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Control and Assembly of Nanoscale Structures: Directed Self-Assembly

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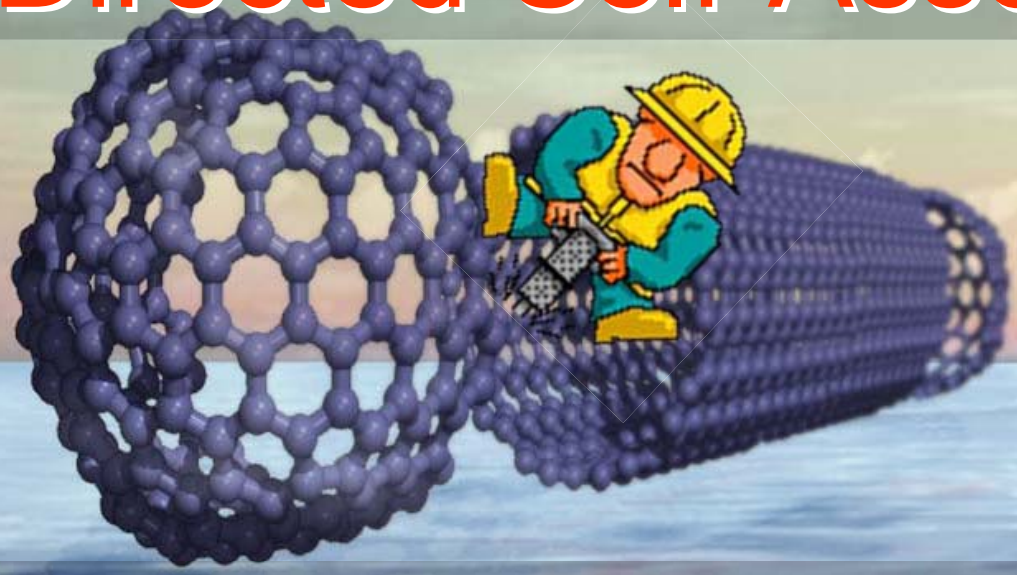
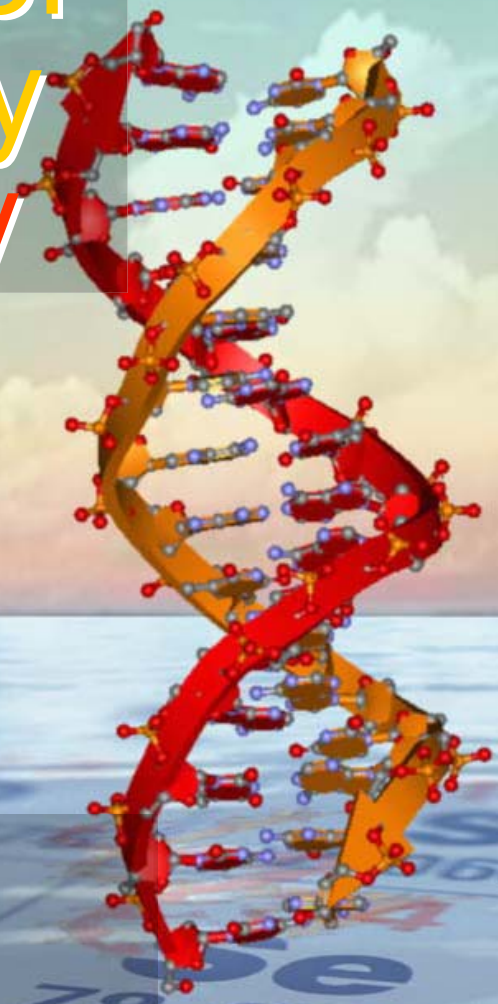
Control and assembly of nanoscale structures by Directed Self-Assembly





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NSF-NIRT

Outline

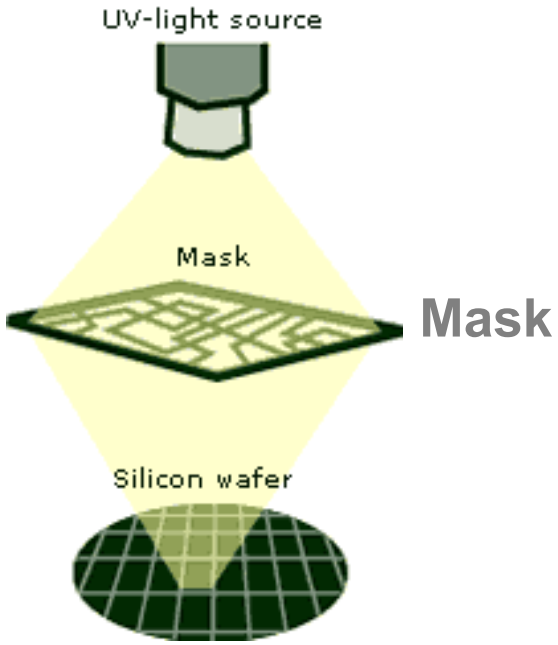
- Introduction: From nanoscience to nanotechnology
  - **From top-down to bottom-up manufacturing**
  - **State of the art of computer simulations**
- The self-assembly way of nanotechnology
  - **Long chain alkanes on HOPG**
  - **Functionalized-C_{60} (F-C_{60}) on HOPG and Ag(111)**
- Nano-engineering with atomic-scale defects
  - **Defect-assisted fusion of fullerenes**
  - **Defect-assisted fusion of nanotubes**
  - **Defect-assisted scroll-nanotube conversion**
  - **Self-trimming of rough graphene nanoribbons**
- The nano-pecker as a probe of defects
  - **Unique capabilities of a dynamic AFM**
  - **Probing morphology and vibrational modes**
- Summary and conclusions

It is never late …

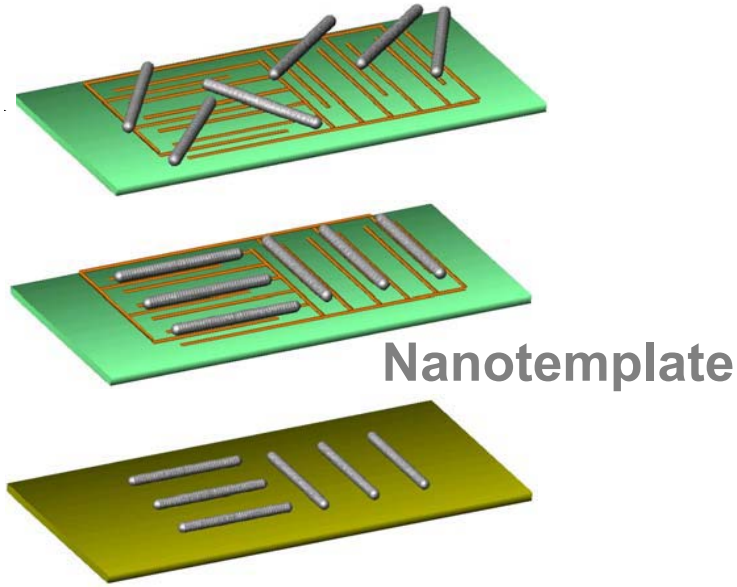
… to get excited

From Top-Down to Bottom-Up Manufacturing

Top-down:
Efficient, but resolution limited by mask



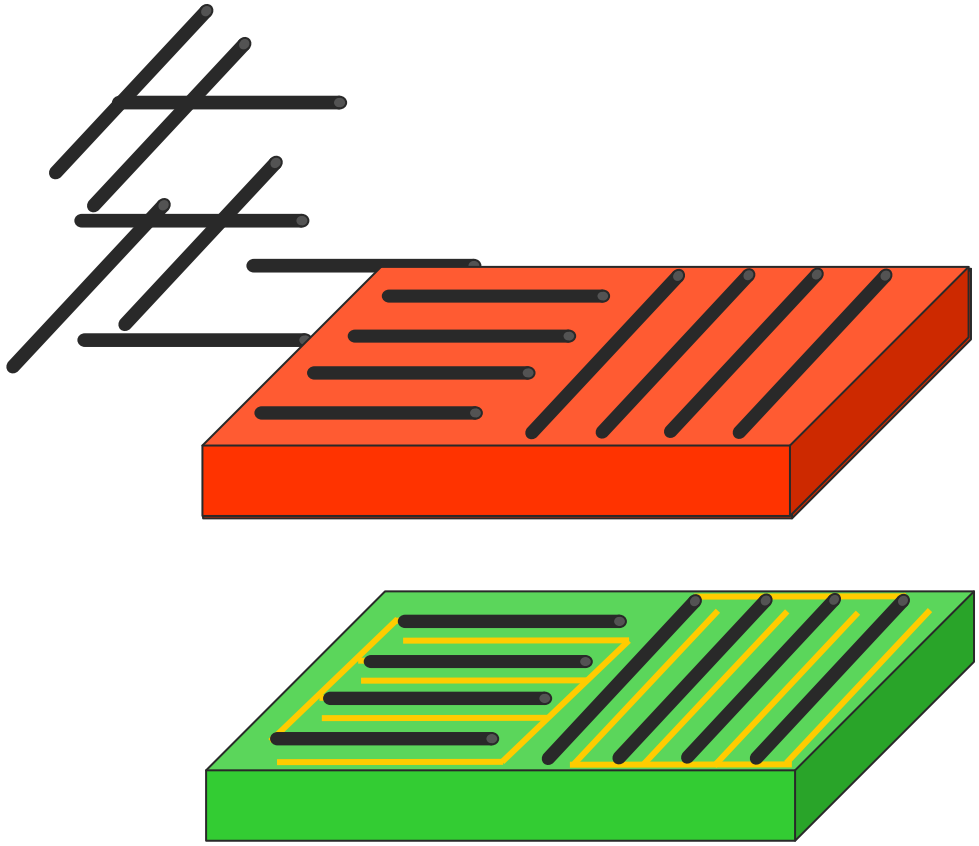
Bottom-up:
Nanotemplate-based imprint lithography for high rate



State of the Art:
➢ A single mask can be used for more than 100,000 Si wafers

Challenge:
➢ Create nanotemplates that can be used many times

How can we harness self-assembly for nanotemplate-based imprint lithography?



How can design and optimize this process using computer modeling?

Some computational approaches

- ***Ab initio***
  - HF (Hartree-Fock)
  - HF-CI (Hartree-Fock with Configurational Interaction)
  - DFT (Density Functional Theory)
  - TDDFT (Time Dependent Density Functional Theory)
  - GW
  - BSE (Bethe-Salpeter Equation)
- **Parameterized**
  - TB (Tight-Binding)
  - EH (Extended Huckel)
  - KISS (Keep It Simple, Stupid!)
  - CNDO (Complete Neglect of Differential Orbitals)
  - CNE (Complete Neglect of Everything)

State-of-the-art ground state electronic structure calculations

- *Ab initio* Density Functional Theory

  Total energy: $E_{tot} = E_{tot}[\,\rho\,]$

  Self-consistent approach:

  $$\{ -\tfrac{1}{2}\nabla^2 + V_{ext} + V_H(\,\rho\,) + V_{XC}[\,\rho\,] \}\,\psi_{nk}(\mathbf{r}) = \varepsilon_{nk}\,\psi_{nk}(\mathbf{r})$$

  $$\rho\,(\mathbf{r}) = \Sigma_{nk} |\,\psi_{nk}(\mathbf{r})|^2$$

- SIESTA code
  - Local Density Approximation
  - Double- ζ + polarization
  - Troullier-Martins pseudopotentials
  - Perdew-Zunger exchange-correlation functional
  - 200 Ry mesh cutoff energy

Ab initio

Latin; "from first principles"

Prague
≈1500 – 1600

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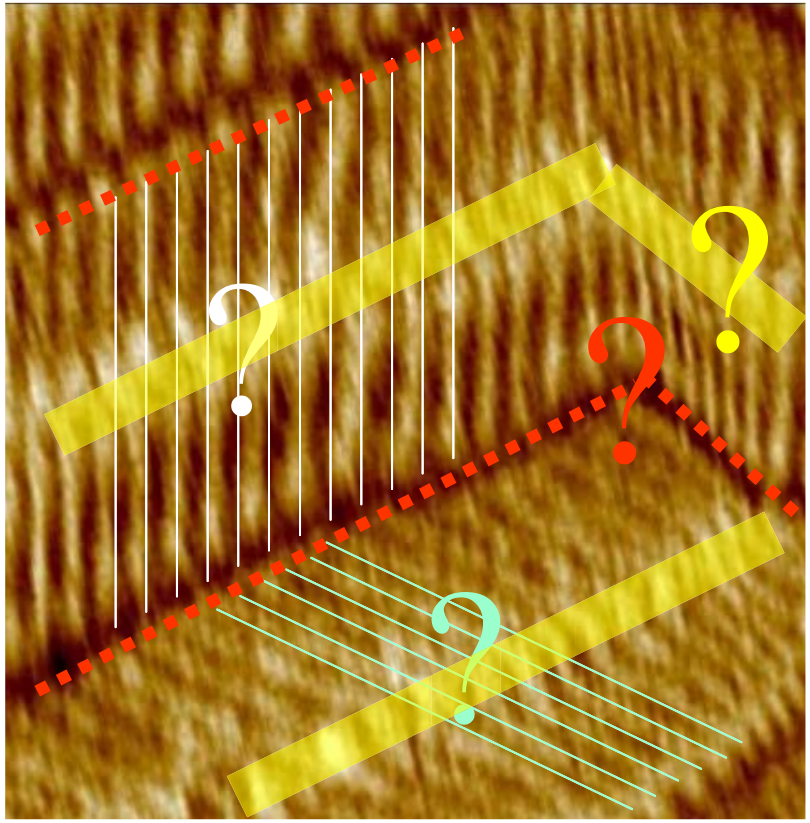
Self-assembly of polymers and fullerenes on surfaces

Long chain alkanes on HOPG

- Long chain alkanes on graphite: **Why** and **how** do self-assembled monolayers (SAMs) form?

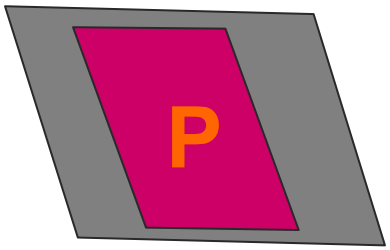


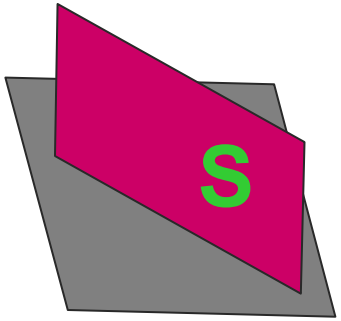
What causes such complex patterns?

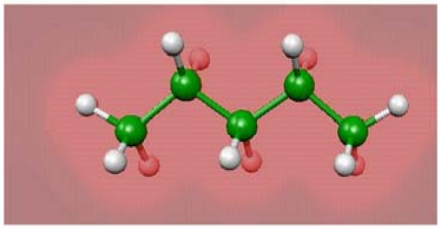
Teng Yang, Savas Berber, Jun-Fu Liu, Glen P. Miller, and David Tománek, Self-assembly of long chain alkanes and their derivatives on graphite, J. Chem. Phys. **128** (2008).

Alkane chains on HOPG: which orientation?

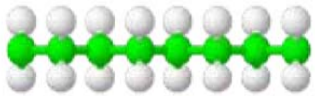
Isolated chains in
P and S configuration:



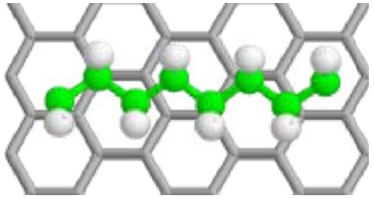




Incommensurate along armchair

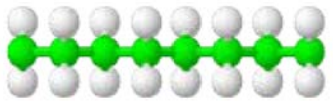


Side view (P)

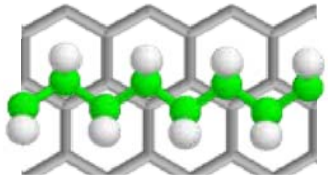


Top view (P)

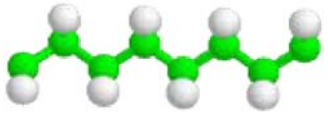
Commensurate along zigzag



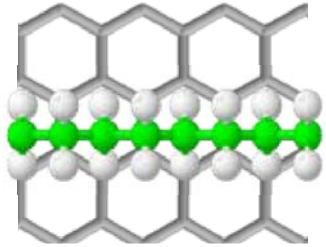
Side view (P)



Top view (P)



Side view (S)

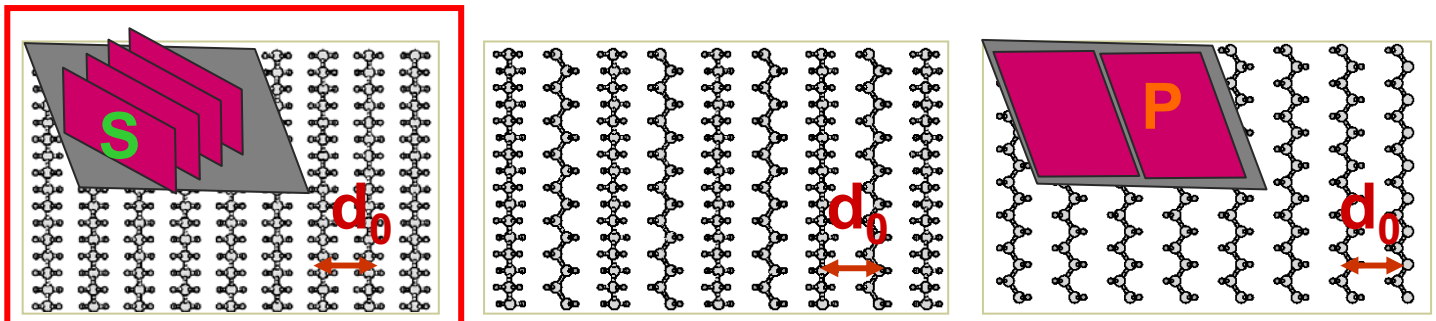


Top view (S)

adsorption energy E_{ad}: **-40 meV**/C_2H_4 **-120 meV**/C_2H_4: **BEST** **-90 meV**/C_2H_4

- Long chain alkanes prefer to align along zigzag direction with P configuration.

Geometry and interactions among polymers in monolayers

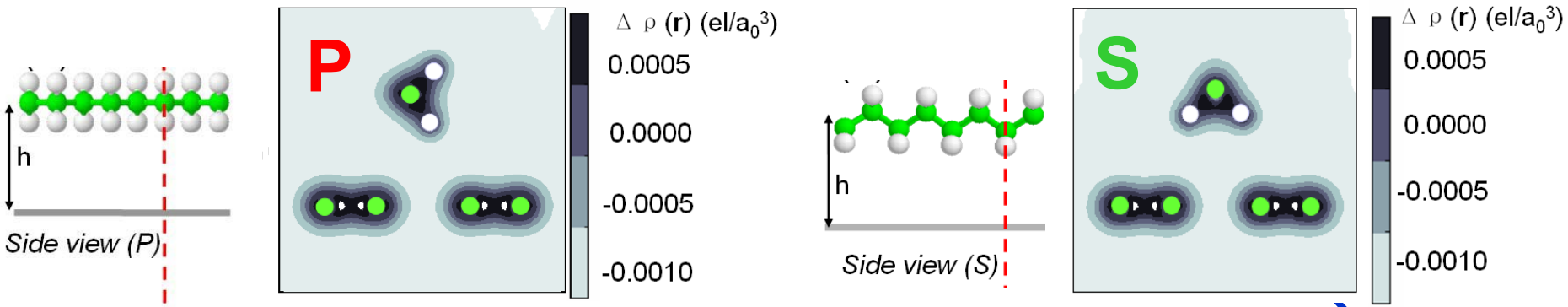


	S-S	P-S	P-P
Inter-polymer interaction E:	-114 meV/C_2H_4	-92 meV/C_2H_4	-65 meV/C_2H_4
Inter-polymer distance d_0:	**3.5 Å**	**4.0 Å**	**4.3 Å**
	BEST		

- Close packing in S-configuration with inter-polymer distance d_0=3.50 Å is best
- Assembly in P-configuration still possible, with inter-polymer distance d_0=4.28 Å

Nature of the alkane-graphite bond

Alkane chains are commensurate with the zigzag graphitic direction



E_{ad} =**-0.12 eV**/C_2H_4

E_{ad} =**-0.09 eV**/C_2H_4

Charge accumulation

Charge depletion

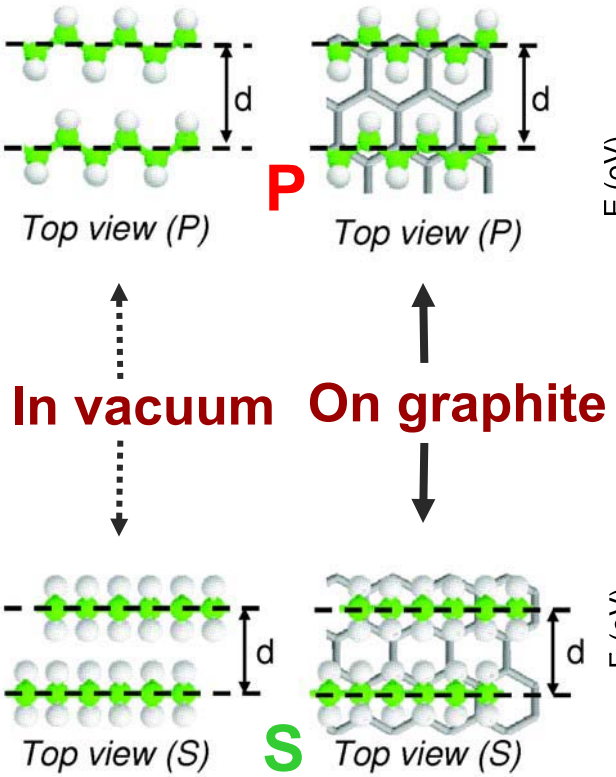
$\Delta\ \rho$ = ρ **(alkanes/graphite)** – ρ **(graphite)** – ρ **(alkane)**

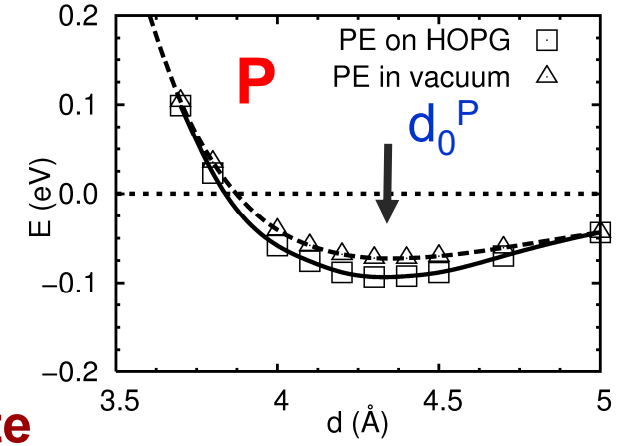
charge density difference

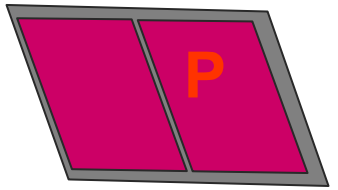
- Charge density difference map suggests weak covalent bonds
- Small charge accumulation in P orientation, small charge depletion in S orientation suggests a slightly stronger adsorption in the P than in the S orientation.

How strong is the alkane-alkane interaction?
Is it affected by the presence of graphite substrate?

Effect of graphite on inter-chain interaction

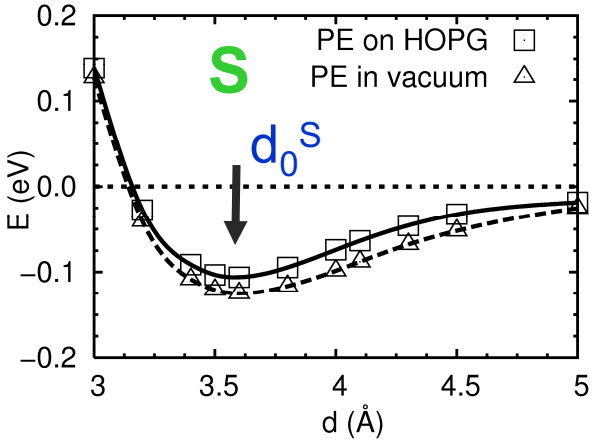


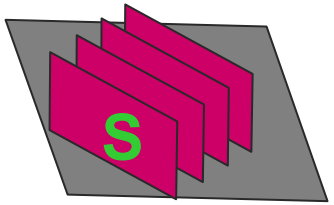




$\Delta E \approx$ -0.1 eV/C_2H_4

d_0^P = 4.26 Å





$\Delta E \approx$ -0.1 eV/C_2H_4

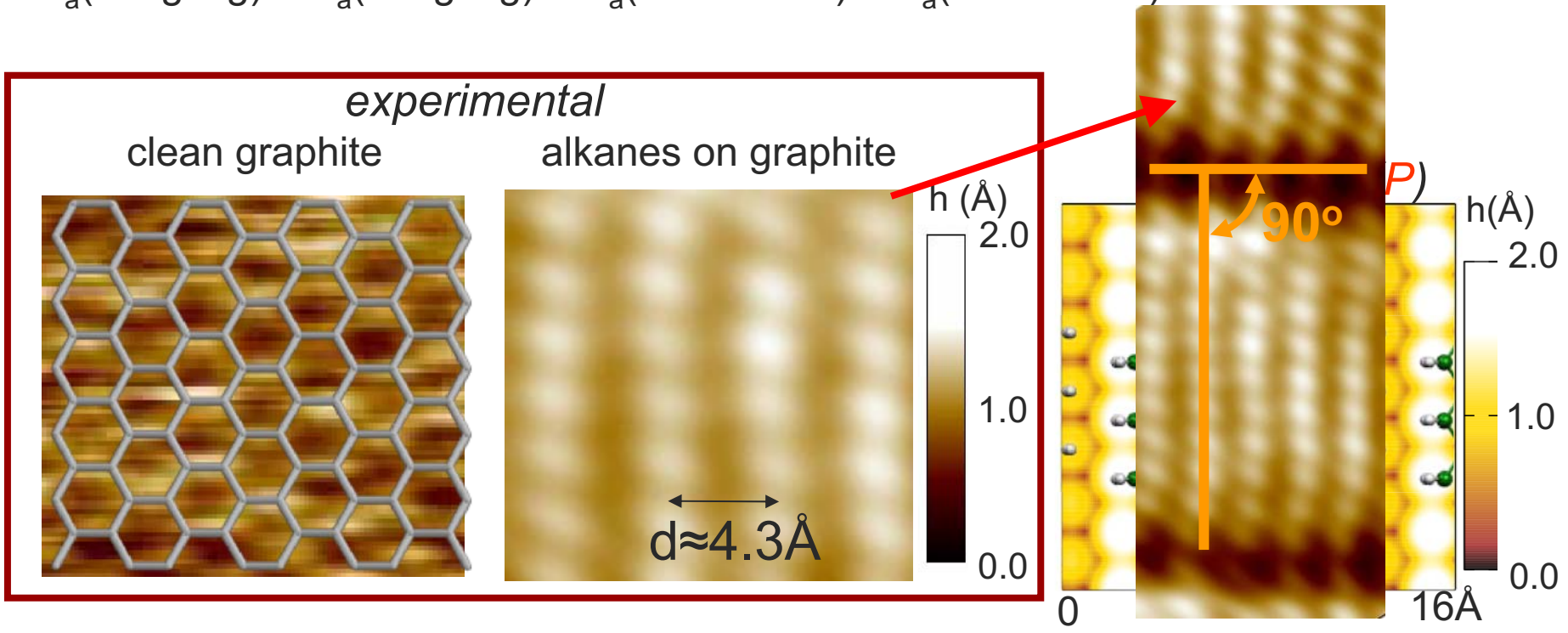
d_0^S = 3.50 Å

- Inter-chain interaction stabilizes the self-assembled monolayer by $\approx$0.1 eV/C_2H_4 both in P and S arrangement
- Interaction with graphite does not affect the inter-chain interaction.

What patterns are expected on graphite?

Energy hierarchy and adsorption patterns

Adsorption pattern is determined by the **hierarchy of interactions**:
E_a(P/zigzag) < E_a(S/zigzag) < E_a(P/armchair) < E_a(S/armchair)



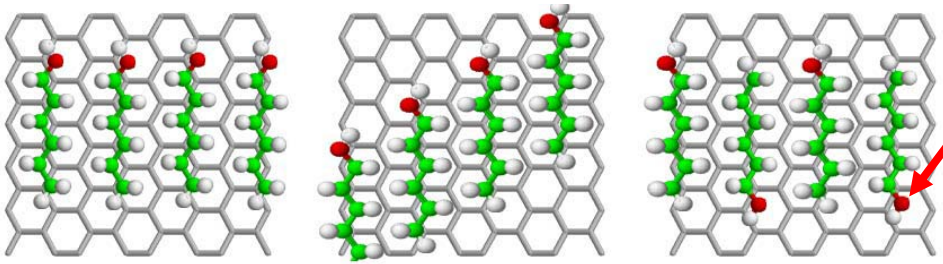
STM images confirm that alkanes form self-assembled monolayers on graphite:

- Preferential alignment: along graphite zigzag direction with P orientation
- Optimum arrangement: 90º angle between domain boundary and alkane chain

Can functional groups modify the patterns?

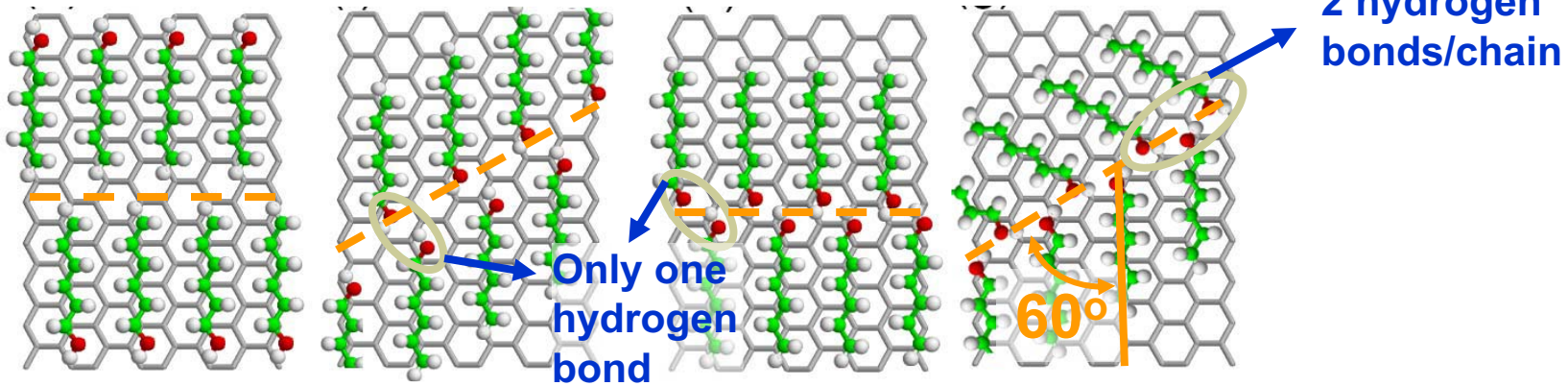
Domain formation in long chain alcohols ($C_6H_{13}OH$)

Single domain: head-to-head or head-to-tail?



E_{ad} = **-1.00 eV** **-0.95 eV** **-0.98 eV** per C_6H_{13}**OH**

Multiple domains: which arrangement?



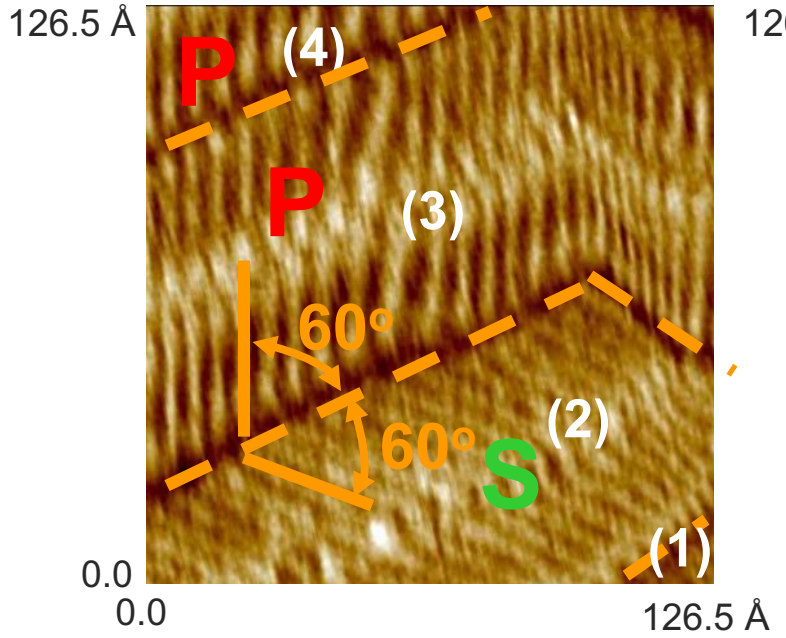
E_{ad} = **-1.03 eV** **-1.20 eV** **-1.45 eV** **-1.60 eV**

- Head-to-head orientation in a single domain is best for alcohols
- Optimum domain boundaries are stabilized by 2 hydrogen bonds/chain (domain boundary at 60º with respect to chain direction)

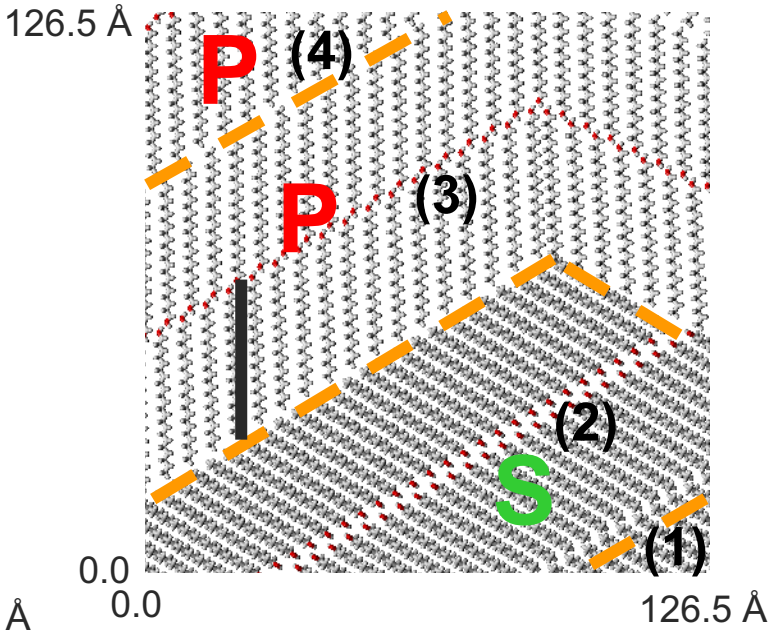
Does this agree with experimental observation?

Comparison with STM images

Experiment



Theory



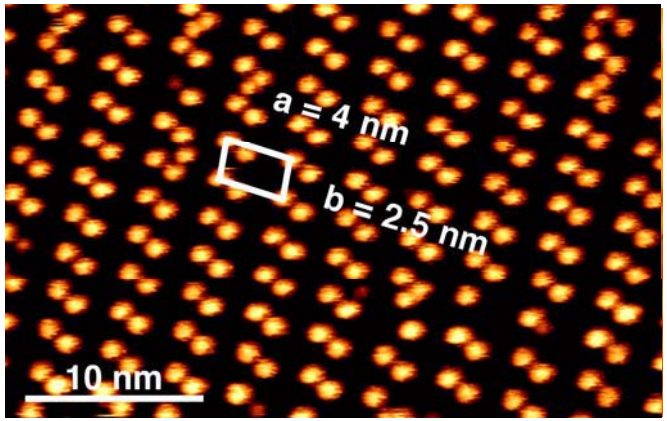
2 domain types: **S**, **P**

Inter chain distance:
d≈3.50 Å **(S)**
d ≈4.28 Å **(P)**

- *Equilibrium geometry given by hierarchy of interactions*

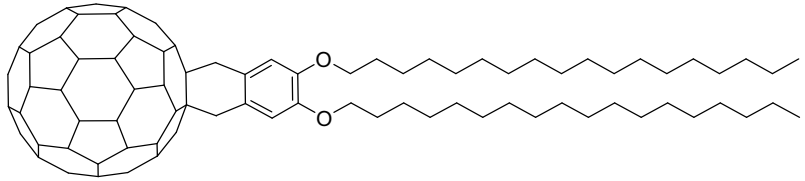
Functionalized-C_{60} (F-C_{60}) on HOPG and Ag(111)

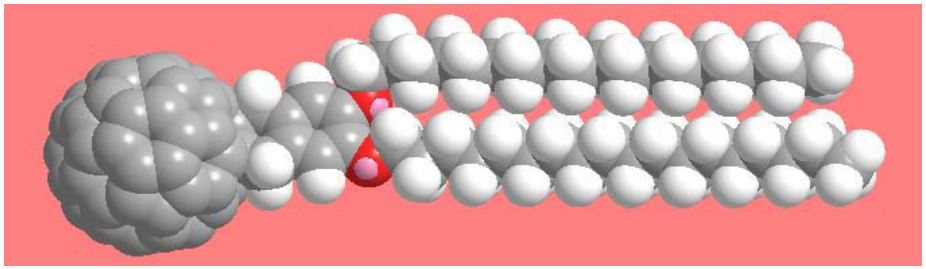
Fullerenes functionalized with two alkyl chains have been synthesized and observed by STM



STM image

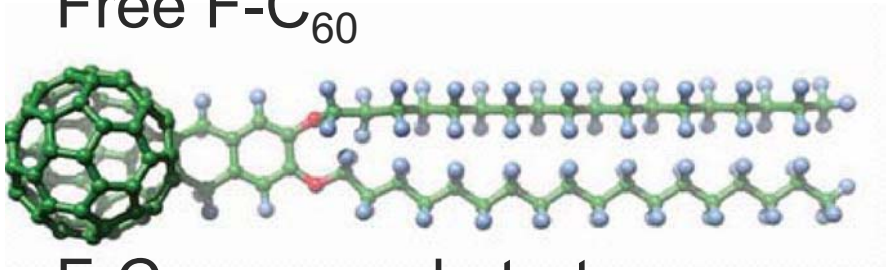
Bogdan Diaconescu, Teng Yang, Savas Berber, Mikael Jazdzyk, Glen P. Miller, David Tománek, and Karsten Pohl, Molecular self-assembly of funtionalized fullerenes on a metal surface, Phys. Rev. Lett. **102**, 056102 (2009).





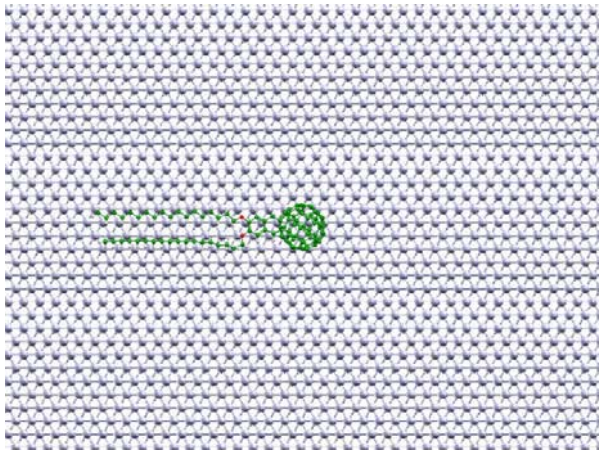
Possible F-C_{60} conformations on a substrate

- Free F-C_{60}

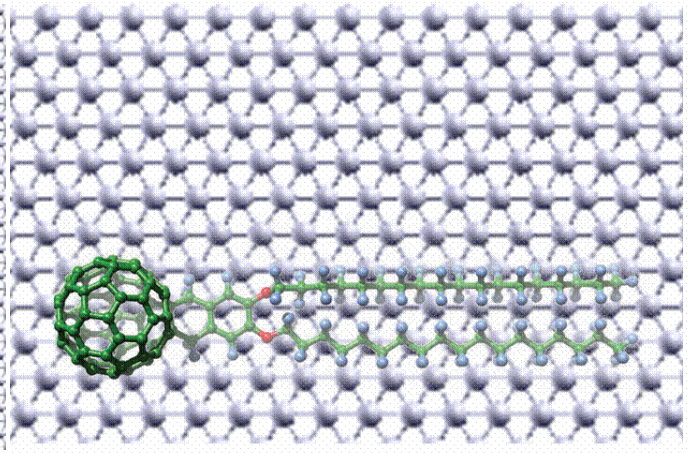


- F-C_{60} on a substrate

Which orientation?

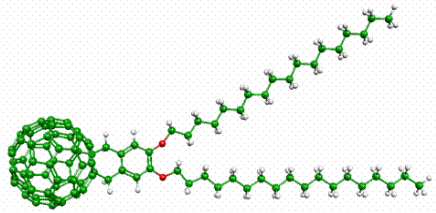


Which shape?



I-shape vs. V-shape

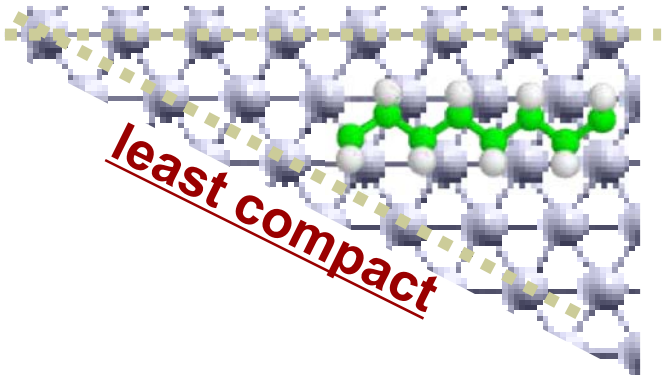
May legs rotate?



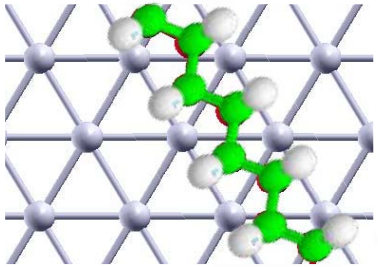
- Will the substrate determine, which it will be?
  - Need to understand hierarchy of interactions in polymer LEGO set

Alkane chains on Ag(111): How different from HOPG?

- Ag(111) surface is a close-packed triangular lattice
- Long chain alkanes are incommensurate with the Ag(111) surface



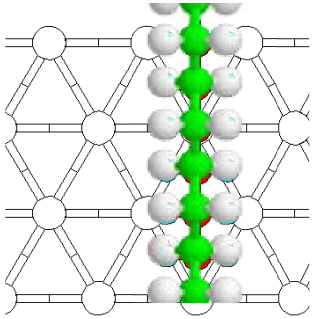
PE-Ag: *P* geometry



E_{ad} = **-223** meV/C_2H_4

BEST

PE-Ag: *S* geometry



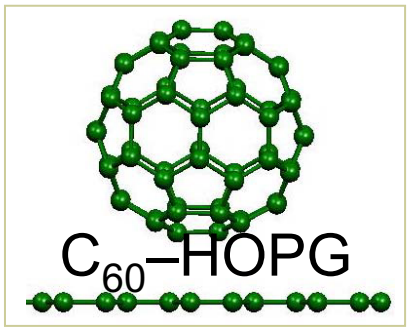
E_{ad} = **-160** meV/C_2H_4

- Long chain alkanes prefer to adsorb in P configuration along the most compact direction (analogy to zigzag direction on HOPG).

Does presence of C_{60} modify the interactions and geometry?

C_{60} on Ag(111): Geometry and interactions

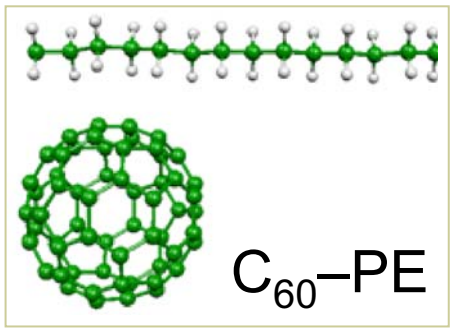
Adsorption energy of C_{60} on HOPG and on Ag(111)



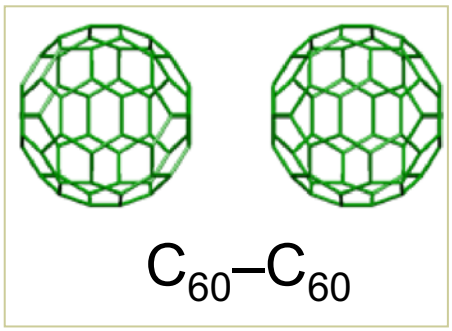
-660 meV

-840 meV

C_{60}-C_{60} and C_{60}-polymer interaction



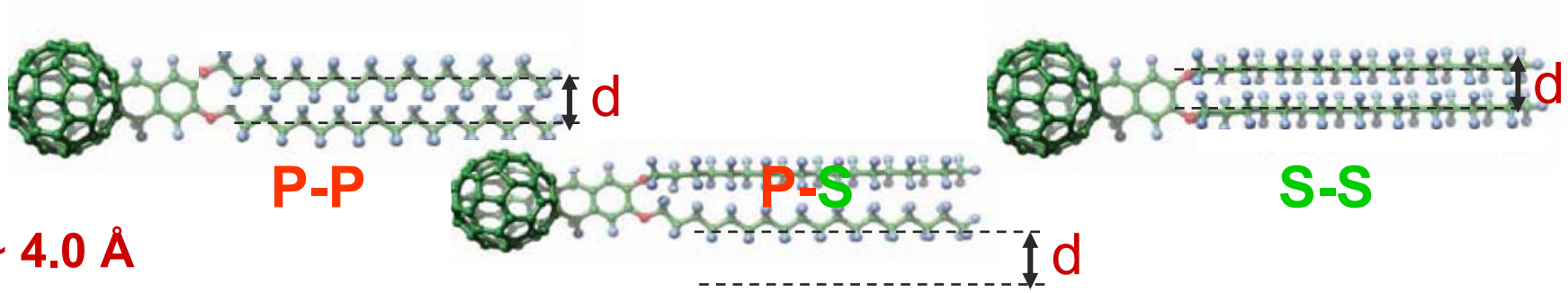
E_{ad} = -273 meV



-150 meV

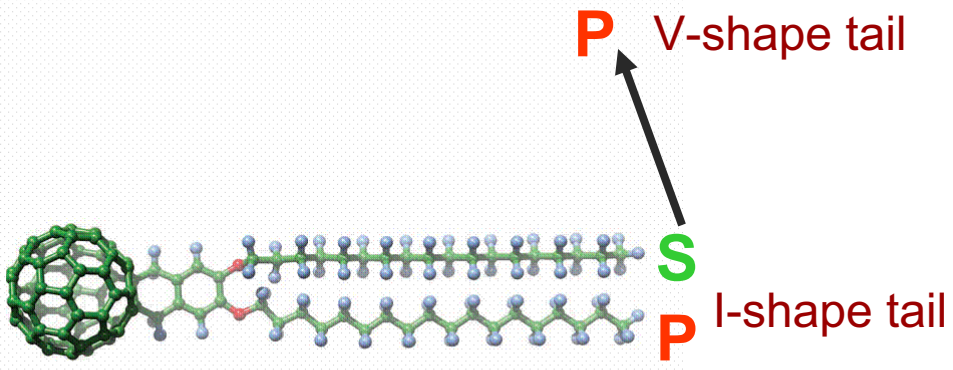
Is this information sufficient to predict adsorption patterns of F-C_{60} on surfaces?

F-C_{60} on HOPG: which conformation?



d ~ **4.0 Å**

polymer-involved E:	**> -2.7eV**	**~ -2.7eV**	**> -2.7eV**



F-C_{60} molecule

Changing I to V shape in vacuum:

ΔE= + 420.6 meV (cost)

Put V shape onto HOPG surface:

$\Delta E_{adsorption}$= - 240 meV (gain)

Net energy loss for V shape on Ag

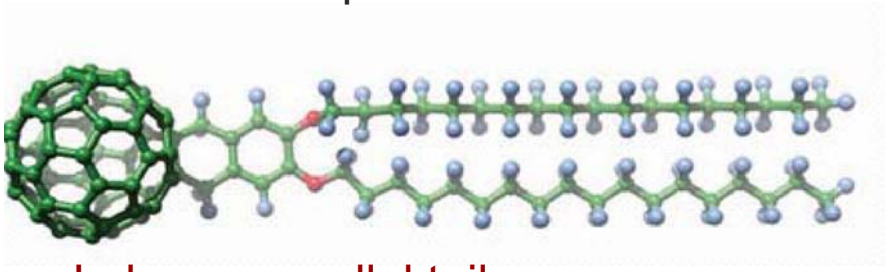
ΔE_{tot}= +181 meV

- On HOPG substrate: **I-shape**
- One chain is in P and the other in S configuration.

Is the shape of F-C_{60} same on Ag(111)?

F-C_{60} on Ag(111): which conformation?

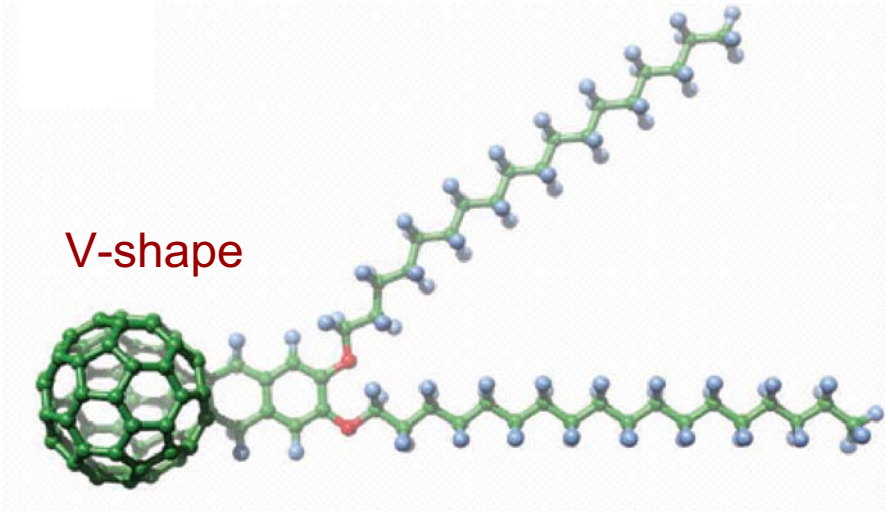
Full structure optimization



I-shape: parallel tails

Changing I to V shape in vacuum:

ΔE= + 420.6 meV



V-shape

Put V shape onto metal surface:

$\Delta E_{adsorption}$= - 480 meV

Net energy gain for V shape on Ag

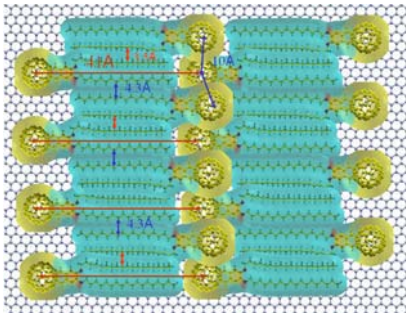
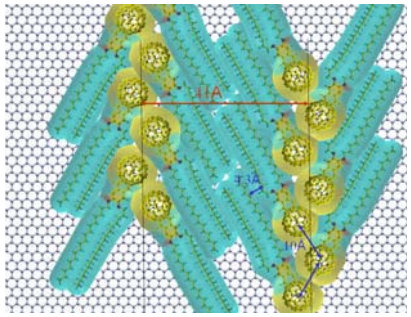
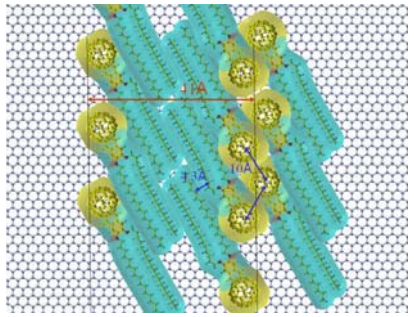
ΔE_{tot}= - 60 meV

- On Ag(111) substrate: **V-shape**
- Chains are both P configuration.

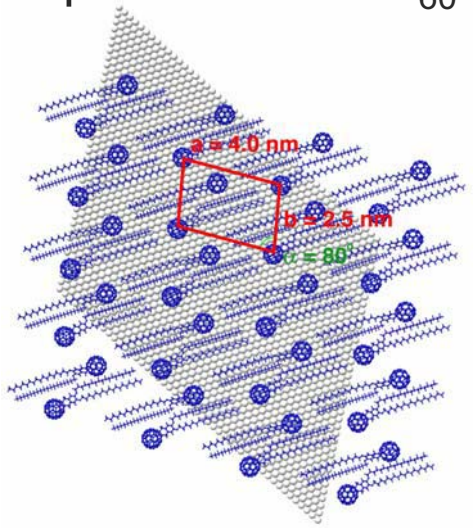
Can the substrate dictate the adsorption pattern?

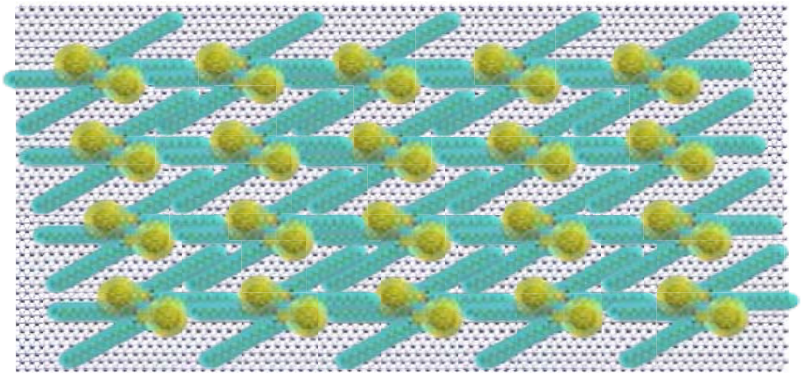
Can self-assembled patterns change from substrate to substrate?

- Possible patterns of F-C_{60} on HOPG

- Possible patterns of F-C_{60} on Ag(111)



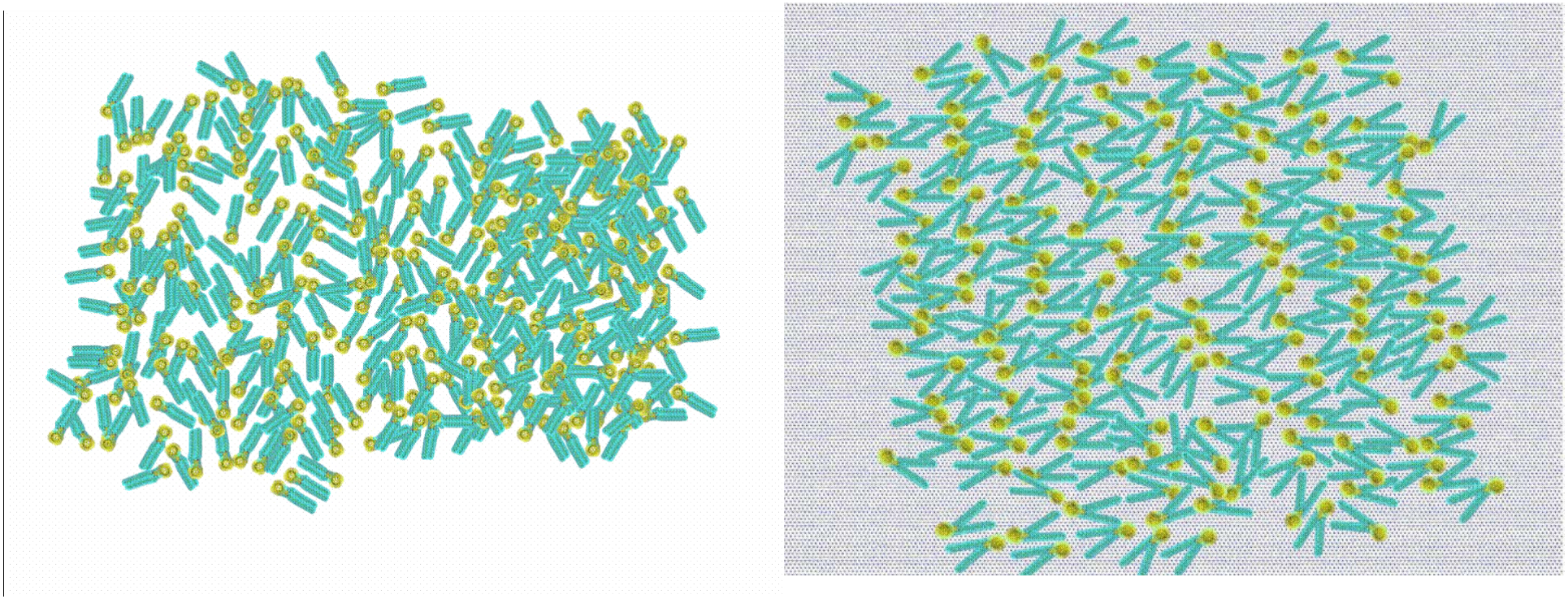


Which ones do really form, and how?

Which patterns do really form, and how?

After considering all interactions, we propose the following assembly dynamics:

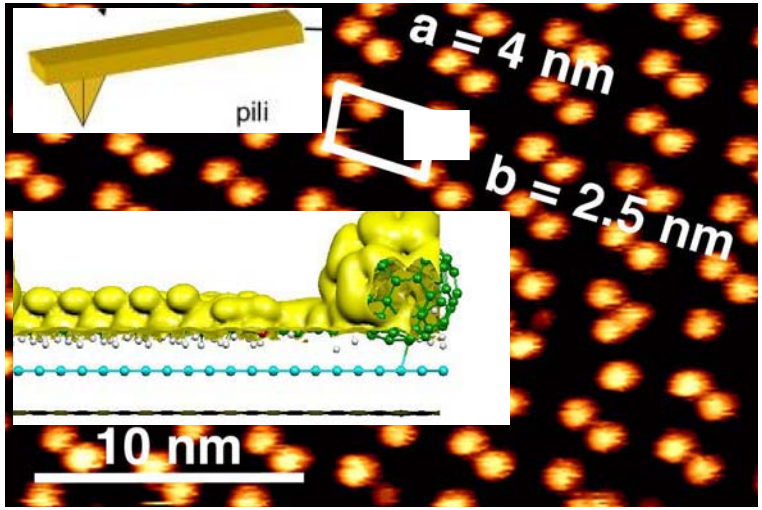
HOPG **Ag(111)**

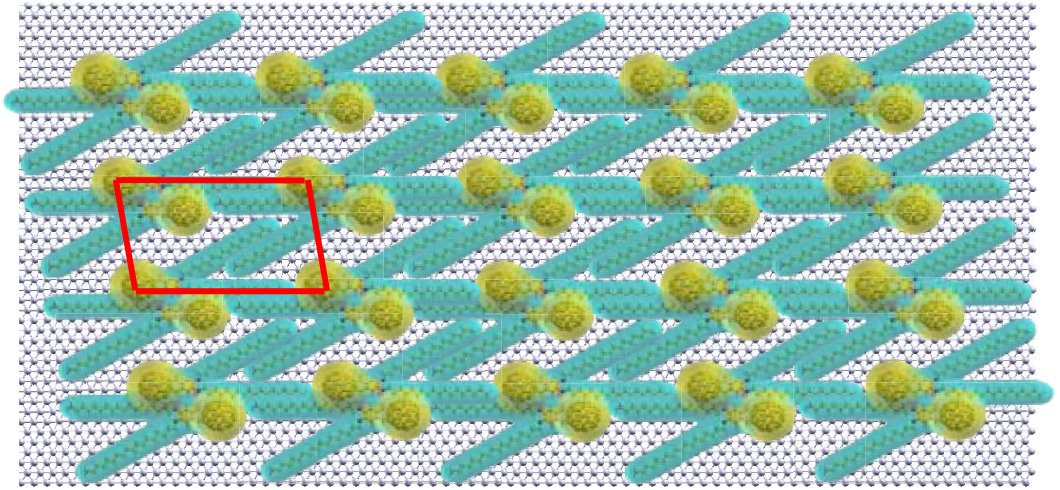


➢Self-assembled patterns depend sensitively on the substrate

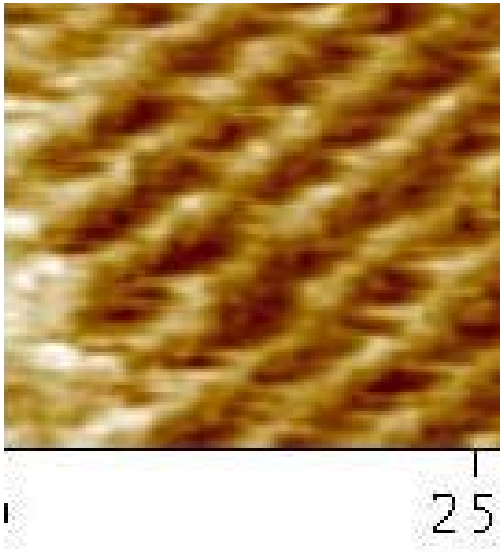
Is there experimental evidence?

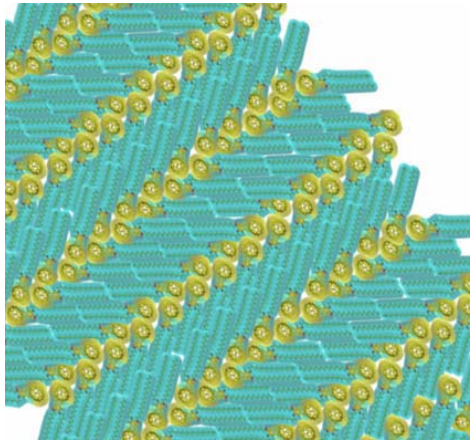
Experimental confirmation of F-C_{60} pattern on Ag(111) and HOPG

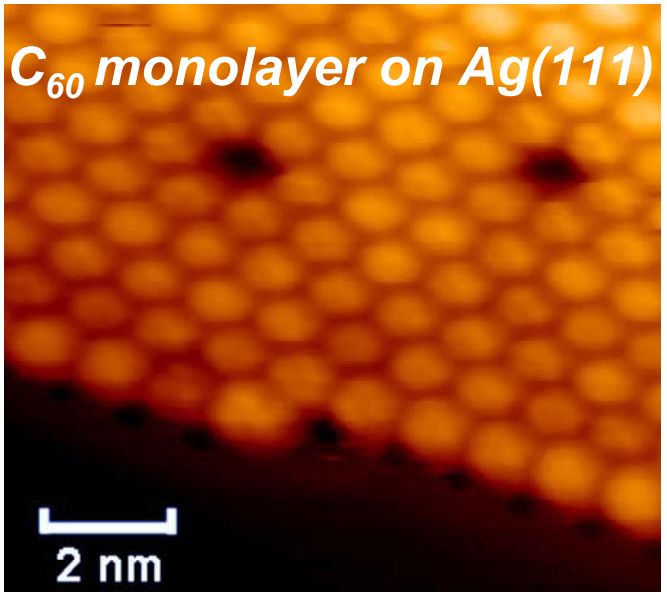




STM image







➢Unit cell can be changed by modifying chain length in F-C_{60}

Outline

- Introduction: From nanoscience to nanotechnology
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  - **Long chain alkanes on HOPG**
  - **Functionalized-C_{60} (F-C_{60}) on HOPG and Ag(111)**
- Nano-engineering with atomic-scale defects
  - **Defect-assisted fusion of fullerenes**
  - **Defect-assisted fusion of nanotubes**
  - **Defect-assisted scroll-nanotube conversion**
  - **Self-trimming of rough graphene nanoribbons**
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  - **Unique capabilities of a dynamic AFM**
  - **Probing morphology and vibrational modes**
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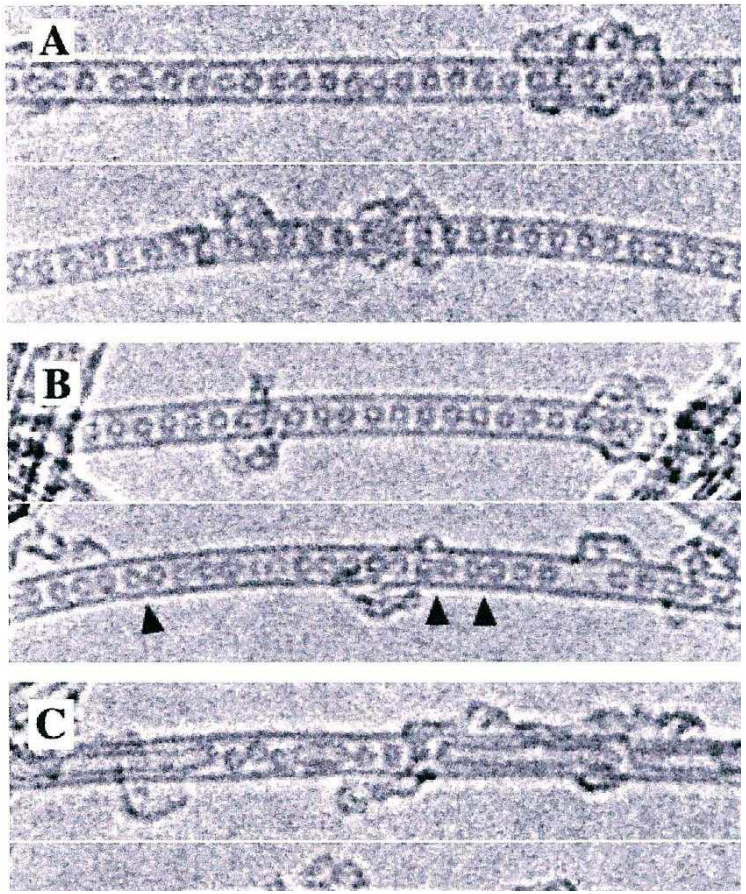
Nano-engineering with atomic-scale defects

Defect-assisted fusion of fullerenes



T=1,100ºC

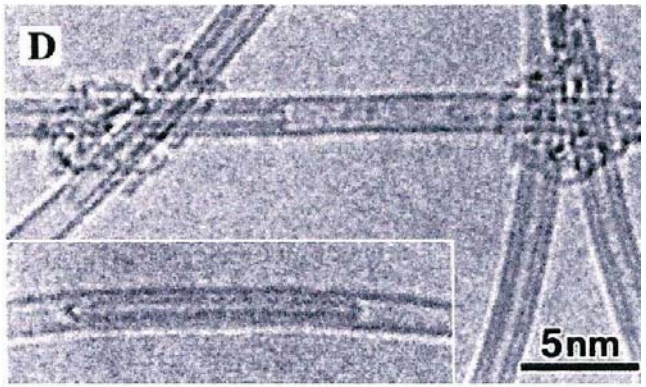
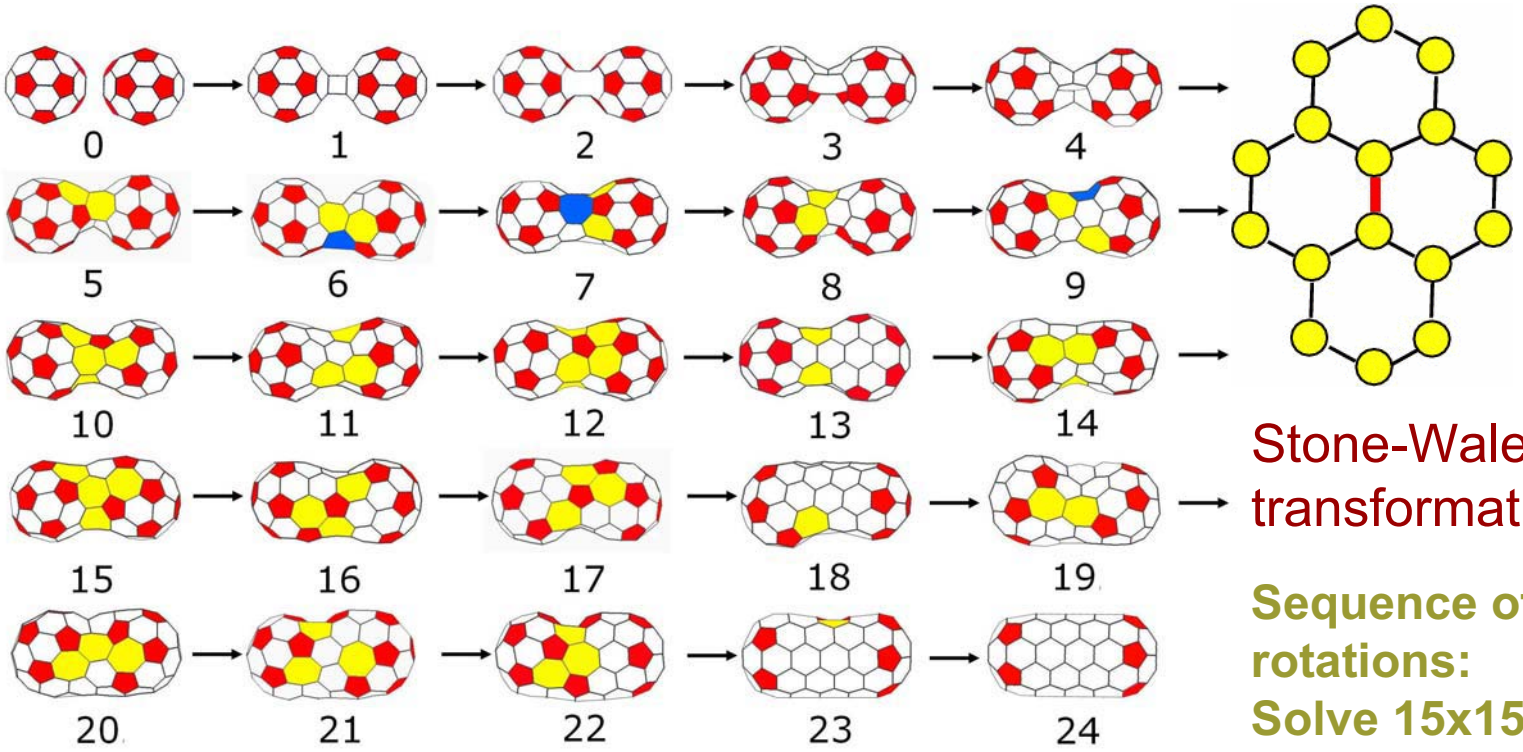


Fig. 1. Transmission electron microscopy images. (A) is for $(C_{60})_n$ @SWNTs, (B) for $(C_{60})_n$@SWNTs heated in ($<10^{-6}$ Torr) at 800°C for 14 h (HT800), (C) for HT100 (D) for HT1200. A and B indicate similar electron micro images, but in B we can occasionally find that some adjacent C_{60} molecules are linked together as indicat arrowheads. In C, some of the C_{60} molecules coalesce tog and transform to a tubular structure. In D, no C_{60} molecu be observed but we easily find DWNTs; in some of ther inside-tubes are terminated by caps and the lengths a order of ~10 nm.

[S. Bandow, M. Takizawa, K. Hirahara, M. Yudasaka, and S. Iijima, Chem. Phys. Lett. 337, 48 (2001)]

The Stone-Wales rearrangement pathway of fullerene fusion



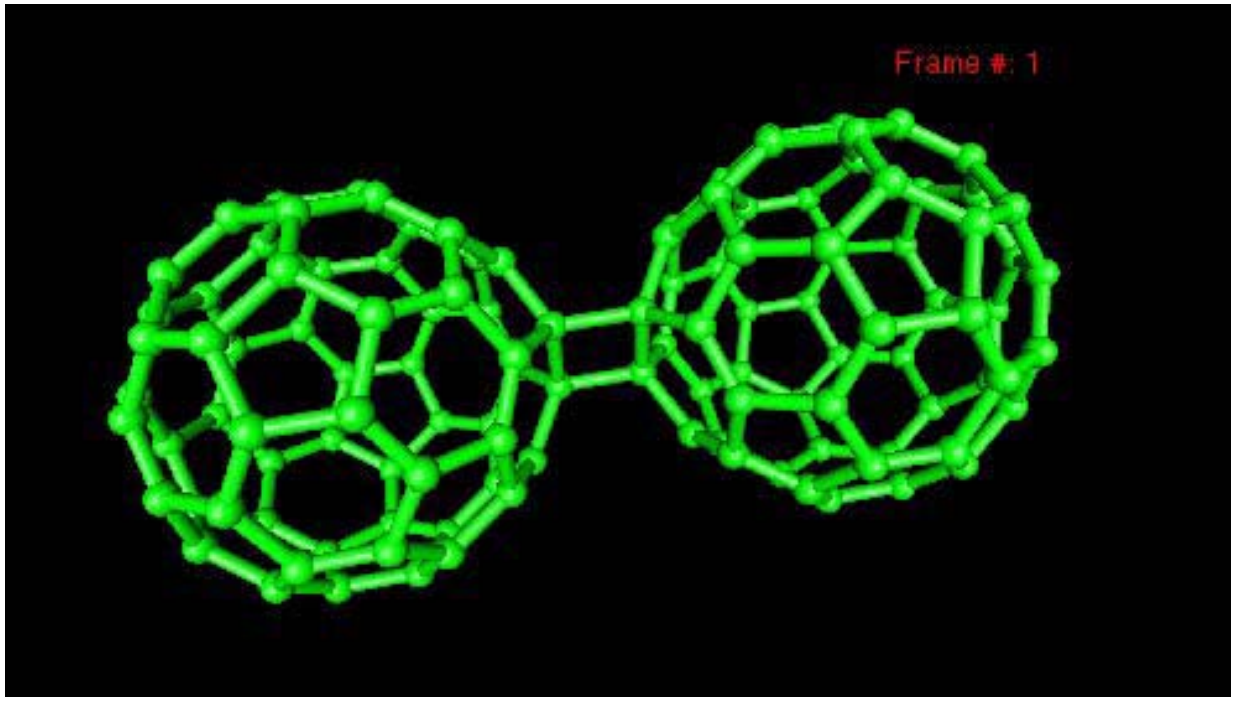
Stone-Wales transformation

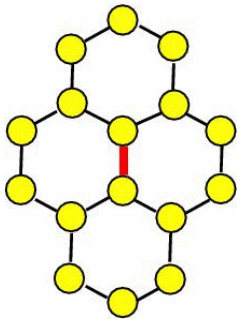
Sequence of bond rotations: Solve 15x15x15 Rubik's Cube puzzle

[Hiroshi Ueno, Shuichi Osawa, Eiji Osawa, and Kazuo Takeuchi, Fullerene Science and Technology **6**, 319-338 (1998)]

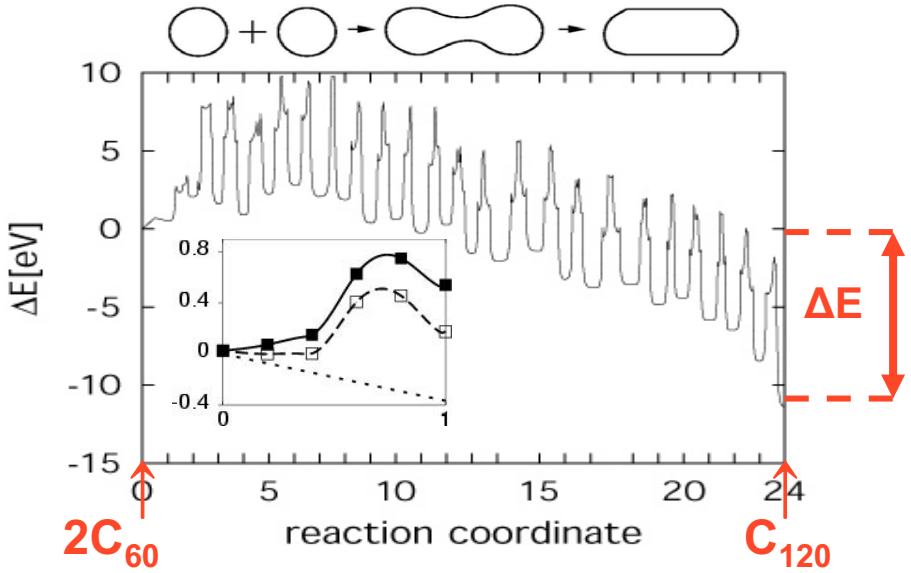
- **Do we understand the energetics?**

Minimum energy path for the $2C_{60} \rightarrow C_{120}$ fusion





Sequence of Stone-Wales transformations

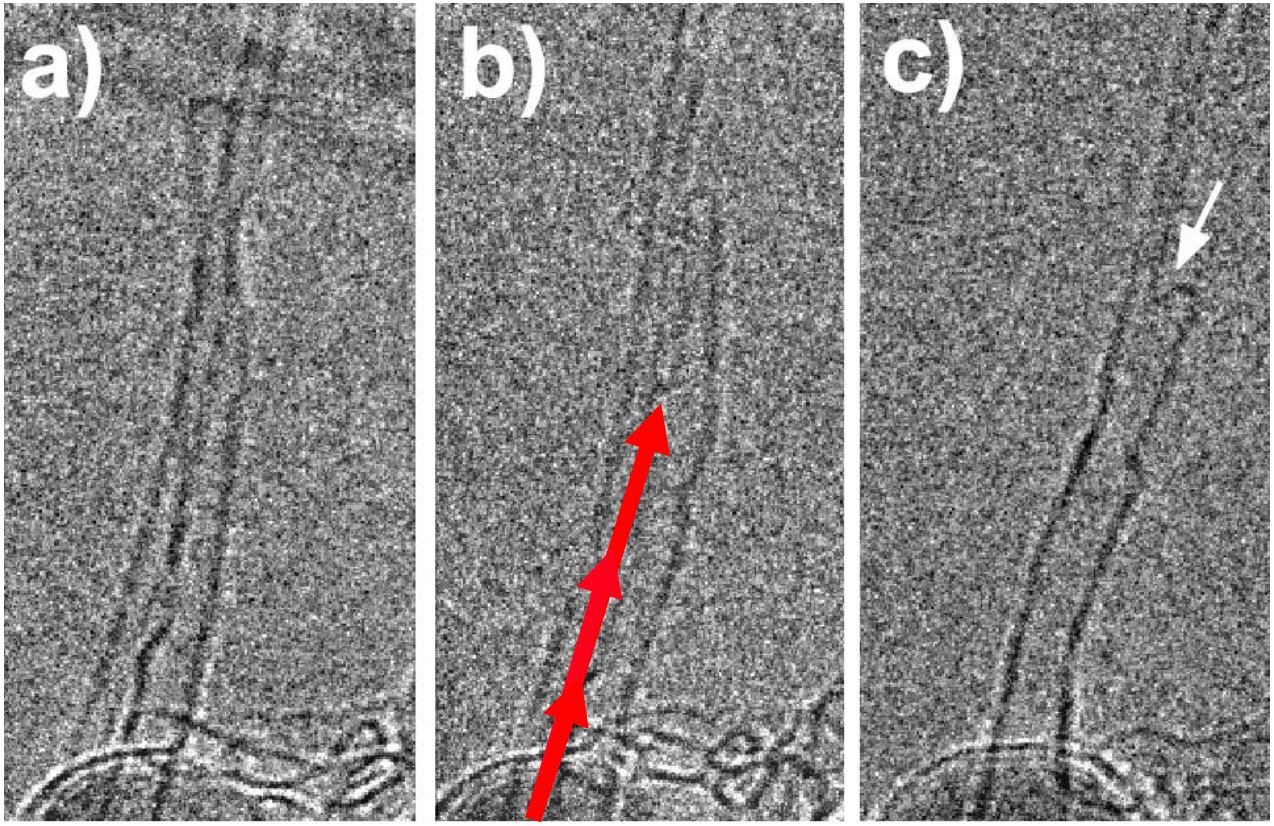


- Conclusions:
  - -Fusion is exothermic.
    Energy gain $\Delta E \approx 1$Ry.
  - -Essential initial step:
    (2+2) cycloaddition

Seungwu Han, Mina Yoon, Savas Berber, Noah Park, Eiji Osawa, Jisoon Ihm, and David Tománek, Microscopic Mechanism of Fullerene Fusion, Phys. Rev. B **70**, 113402 (2004).

Defect-assisted fusion of nanotubes

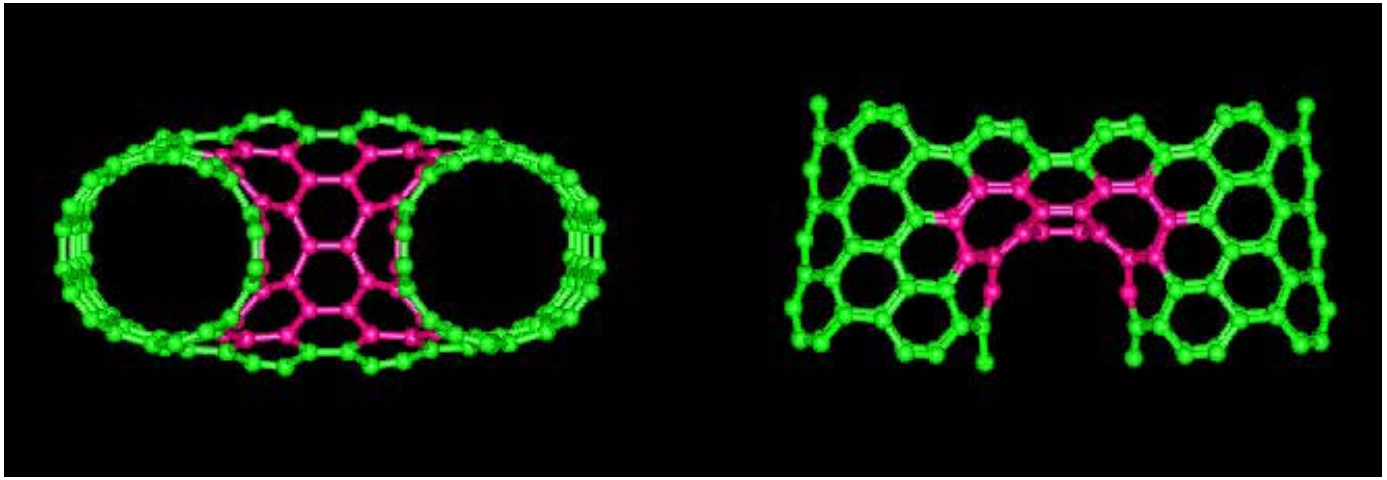
The zipper mechanism

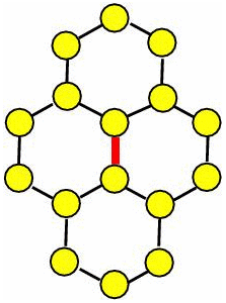


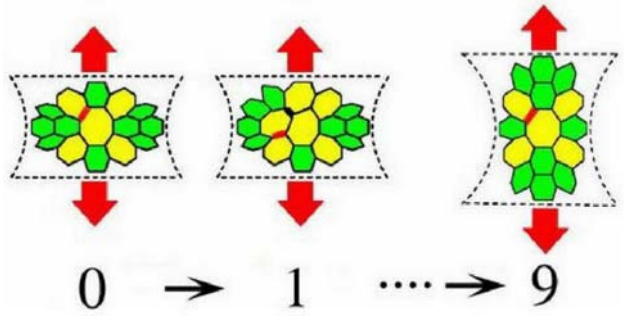
Zipper

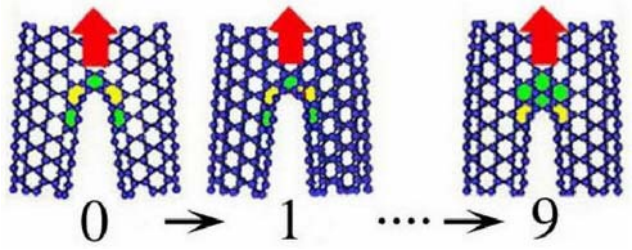
M. Yoon, S. Han,
G. Kim, S. Lee, S. Berber,
E. Osawa,
J. Ihm, M. Terrones,
F. Banhart, J.-C. Charlier,
N. Grobert, H. Terrones,
P. M. Ajayan, D. Tománek,
Phys. Rev. Lett. 92,
075504 (2004).

Minimum energy path for the (5,5)+(5,5)→(10,10) fusion

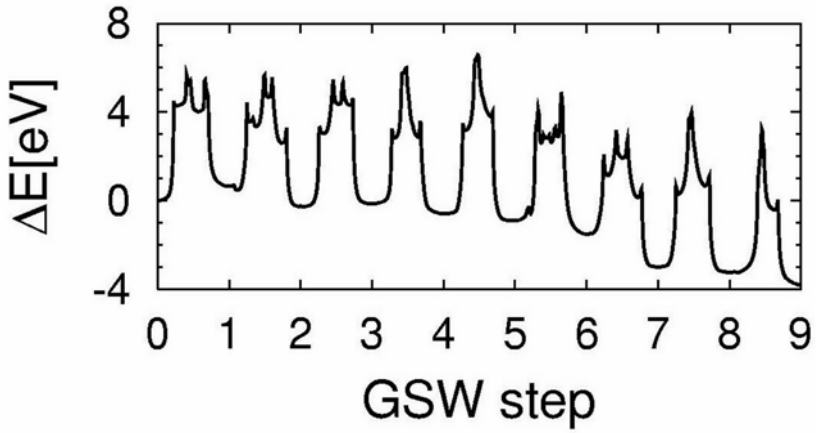








Sequence of Stone-Wales transformations

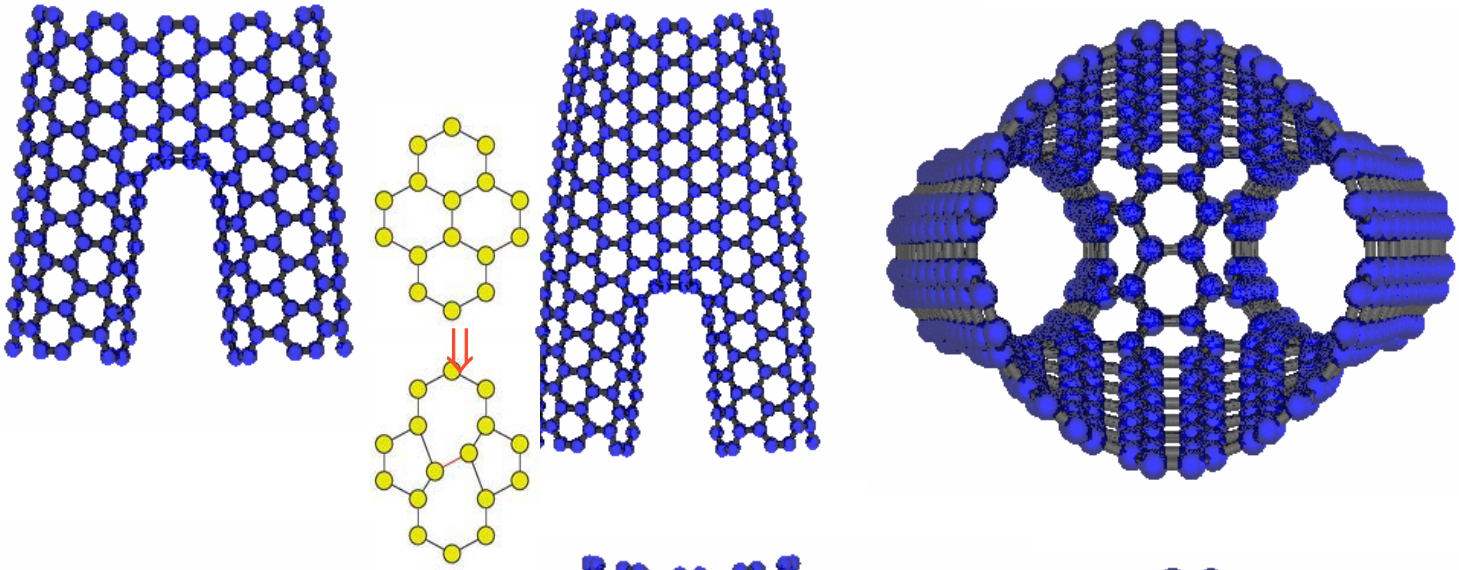


- Fusion is exothermic
- Fusion can be achieved by a sequence of Stone-Wales transformations

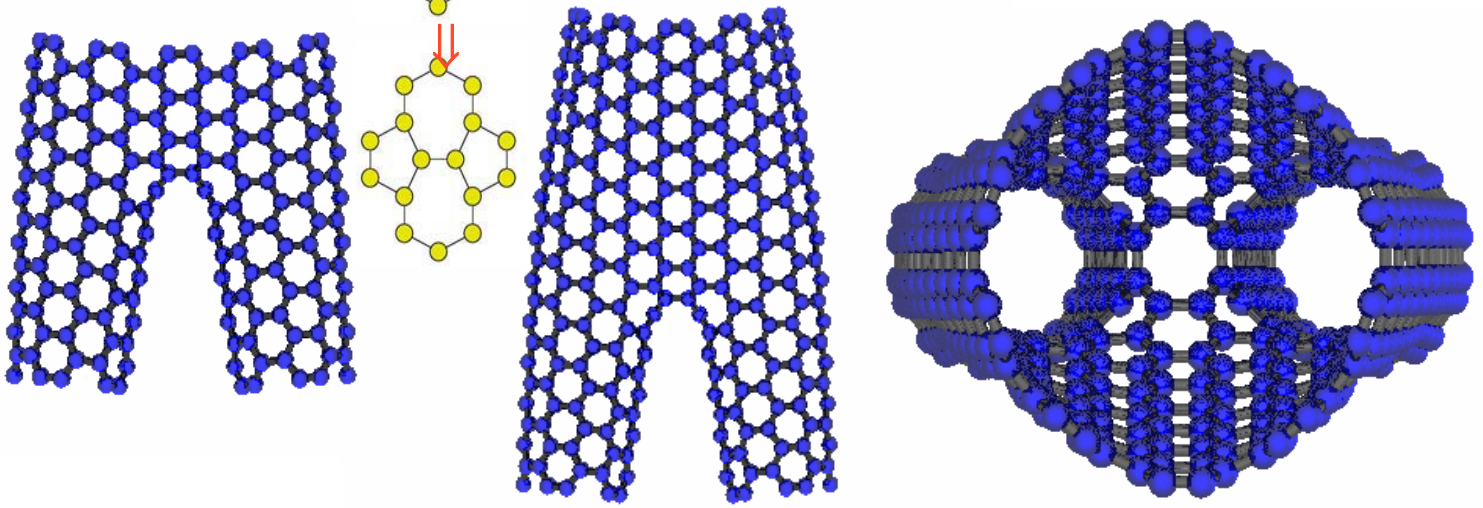
Geometry of fusing nanopants

front view **bottom view**

Type A:
6 heptagons in junction area

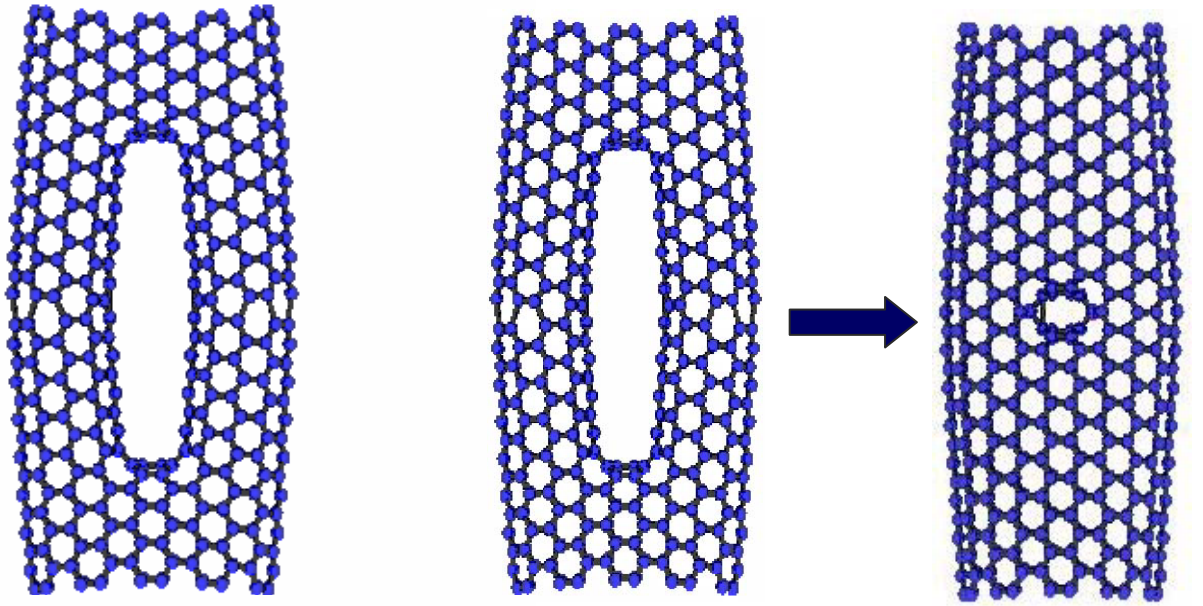


Type B:
1 octagon, 4 heptagons in junction area

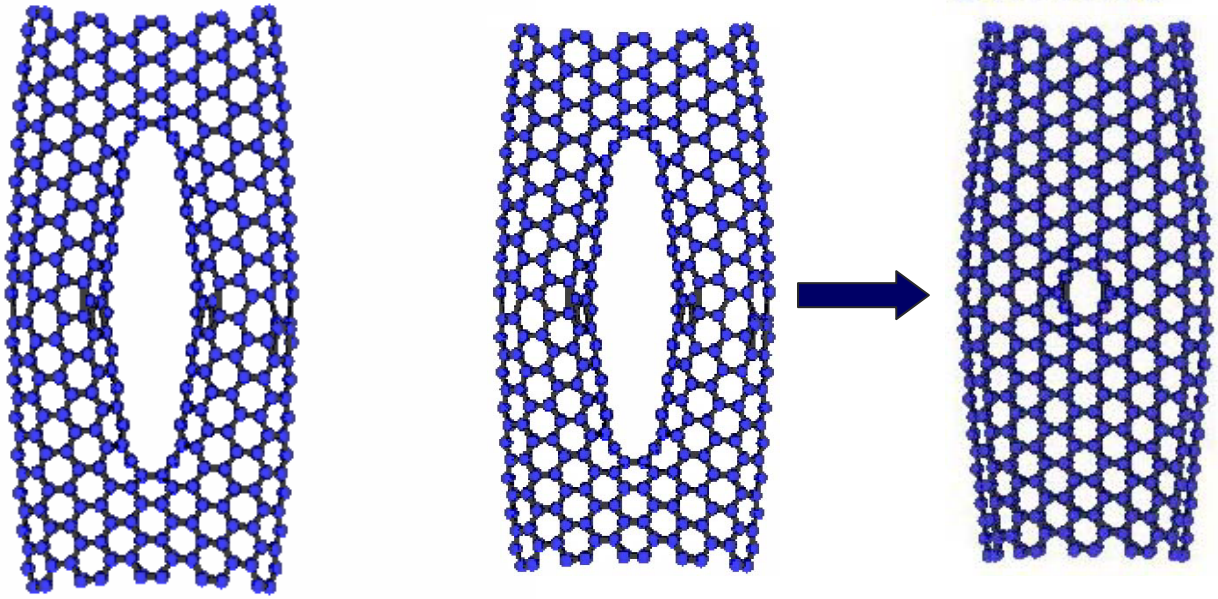


Nanotorus geometry

Type A:
Two hexagons in NP junction area

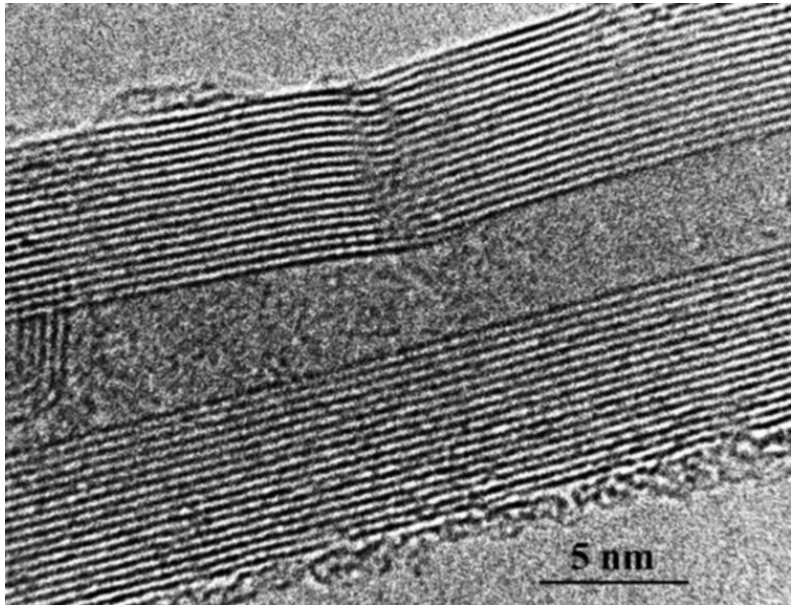


Type B:
One octagon in NP junction area



Defect-assisted scroll-nanotube conversion

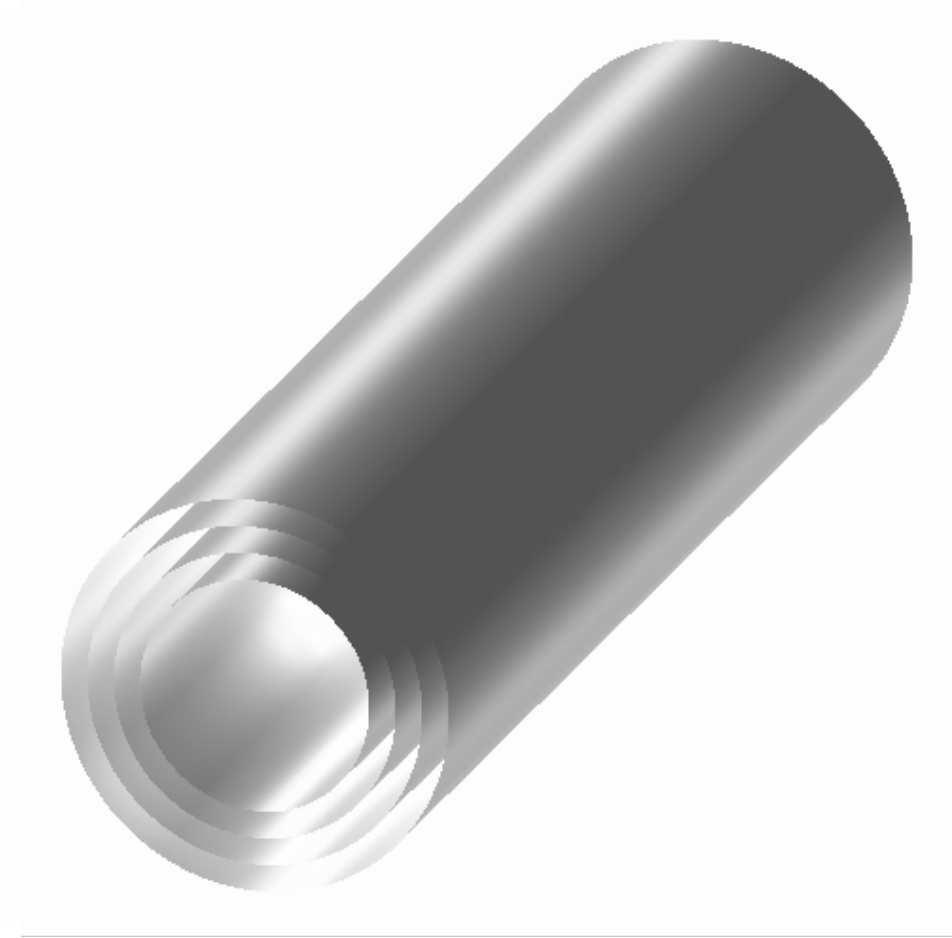
Can scrolls and nested tubes …



HRTEM image

Shekhar Subramoney, Gerry Lavin, Rodney Ruoff, David Tománek, Savas Berber, Carbon 40, 1123 (2002)

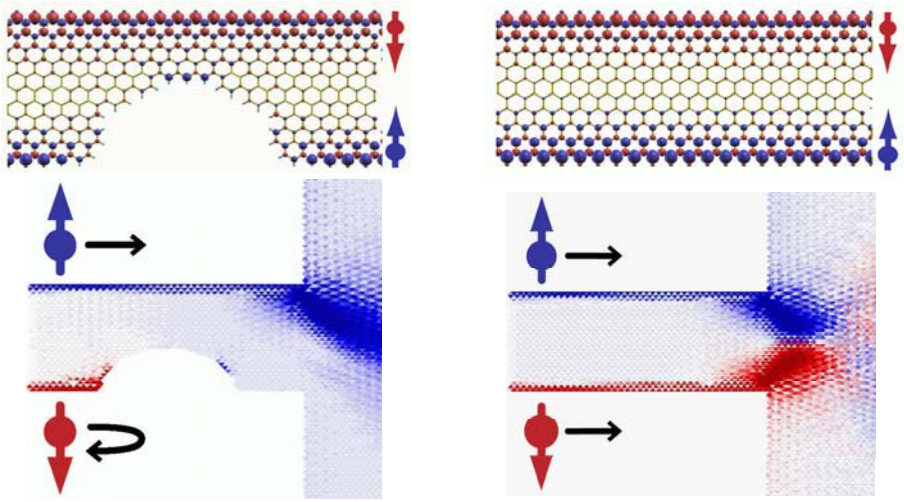
…coexist?



…or transform?

Self-trimming of rough graphene nanoribbons

- How dangerous are edge defects for transport in graphene?



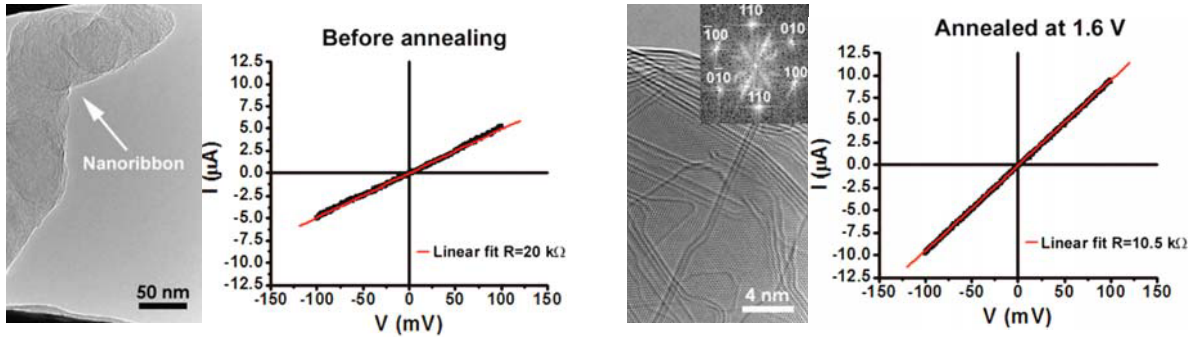
•Edge states dominate transport

•Two-wire model:
Current is confined to edges

•Edge defects suppress current

Michael Wimmer, Inanc Adagideli, Savas Berber, David Tománek, and Klaus Richter, Phys. Rev. Lett. 100, 177207 (2008).

- Can edge defects be removed?



Joule heating
•smoothens edges
•improves conductance

J. Campos-Delgado *et al.*, Nano Lett. 8, 2773 (2008)

- Which is the microscopic mechanism of removing defects?

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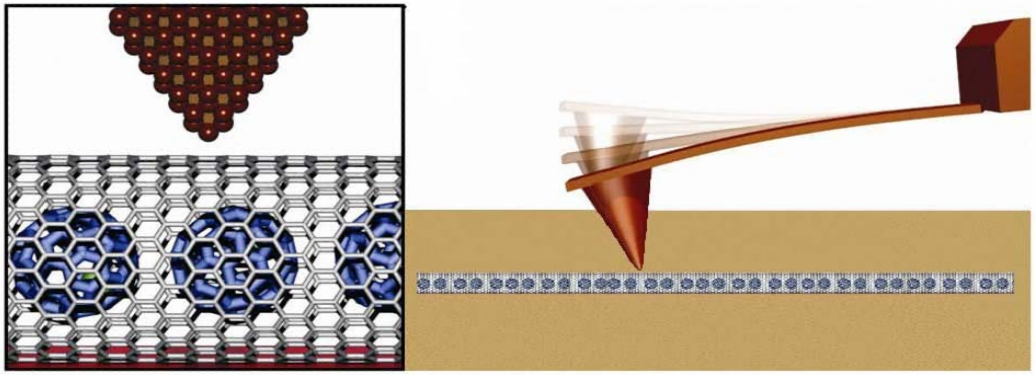
The nano-pecker as a probe of defects

Unique capabilities of a dynamic AFM

A Woodpecker

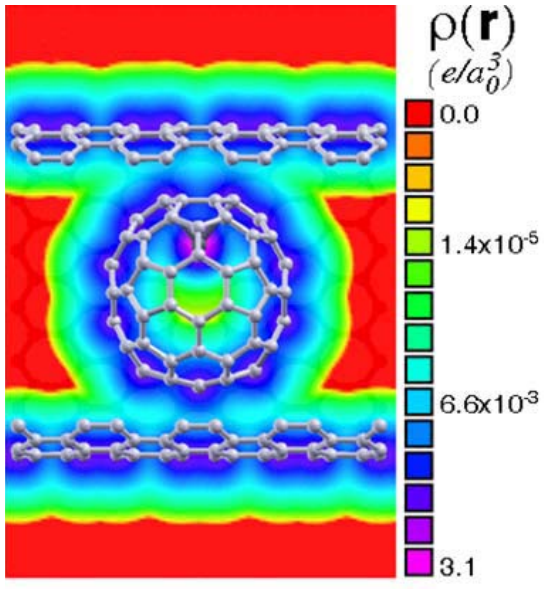
A Noncontact Nano-Pecker (dynamic AFM)



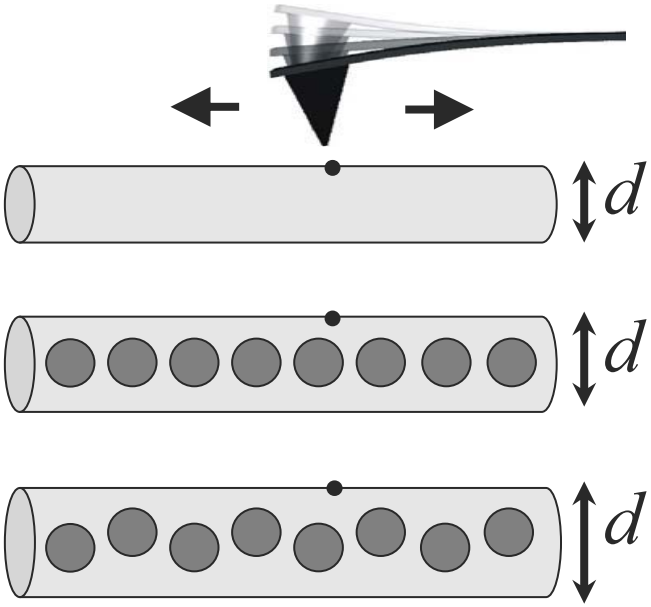
Makoto Ashino, Roland Wiesendanger, Andrei N. Khlobystov, Savas Berber, and David Tománek, Revealing Sub-Surface Vibrational Modes by Atom-Resolved Damping Force Spectroscopy, Phys. Rev. Lett. 102, 195503 (2009).

(Dy@C_{82})$_\infty$@(carbon nanotube): Example of a complex nanostructure

Total charge density



Probing nanotube peapods

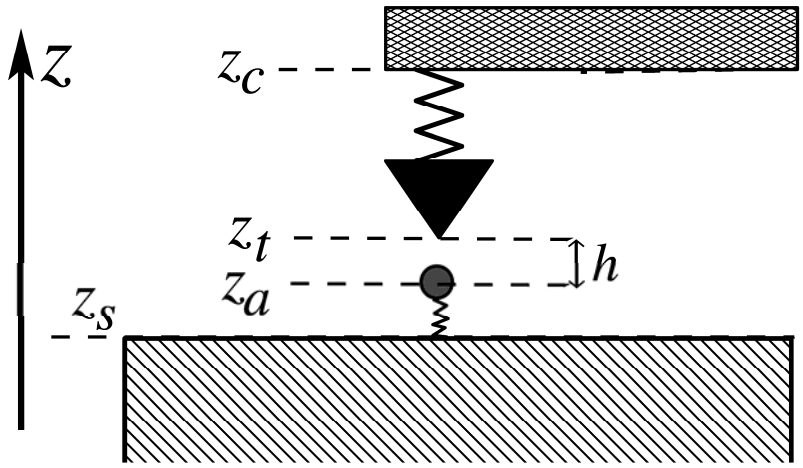


- Empty
- Closely packed
- Loosely packed

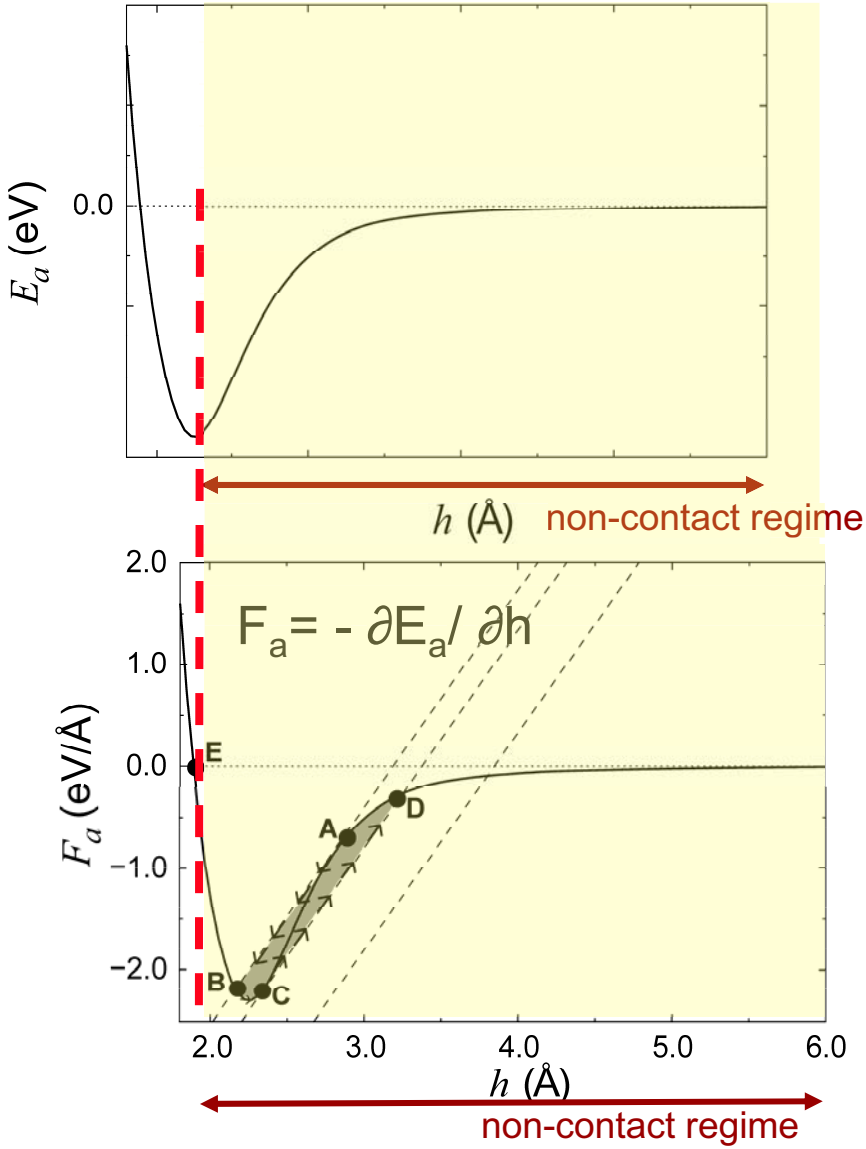
Can we
- obtain atomically resolved topography images?
- get atomically resolved damping signal information?
- distinguish what is inside?

YES WE CAN!

Interaction between an AFM tip and an elastic substrate

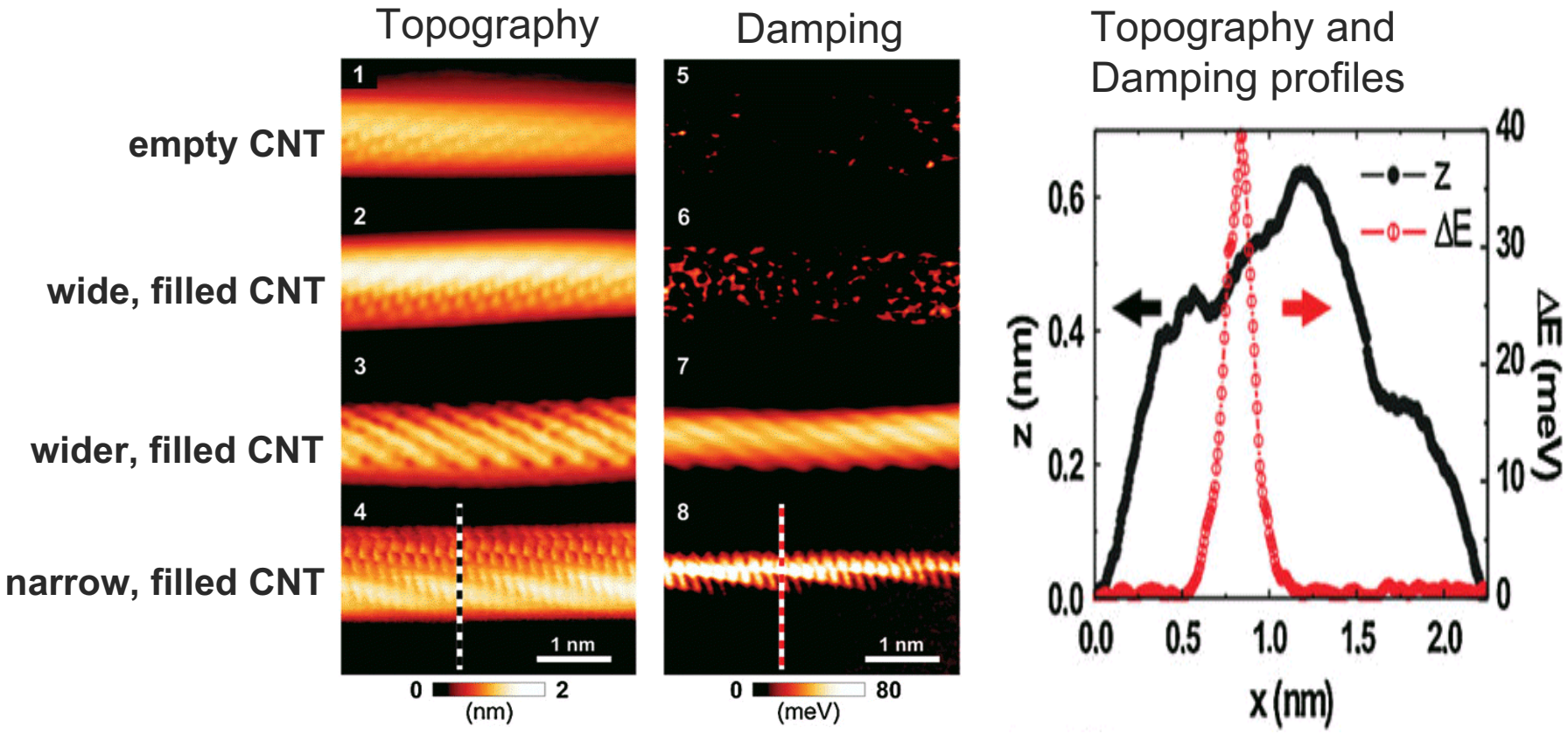


- Hysteresis occurs if cantilever or substrate are soft
- Energy dissipation (“damping”) corresponds to shaded area under the hysteresis curve
- Damping force spectroscopy technique



Probing surface and subsurface morphology and vibrational modes

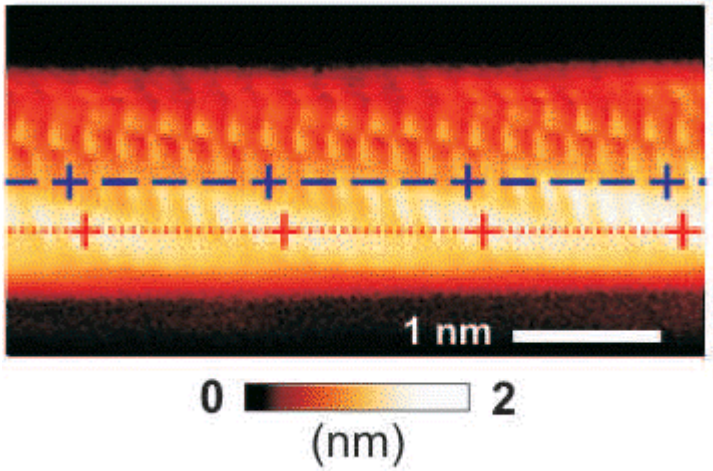
Does topography or damping provide superior information?

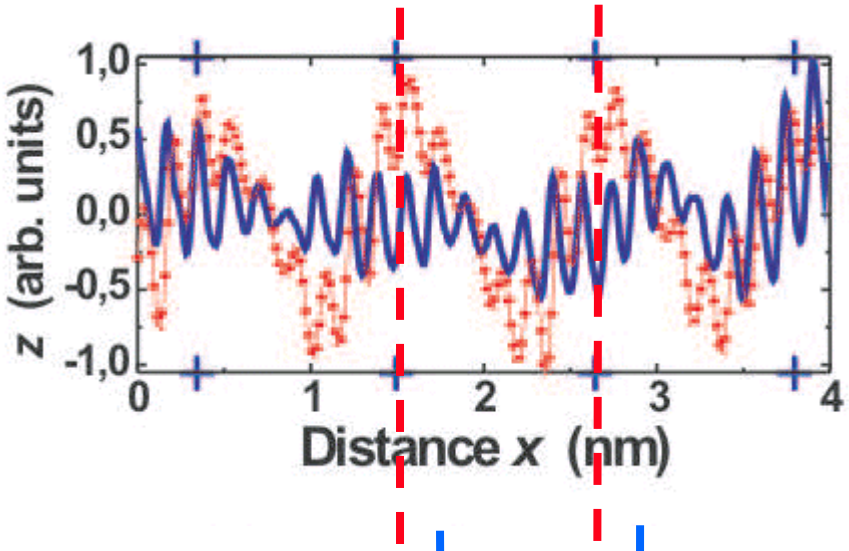


- Topography and damping signals observed simultaneously

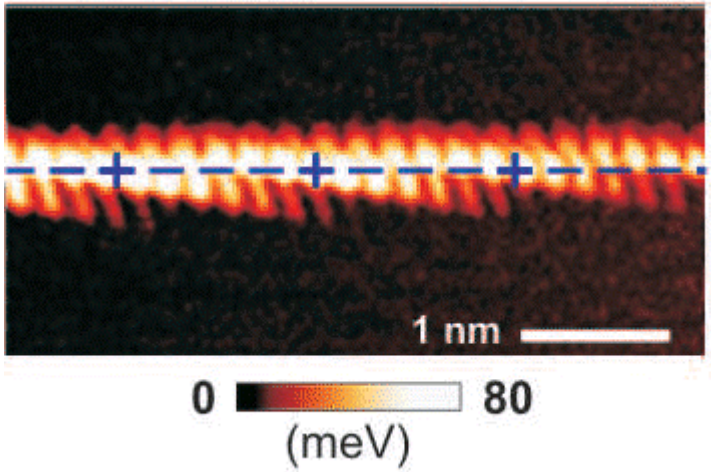
Longitudinal profiles of a densely filled peapod

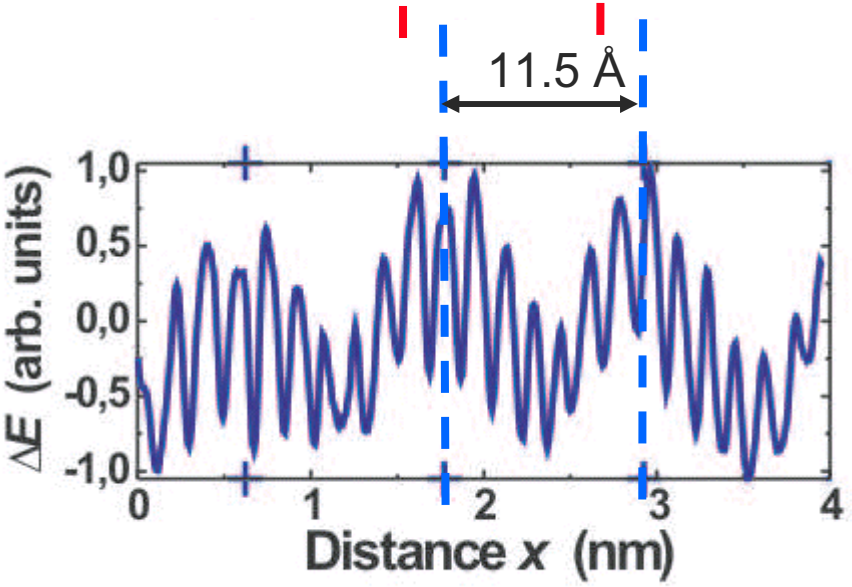
• Topography

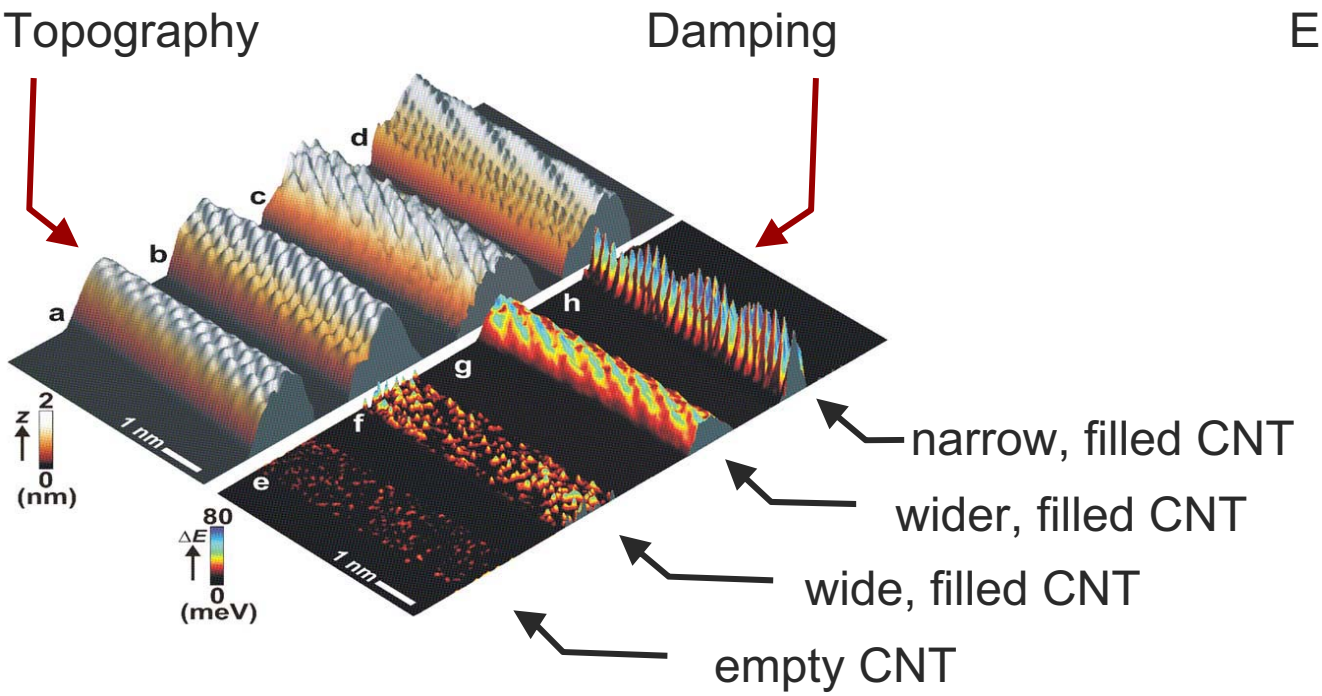




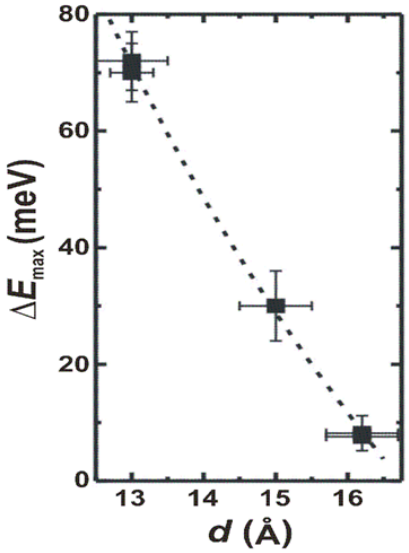
• Damping







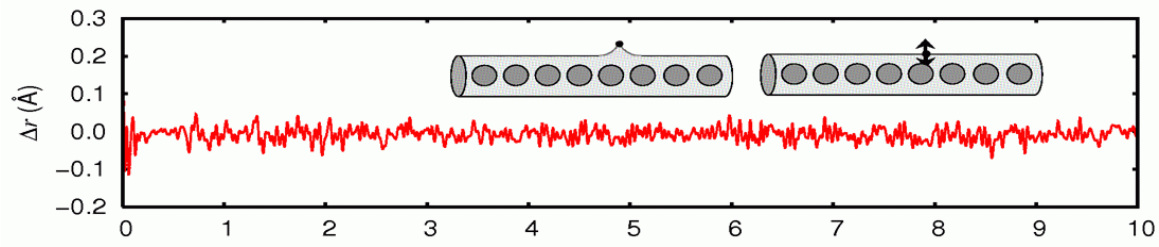
Energy loss per cycle



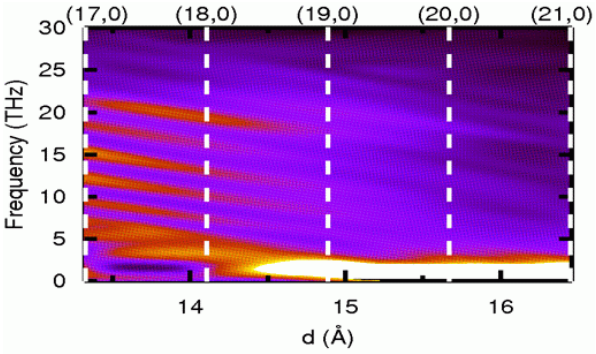
- Non-contact AFM provides atomic resolution superior to the STM
- Damping Force Spectroscopy (DFS) provides similar resolution
- DFS signal is very sensitive to sub-surface morphology and packing
- Damping decreases with increasing nanotube diameter and looser fullerene packing

Molecular dynamics simulations of Damping Force Spectroscopy

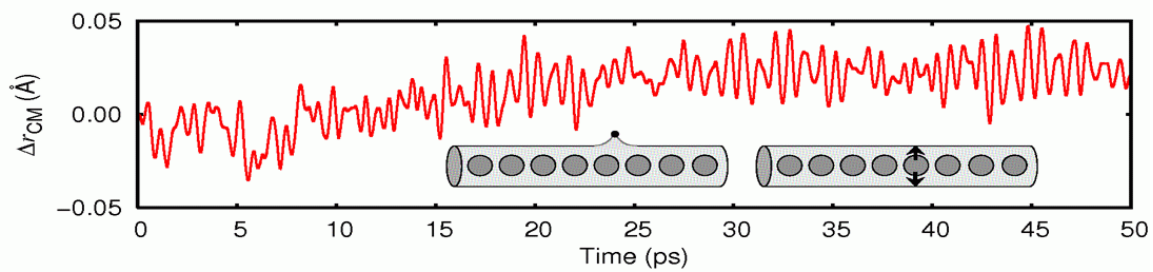
Response of CNT surface atom to radial plucking:



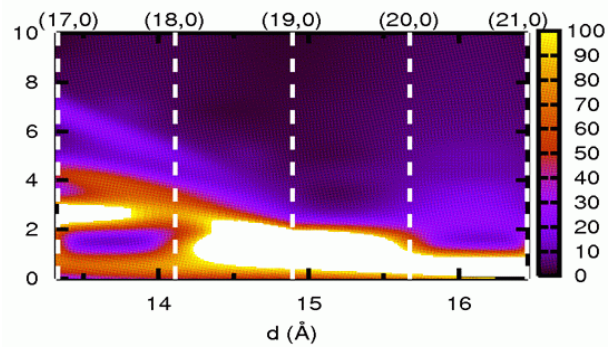
Fourier spectrum:



Response of underlying C_{82} to radial plucking:



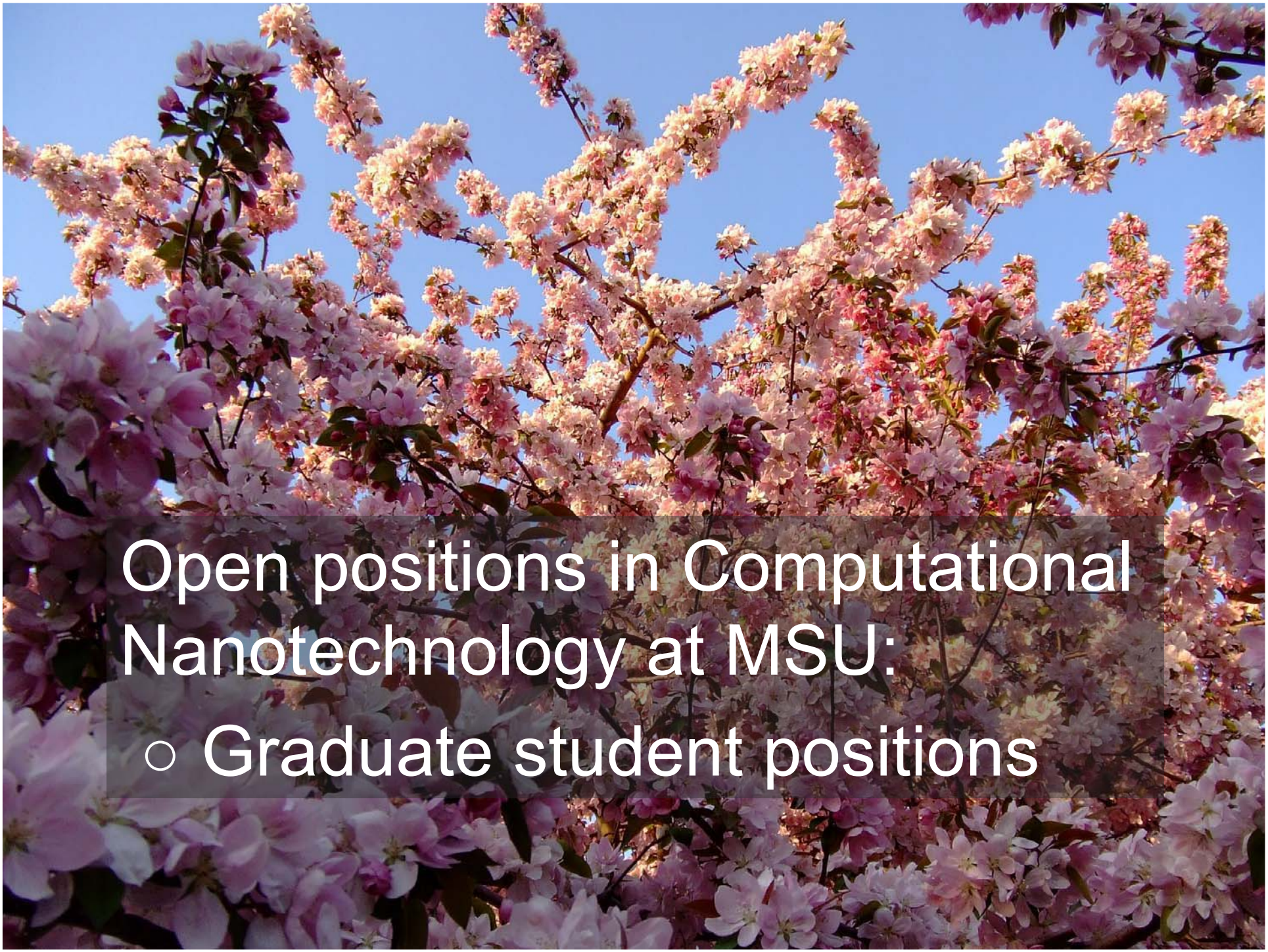
Fourier spectrum:



- Damping is largest when plucking off-center of the underlying fullerene
- Vibration frequencies soften and damping decreases in wide nanotubes

Summary and Conclusions

- Self-assembly of clusters and polymers on surfaces can be understood in terms of the interaction hierarchy, described by a “LEGO” model.
- Designer superlattices of clusters can be formed by tailoring functional groups and utilizing the self-assembly mechanism.
- Defects are useful for structural transformations:
  - Fusion of fullerenes and nanotubes
  - Self-trimming of graphene edges
- Powerful Scanning Probe Microscopy (SPM) techniques are complemented by Damping Force Spectroscopy that probes local surface and sub-surface structure and vibrational modes.


Open positions in Computational Nanotechnology at MSU:
○ Graduate student positions


End
of
Lecture 1