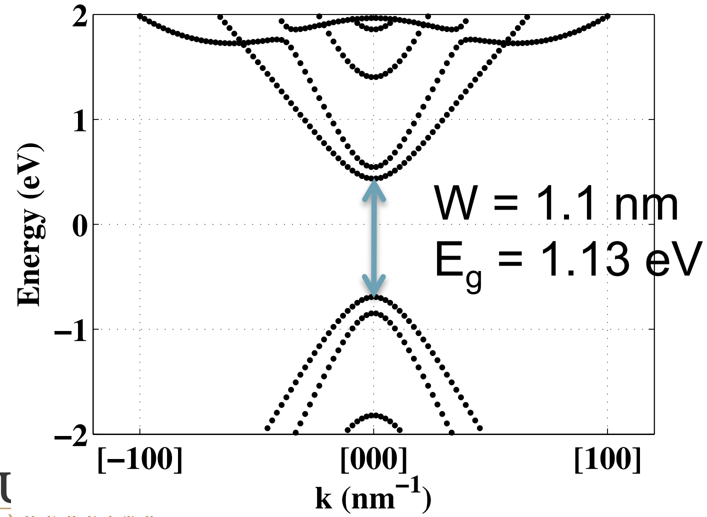


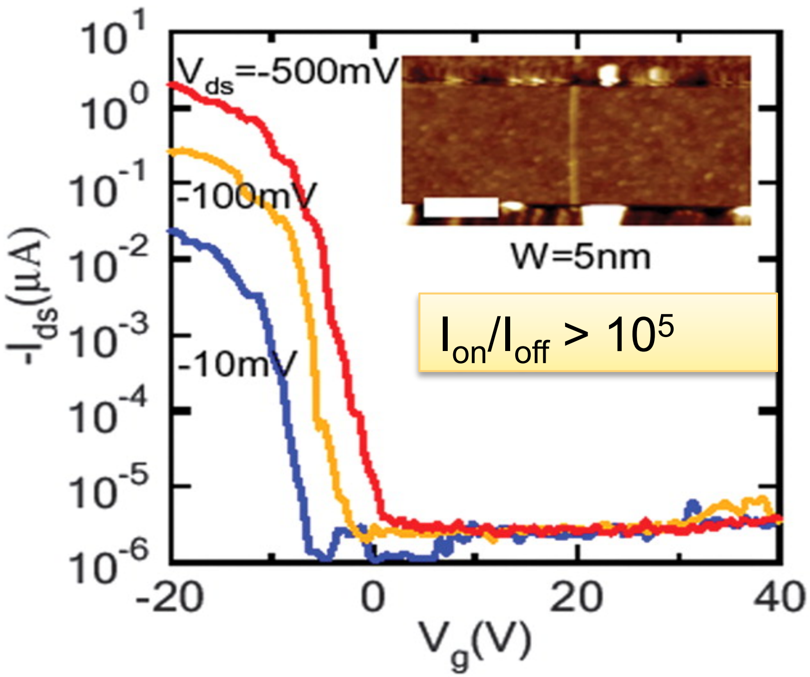
V. Pereira *et al.* Phys. Rev B.80. 045401 (2009)

Graphene Nanoribbon (GNR)









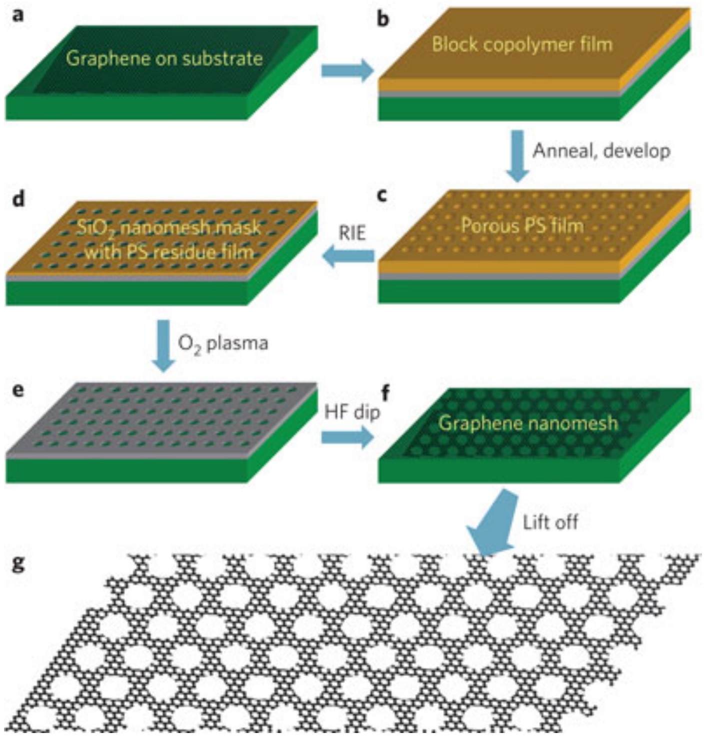
X. Li, *et al.* Science 319, 1229 (2008)

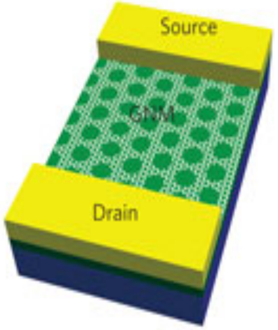
Bandgap opens up in GNR due to lateral confinement, $E_g \sim 1/w^{\alpha}$, with $\alpha \approx 1$

Drawbacks of GNR:

- Lithographical challenges
  - » Very narrow nanoribbons (W < 10 nm), well-defined edges are necessary
- Low driving current
  - » Practical devices or circuits requires production of dense arrays of GNR

The Alternative: Graphene nanomesh (GNM)





Advantages of GNM:

- Easier to process, effectively a dense array of GNR
- Large driving current
- Tunable bandgap

Currently obtainable on-off ratio ~ 100

J. Bai *et al.* Nature Materials 5, 190-194 (2010)

Objectives of this work

- Investigate the properties of Graphene Nanomesh using the computational modeling approach
  - » How does the geometry (hole size, shape) affect electronic properties?
  - » Can we engineer the electronic structure of GNM?
  - » Is GNM fit for nanoelectronics applications?
- Methodology: Nearest neighbor tight-binding model
  - » The GNM structures to be modeled contain hundreds of atoms
  - » Tight-binding method is good at handling such large computational intensive tasks, and reproducing the essential physics

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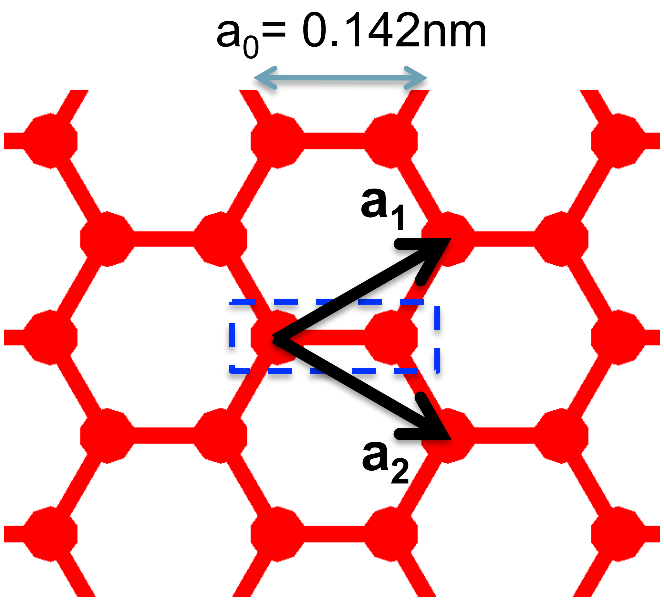
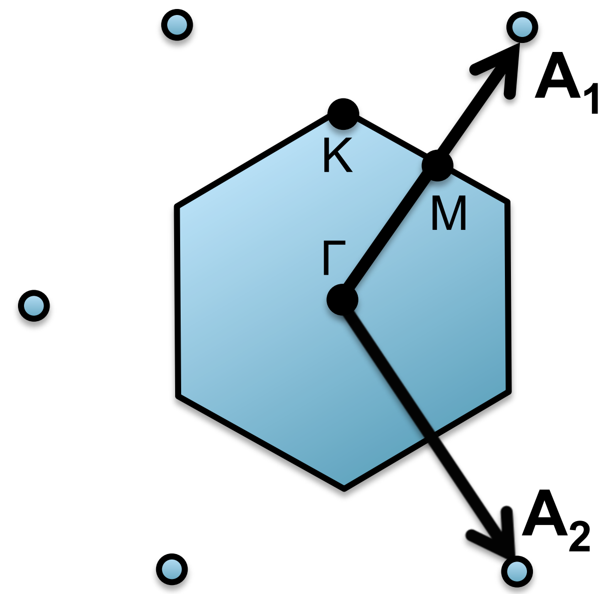
Graphene Lattice and Brillouin Zone





Lattice basis:

$$\vec{a}_1 = \frac{3a_0}{2}\hat{x} + \frac{\sqrt{3}a_0}{2}\hat{y}$$

$$\vec{a}_2 = \frac{3a_0}{2}\hat{x} - \frac{\sqrt{3}a_0}{2}\hat{y}$$

Reciprocal lattice basis:

$$\vec{A}_1 = \frac{2\pi}{3a_0}\hat{x} + \frac{2\pi}{\sqrt{3}a_0}\hat{y}$$

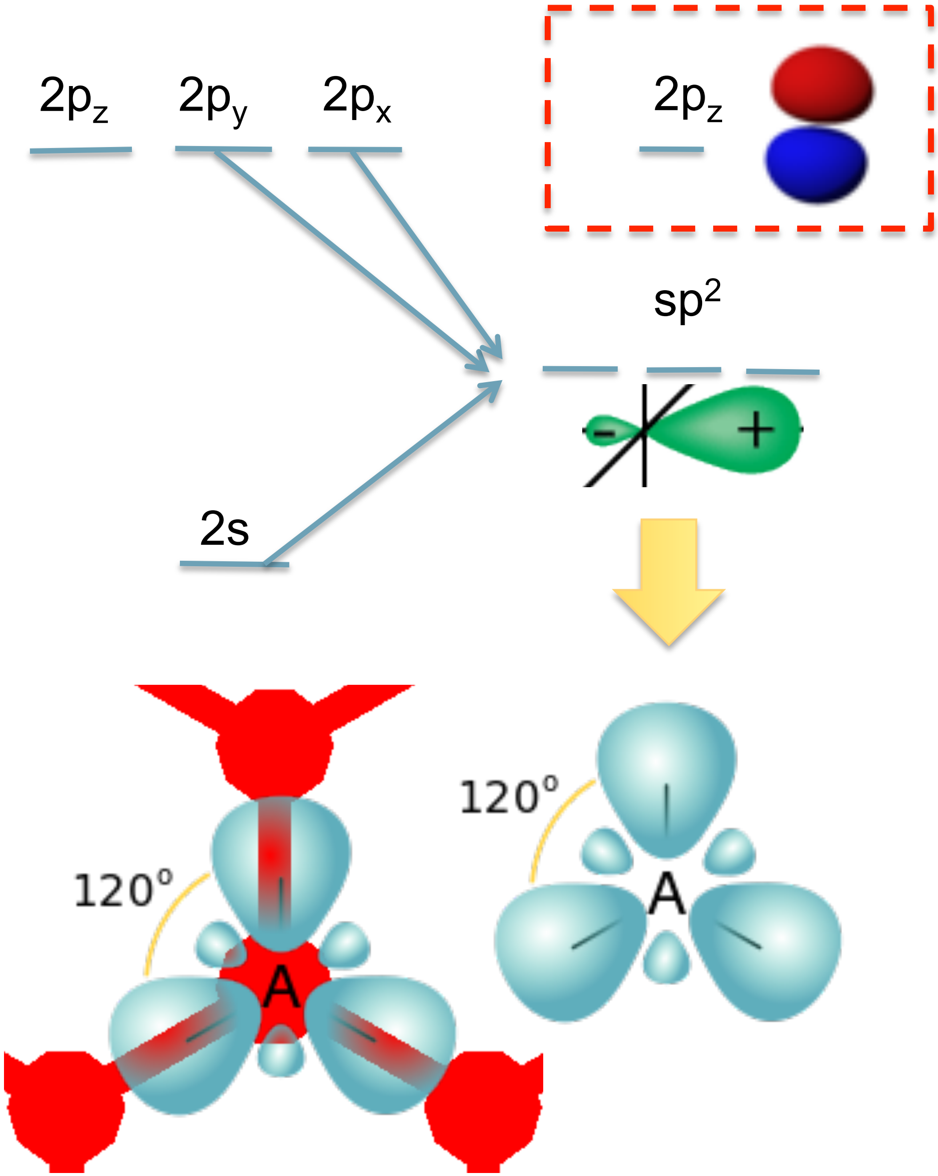
$$\vec{A}_2 = \frac{2\pi}{3a_0}\hat{x} - \frac{2\pi}{\sqrt{3}a_0}\hat{y}$$

Symmetry points:

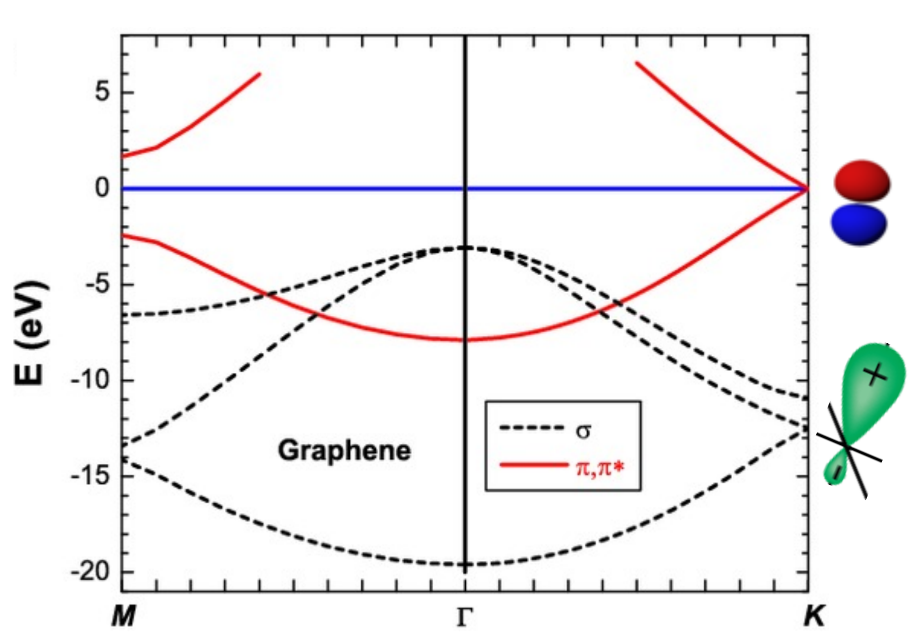
$$K : \frac{1}{3}\vec{A}_1 - \frac{1}{3}\vec{A}_2$$

$$M : \frac{1}{2}\vec{A}_1$$

Tight-binding Model

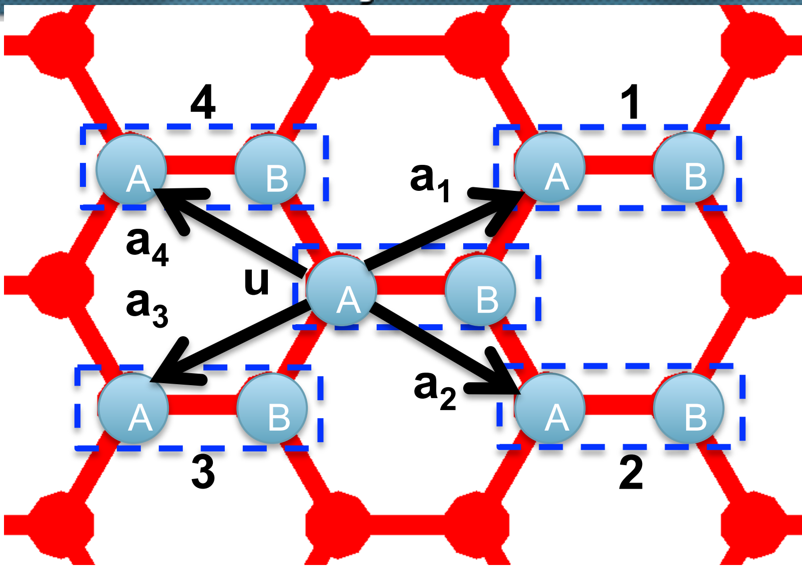


Y. Zhang and R.Tsu, Nanoscale Research Letters Vol. 5 Issue 5



- p_z orbital is well separated in energy from the sp^2 orbitals
- More importantly, only the p_z electron is close to the Fermi level
- Therefore, the common tight-binding method for graphite/graphene considers only the p_z orbital (P.R. Wallace, PRB 1947)

pz tight-binding Model



$$E\{\phi\} = [h(\vec{k})]\{\phi\}$$

$$[h(\vec{k})] = \sum_m [H_{nm}] e^{i\vec{k}\bullet(\vec{d}_m - \vec{d}_n)}$$

- {Φ}: (2 x 1) vector; [H]: (2 x 2) matrix since there are 2 orbitals per unitcell

$$[h(\vec{k})] = \begin{bmatrix} \varepsilon & -t \\ -t & \varepsilon \end{bmatrix} + \begin{bmatrix} 0 & 0 \\ -t & 0 \end{bmatrix} e^{i\vec{k}\bullet\vec{a}_1} + \begin{bmatrix} 0 & 0 \\ -t & 0 \end{bmatrix} e^{i\vec{k}\bullet\vec{a}_2} + \begin{bmatrix} 0 & -t \\ 0 & 0 \end{bmatrix} e^{i\vec{k}\bullet\vec{a}_3} + \begin{bmatrix} 0 & -t \\ 0 & 0 \end{bmatrix} e^{i\vec{k}\bullet\vec{a}_4}$$

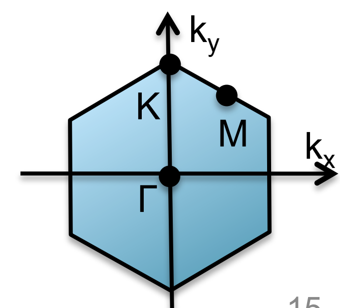
u | u → 1 | u → 2 | u → 3 | u → 4

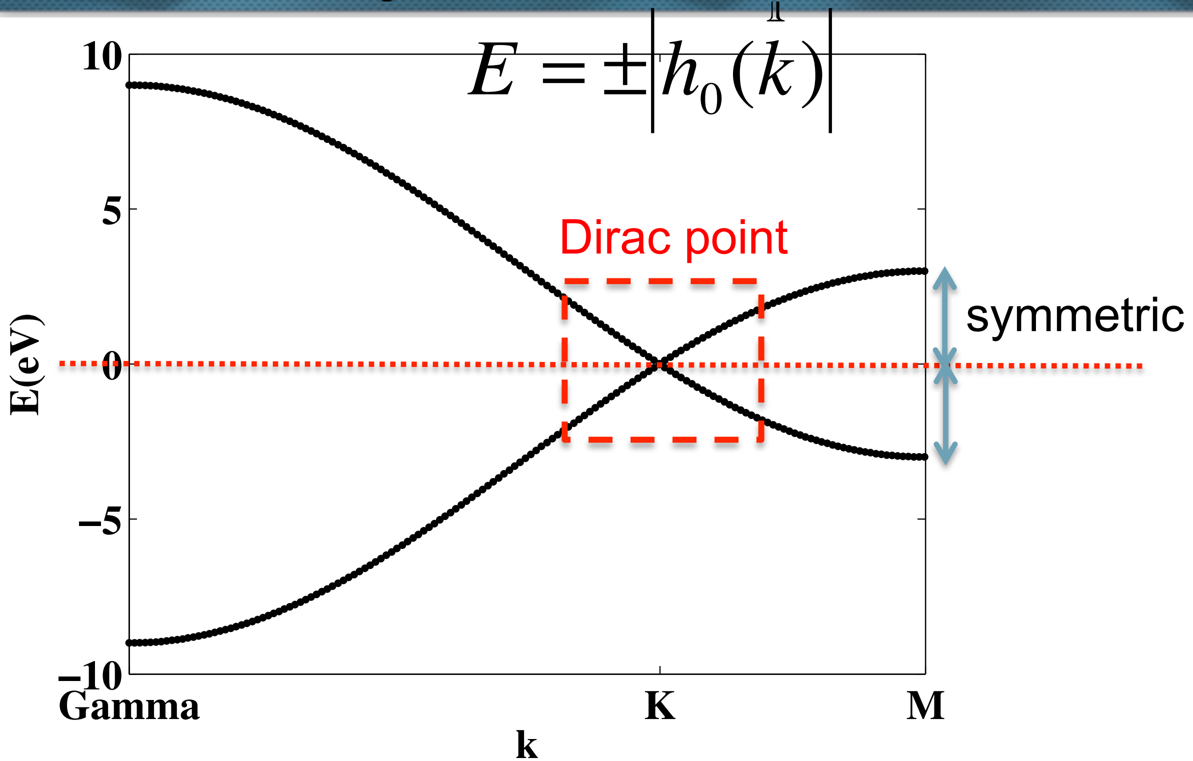
$$[h(\vec{k})] = \begin{bmatrix} \varepsilon & h_0(\vec{k}) \\ h_0(\vec{k}) & \varepsilon \end{bmatrix}$$

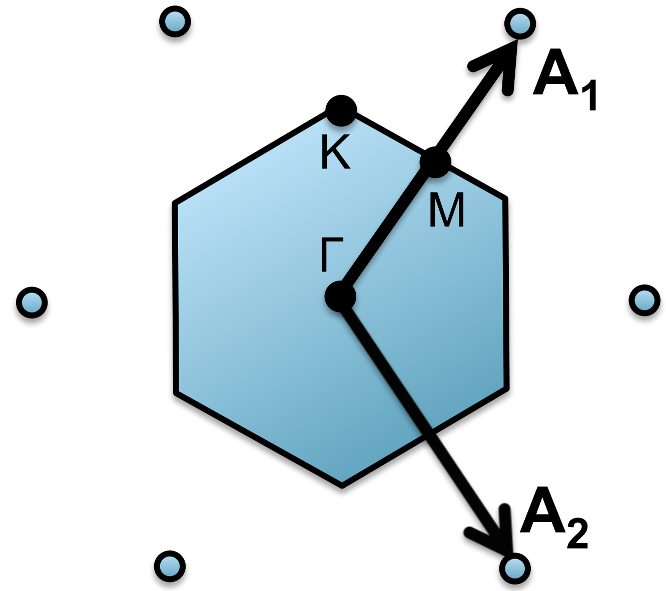
diagonalize →

$$E = \pm\left|h_0(\vec{k})\right|$$ (if ε = 0)

$$= \pm t\sqrt{1 + 4\cos k_y b \cos k_x a + 4\cos^2 k_y b}$$



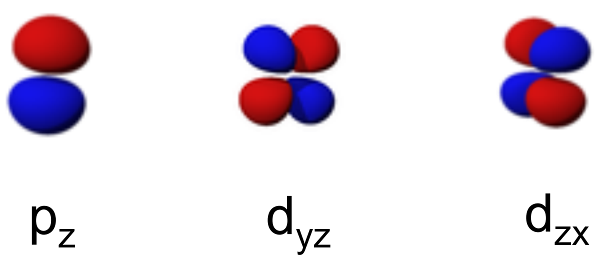


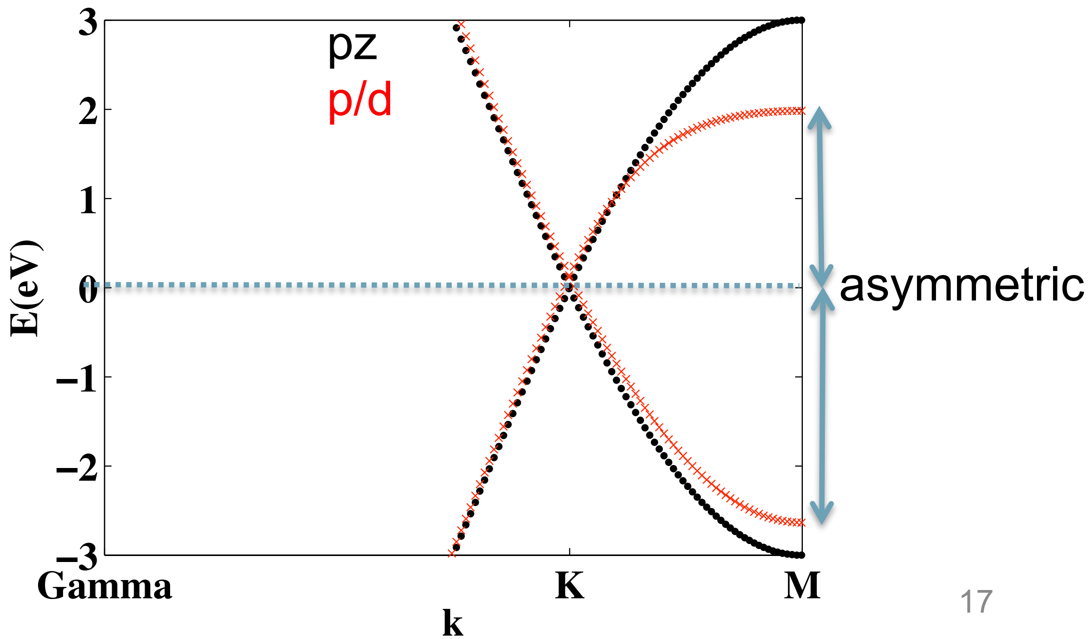


- Features of graphene bandstructure
  - » Conduction and valence bands cross at K points of Brillion zone, forming Dirac cones
  - » At M points in the Brillouin zone, band edges are symmetric around the Dirac point (since $E = \pm|h_0(\vec{k})|$ is symmetric around E = 0 eV)

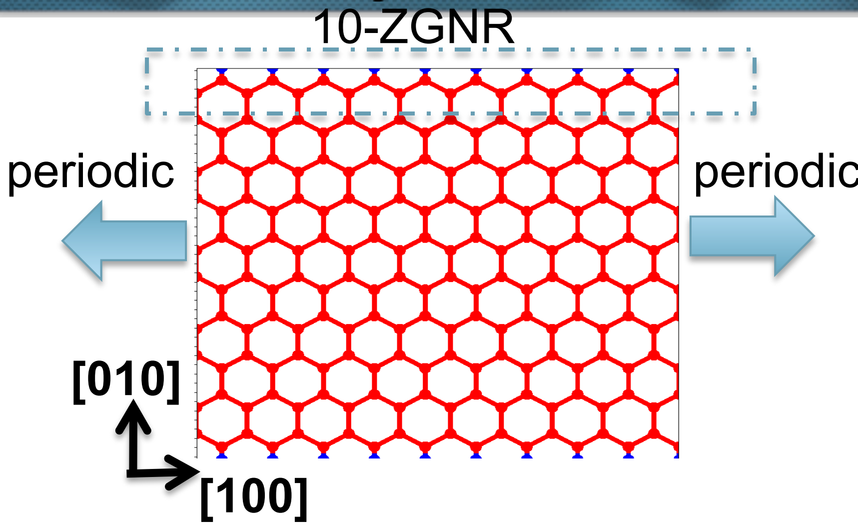
P/D Model
(Boykin et al., *J. Appl. Phys.* 2011)

- Flaws of the pz model
  - » Could not reproduce the asymmetry of bands
  - » Does not allow proper hydrogen passivation scheme. This is because the single s orbital of hydrogen atom does not have any coupling to the p_z orbital of carbon atom
- The solution: P/D model
  - » Use a set of three orbitals {p_z d_{yz} d_{zx}} to represent each C atom
  - » For hydrogen passivation, also use {p_z d_{yz} d_{zx}} to represent H atom



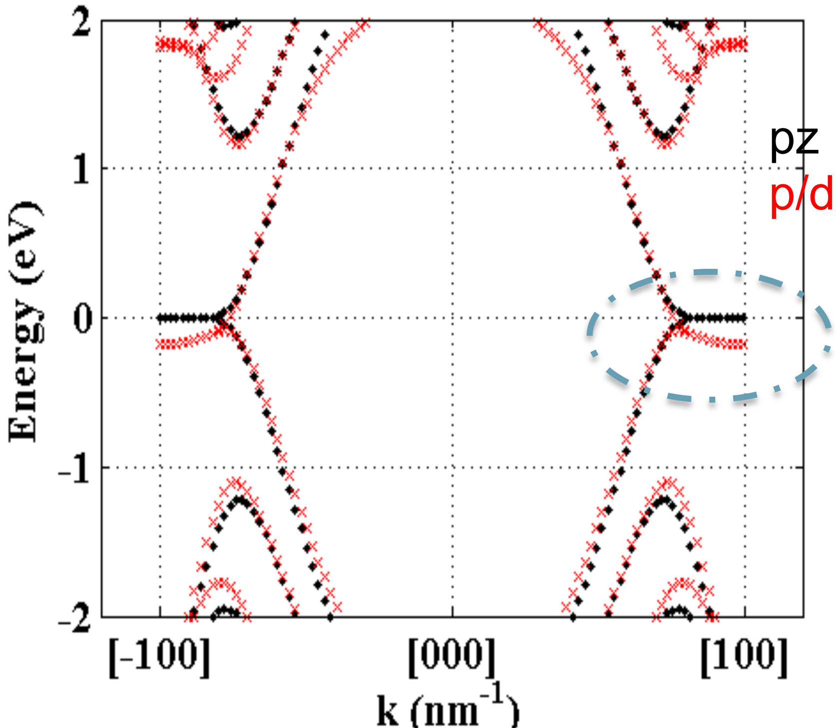


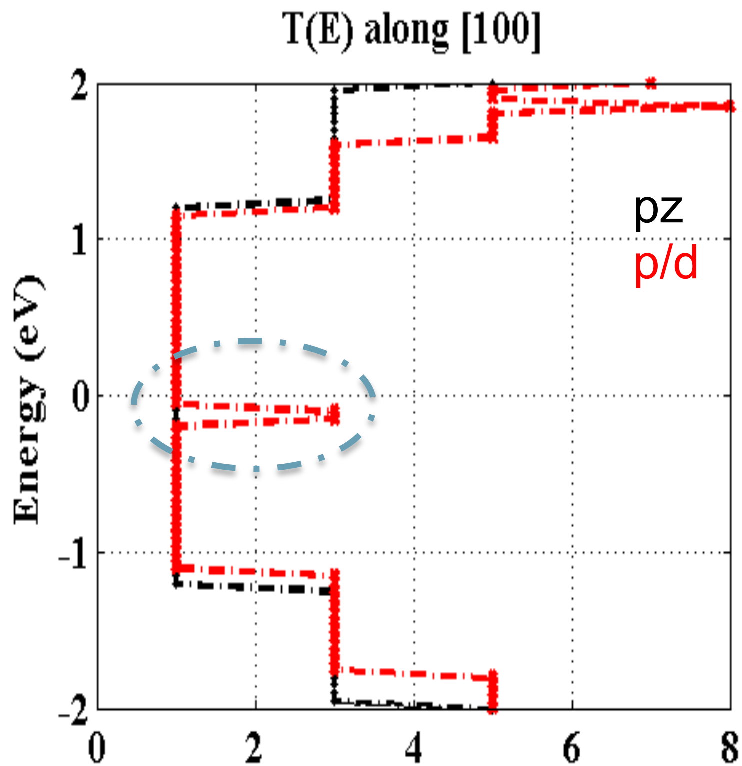
Model validation: zig-zag nanoribbon



- P/D model correctly reproduces the band bending around the E = 0 eV
- As a result, transmission has a 'spike', i.e, T(E≈0) = 3. This matches with DFT results

Nature 444, 347-349 (2006)
J. Comput. Chem., 29: 1073–1083 (2008)





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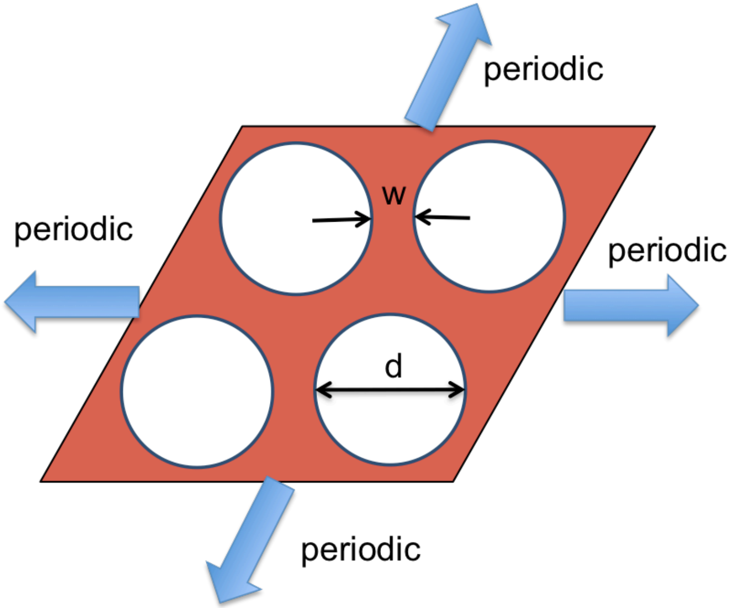
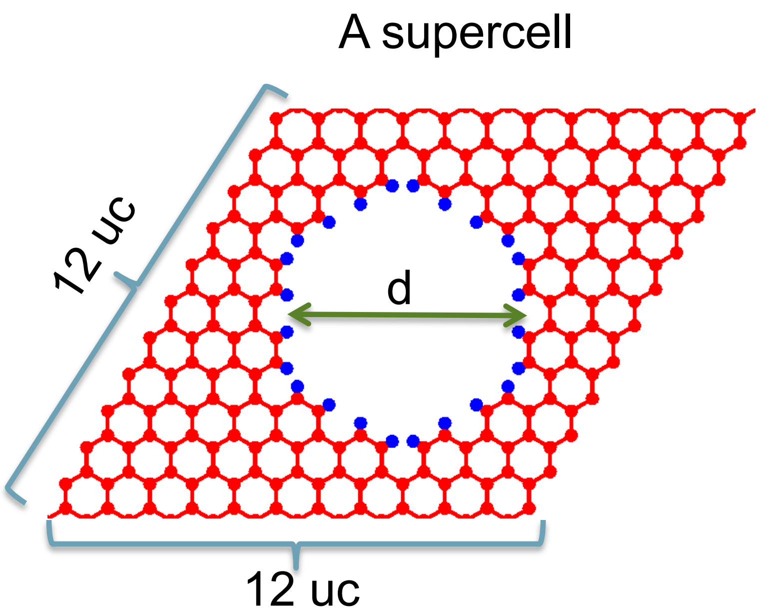
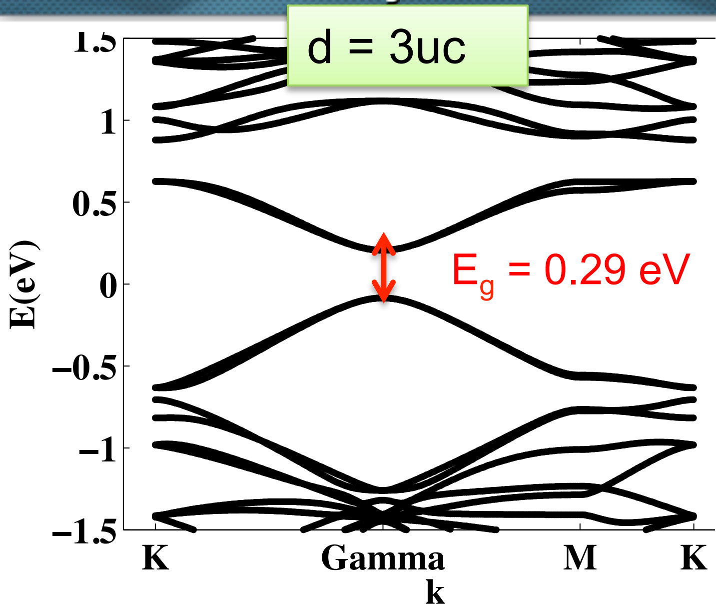
GNM: the structure

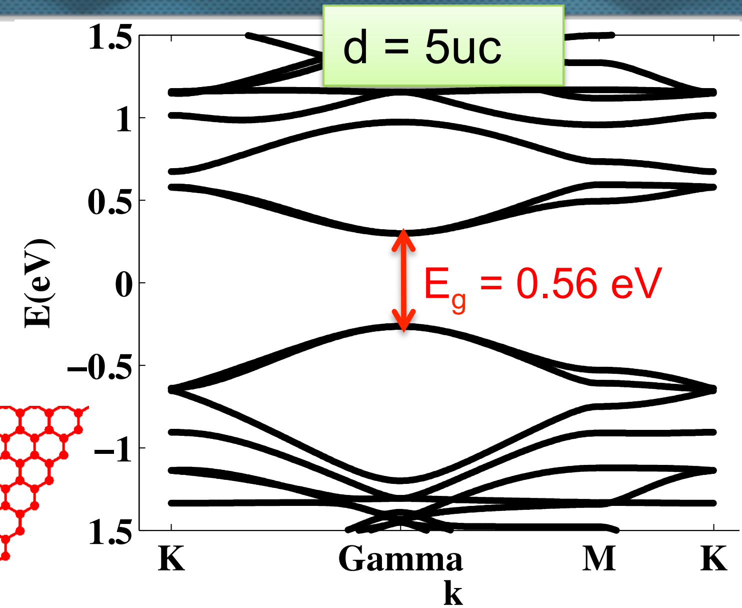


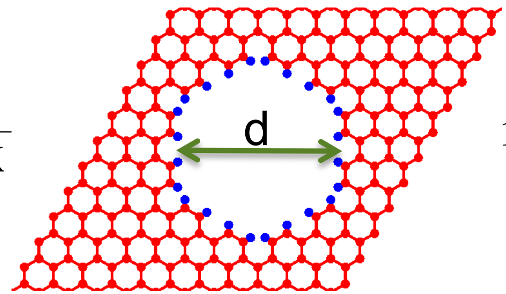


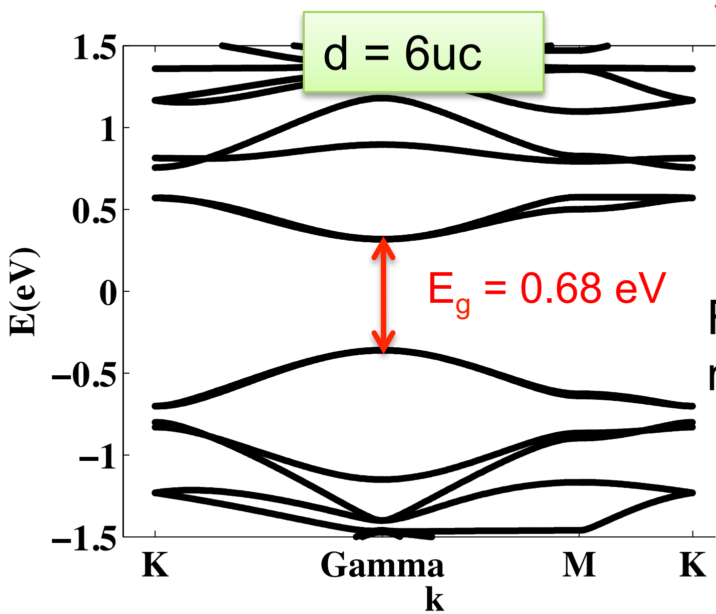
- Periodic structure in 2D
- Edges are passivated by H atoms
- Size of a supercell is 12 graphene primitive unit cells long, or 2.95 nm
- Hole diameter is varying

GNM: Bandstructure

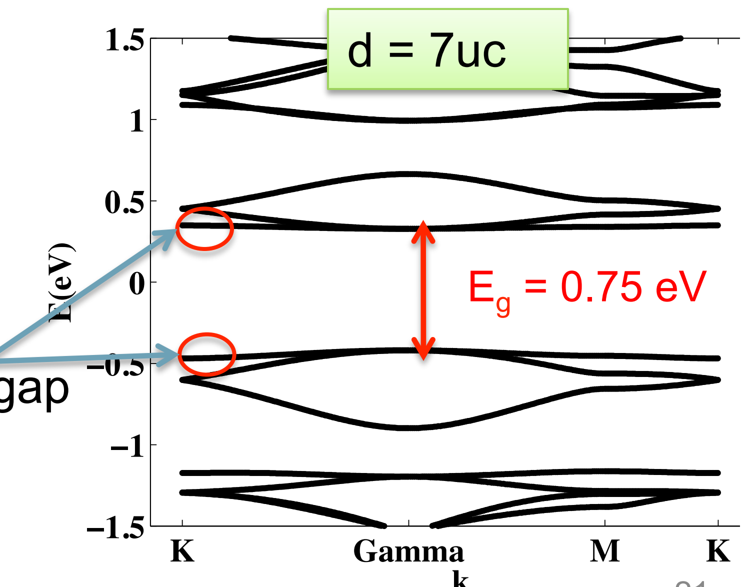




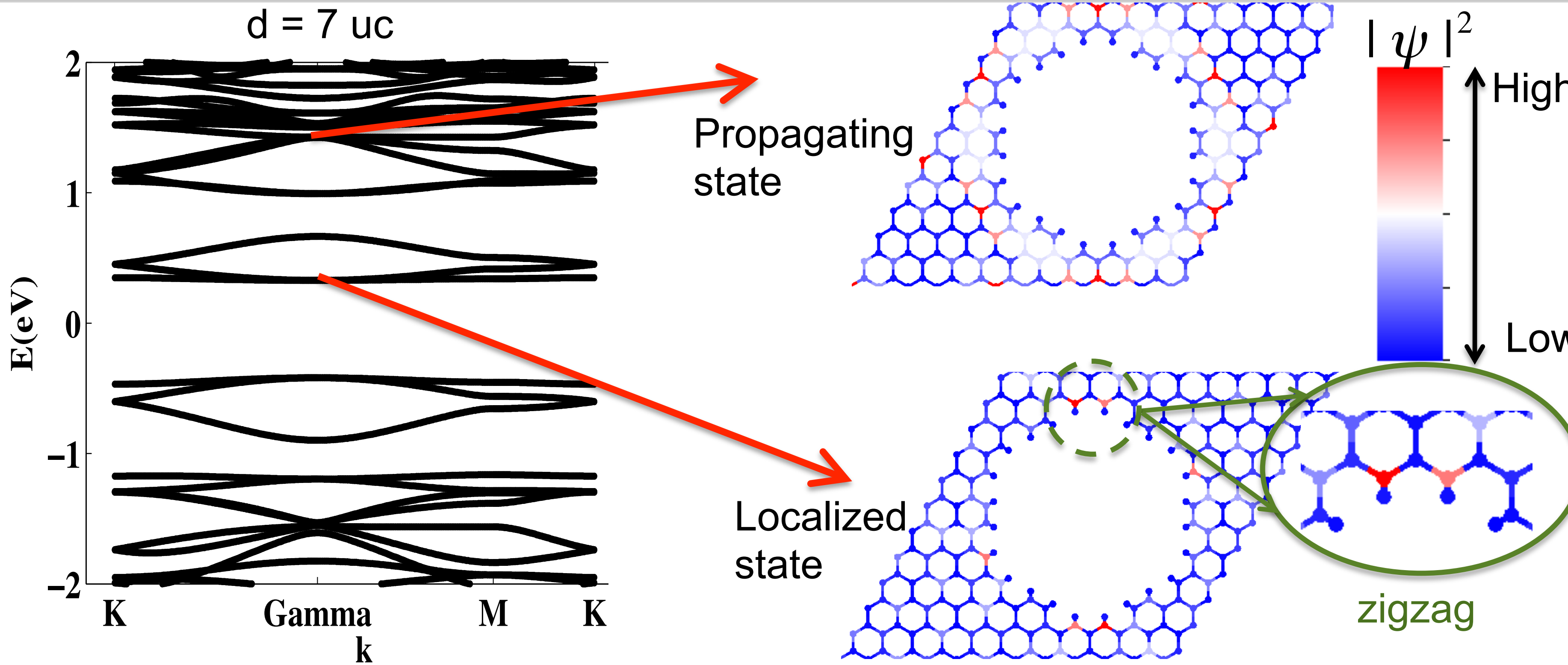




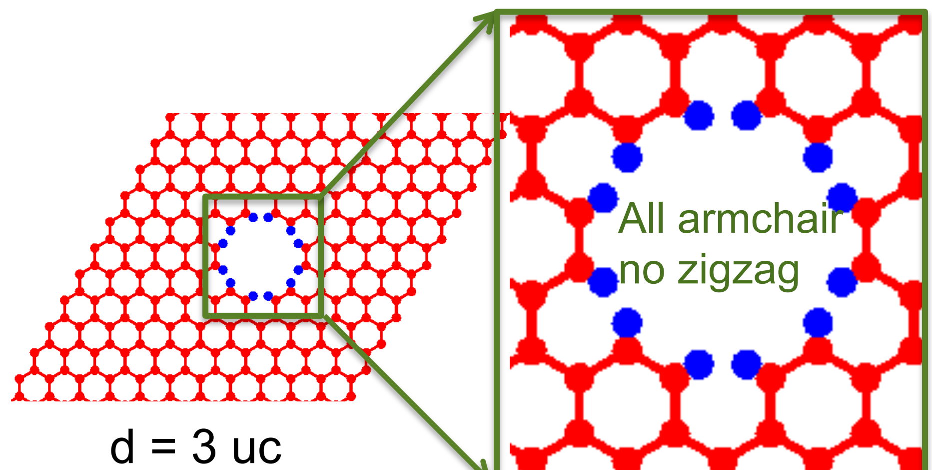
Flat bands in the middle of the bandgap



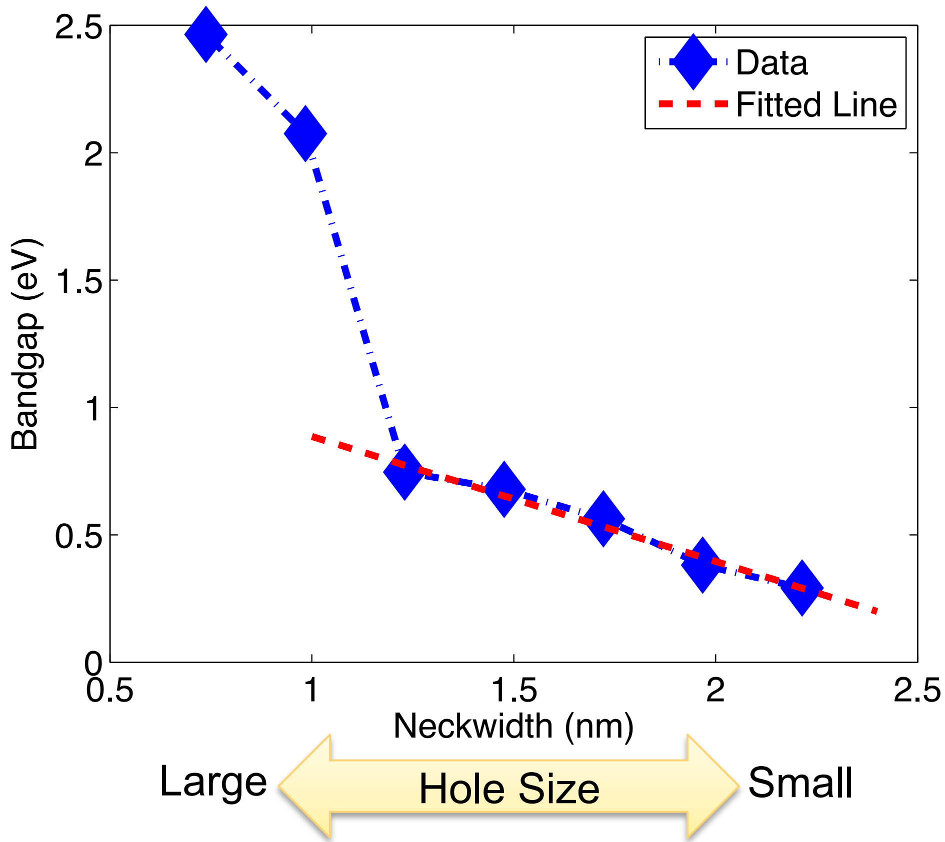
GNM: Edge state



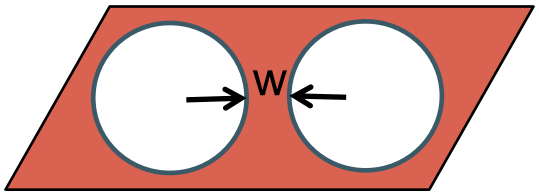
- As hole size get bigger, flat bands apprear in the middle of the bandgap
- Flat bands are edge states, where electron wavefunctions localize on the hole edge
- A closer look at the edge state reveals that wavefunctions tend to localize on the zigzag edge



Bandgap vs. Neckwidth



- At small neckwidth range, bandgap is nearly inversely proportional to neckwidth
- However, as hole size increases, edge effects become more prominent, which induces more localized states (flat bands) in the bandgap.
- As a result, bandgap results deviates from the linear trend at narrow neckwidth.



Short Conclusion

- Graphene with periodic perforation can open up sizeable bandgap, which makes GNM potentially useful for transistor applications.
- However, just like GNR, edge still plays an important role in electronic properties of GNM

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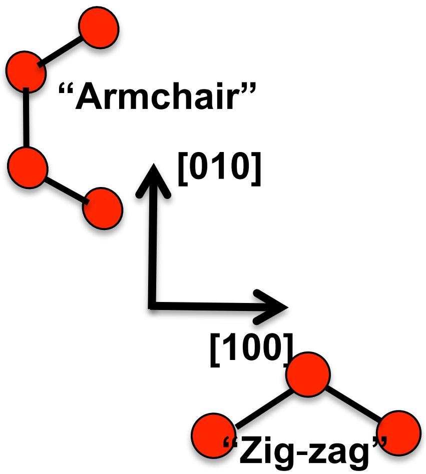
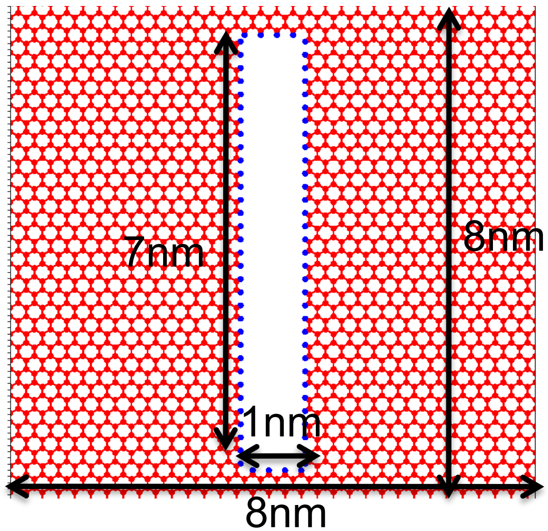
Rectangular hole structure

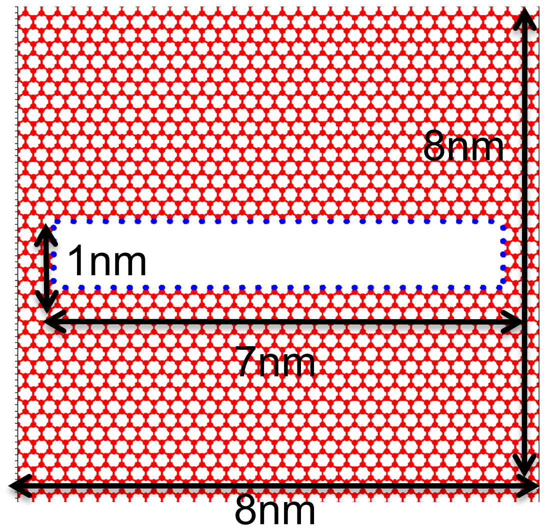
- From previous study, it is learned that edges plays significant role in the bandstructure
- Thus we can expect that different hole geometries leads to different E-k characteristics and electronic properties
- Compare electronic properties between two types of structures "AGNM" and "ZGNM"



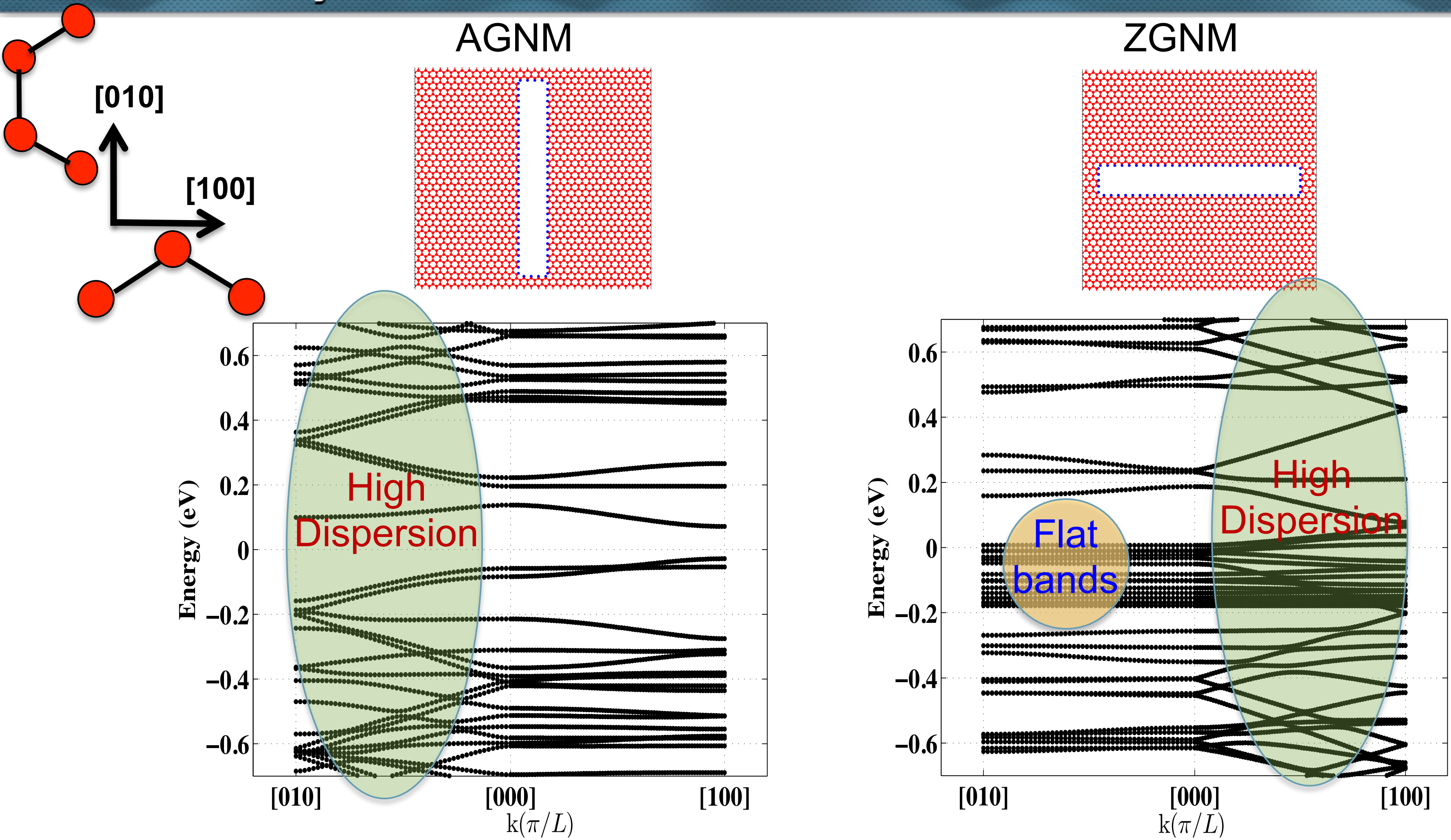
Armchair GNM, or "**AGNM**"



Zigzag GNM, or "**ZGNM**"

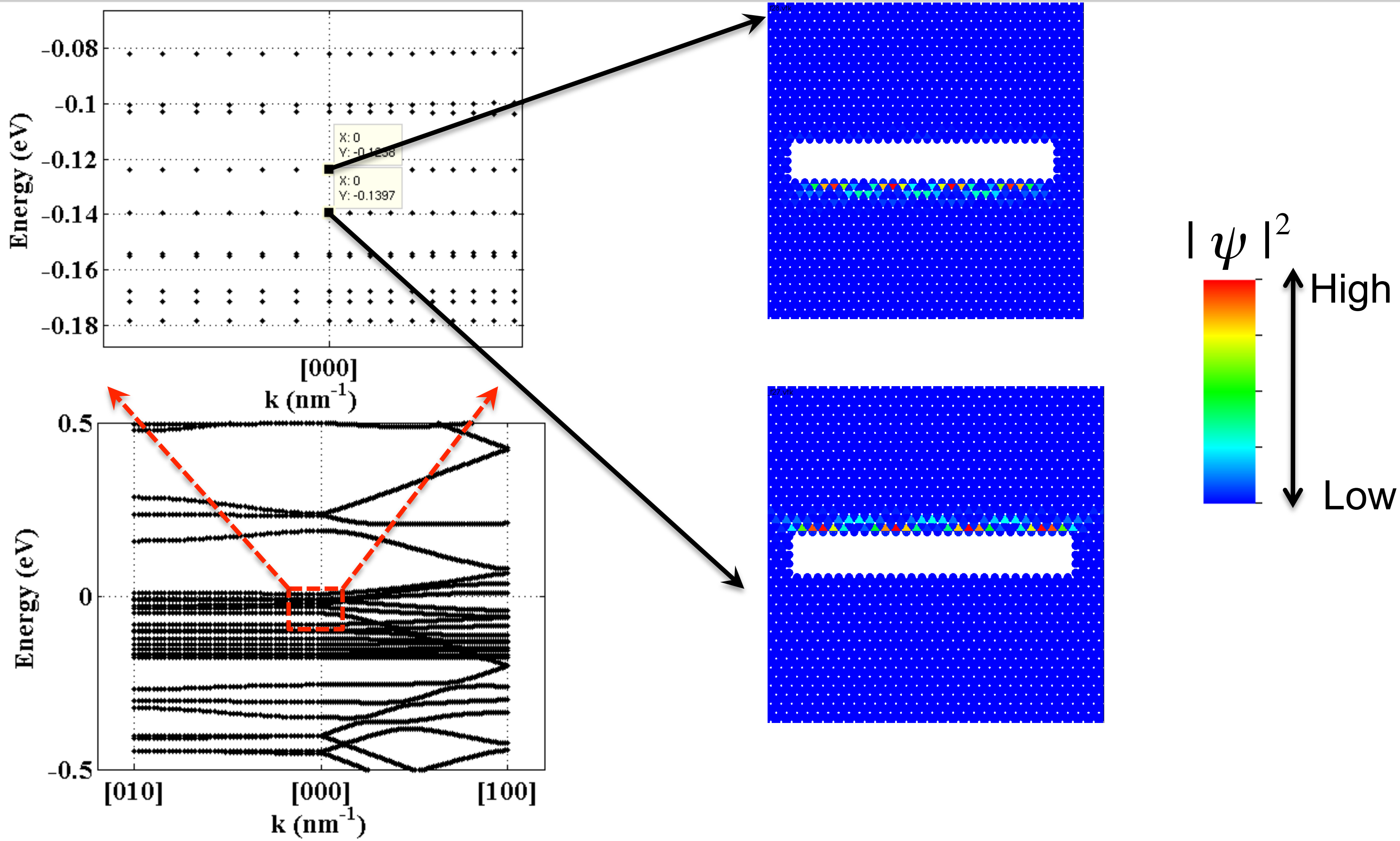


Bandstructure comparision

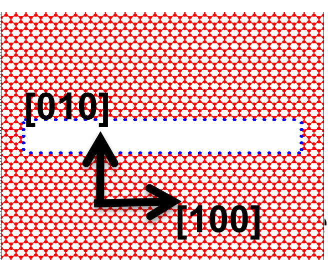


- Dispersion of E-k is significantly larger along the hole direction, i.e, [010] for AGNM and [100] for ZGNM
- Many flat bands in the ZGNM bandstructure

Localized States

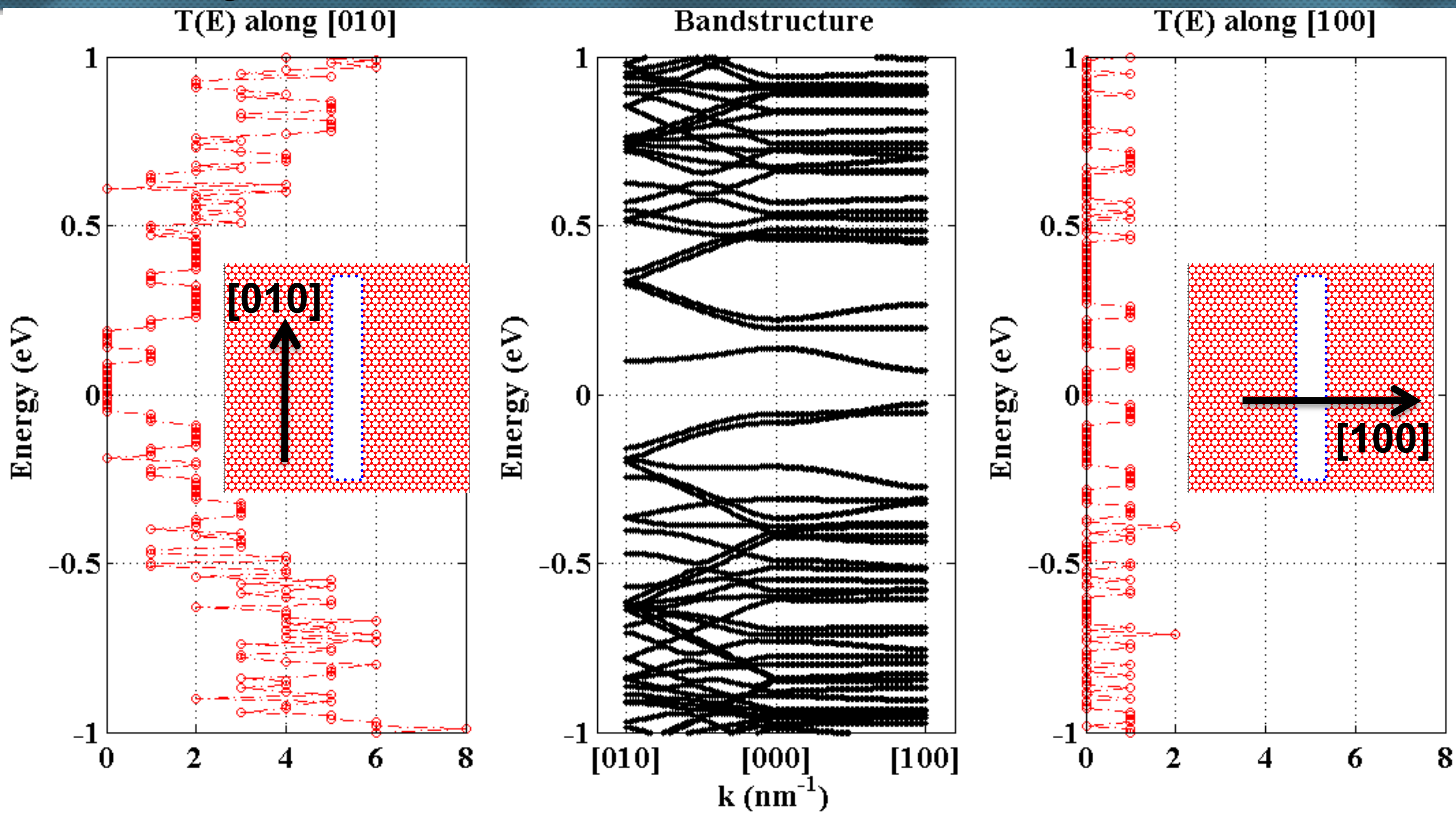


ZGNM



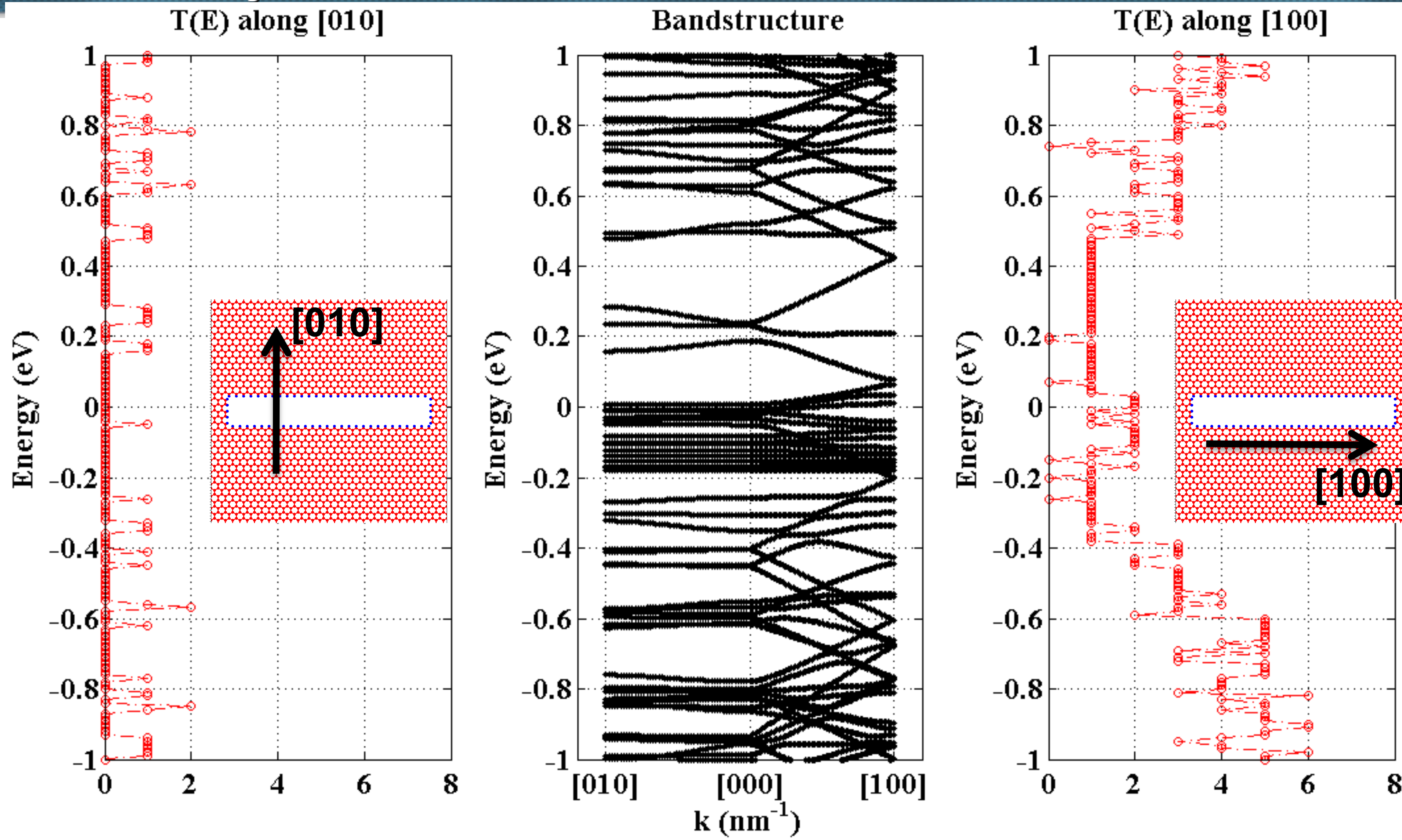
- Flat bands are localized states on the zigzag edge

1x7nm hole



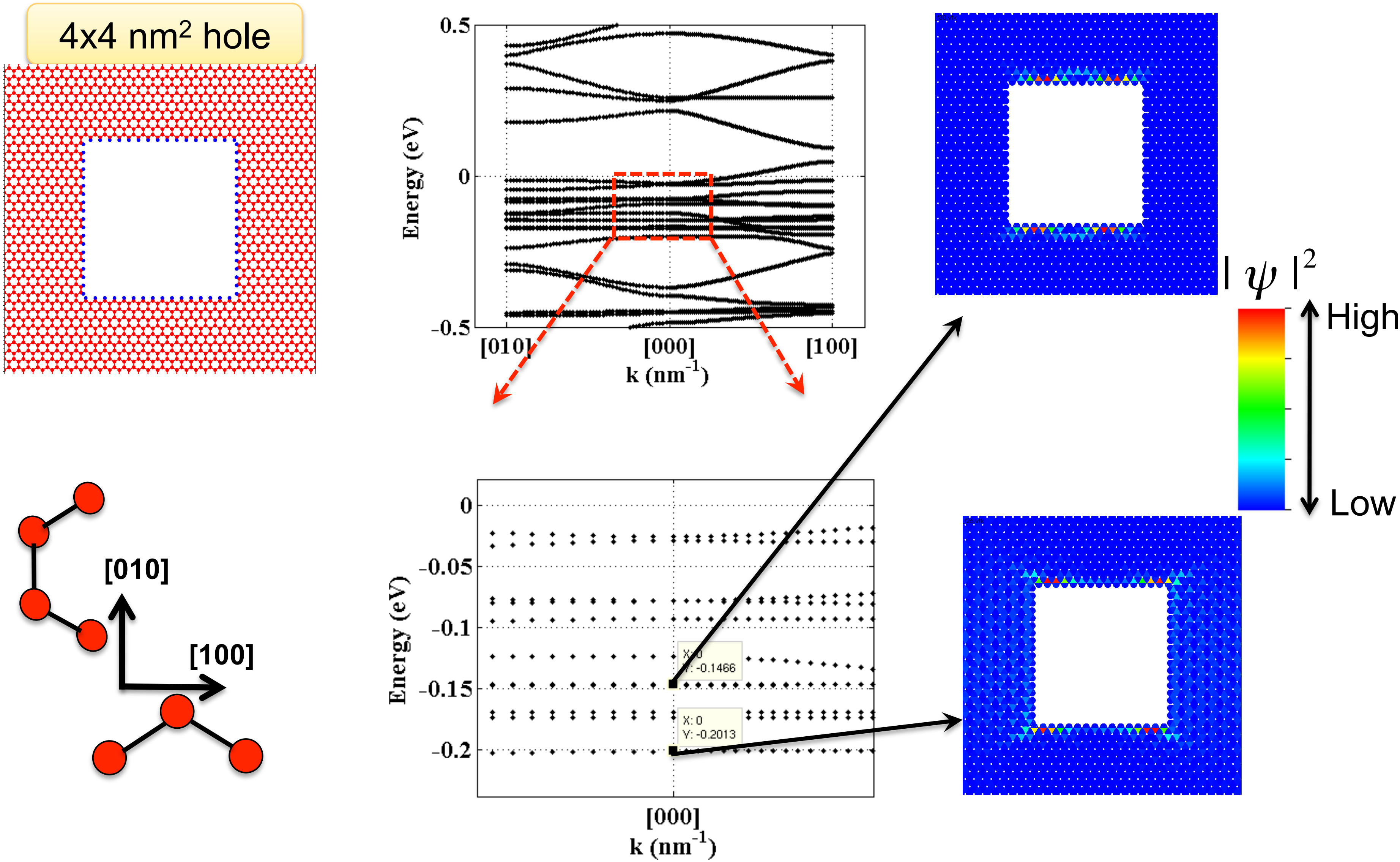
Anisotropic dispersion ➔ Anisotropic transmission

7x1nm hole



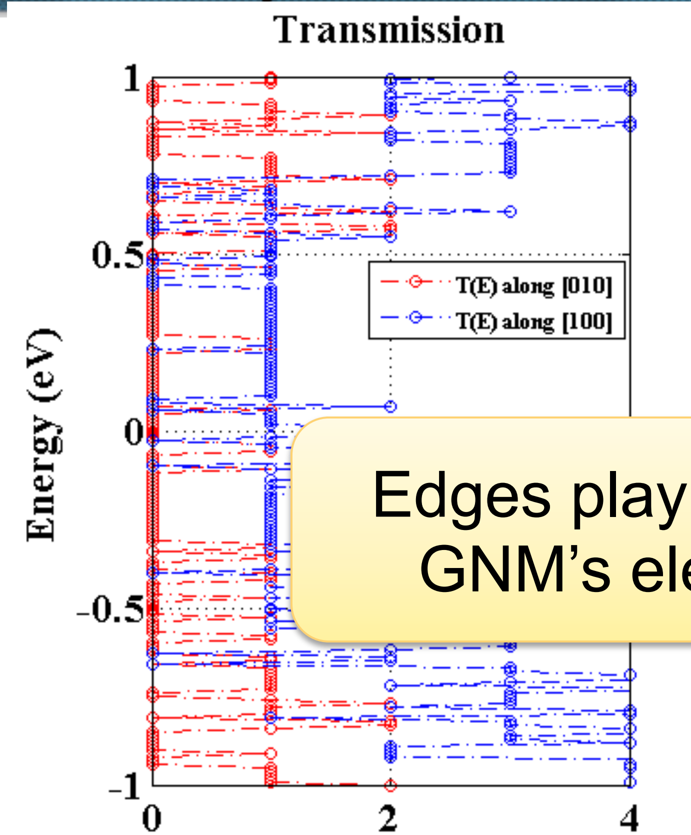
- High (low) dispersion ➔ High (low) transmission
- A rectangular hole serves as a ‘guide’ to electron conductance
- How does the edge affect electron conductance ?

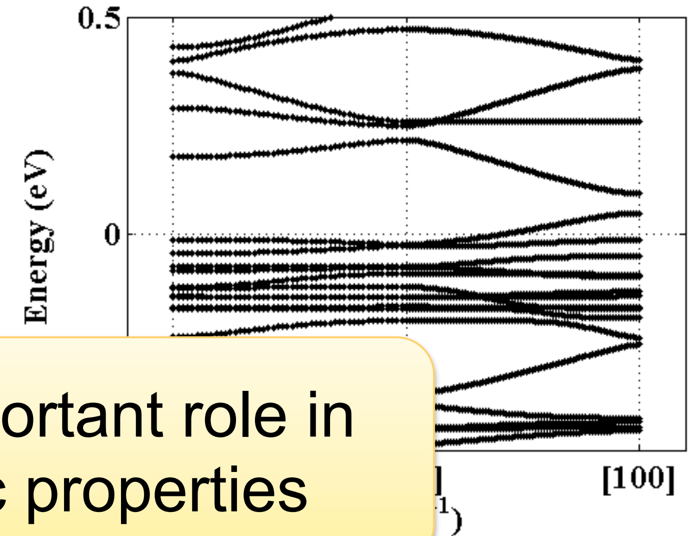
Square Hole



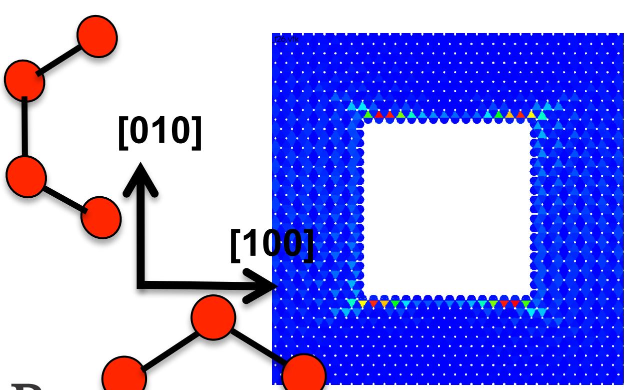
- Same as before, electron wavefunction is localized on the zigzag edge

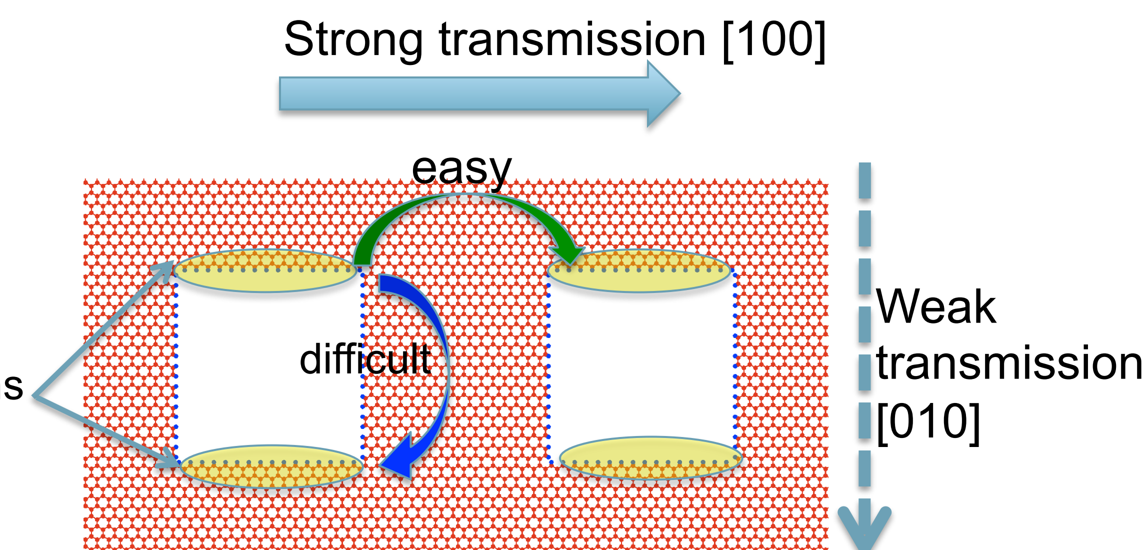
Transmission Comparision





Edges play an important role in GNM's electronic properties





Outline

- Introduction/Motivation
  - » Why graphene is important
  - » Challenges for graphene applications
  - » Graphene nanostructures
- Model Details
  - » Nearest neighbor tight-binding model in graphene
  - » Need for P/D model
- Modeling of Graphene Nanomeshes (GNM)
  - » Circular hole GNM: Bandgap & edge states
  - » Rectangular hole GNM: Anisotropic conductance
- **Conclusion and Future Work**

Conclusion and Future Work

Conclusion:

- Periodic perforations in graphene can open up a sizeable bandgap, making it possible for transistor applications
- The electronic properties of GNM are highly dependent on hole size and geometry. This opens up opportunities for bandstructure engineering in GNM.
- However, atomic precision lithography is still necessary to harness the potential of GNM, since the electronic properties depend heavily on the edge structure

Future Work:

- Full transport simulation with applied bias
- Propose novel device applications utilizing GNM properties, such as band-to-band-tunneling transistors
- Reliability test including edge roughness, hole size fluctuation, tilted angle, etc.

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