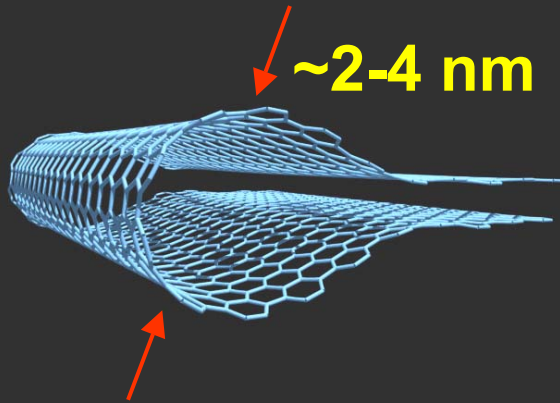
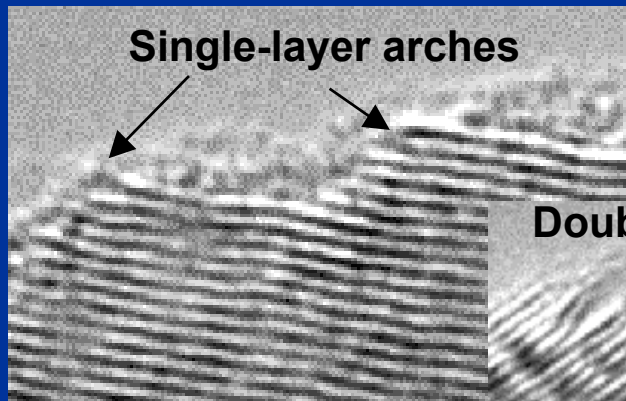
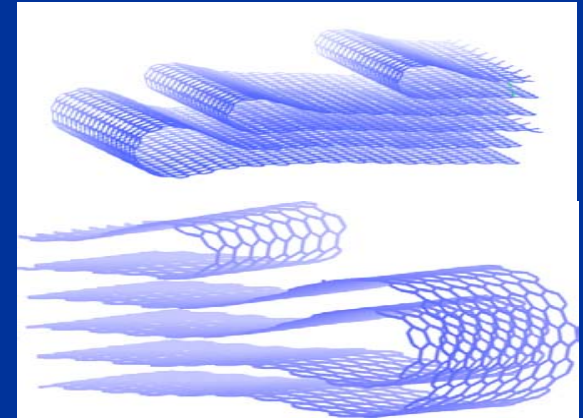


Methods of Continual Modeling for Graphitic Systems: Scrolling at Nanoscale

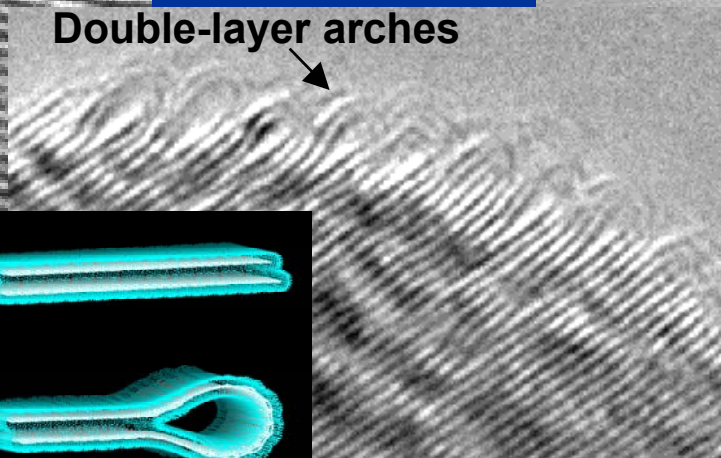
Scrolling at the Nanoscale



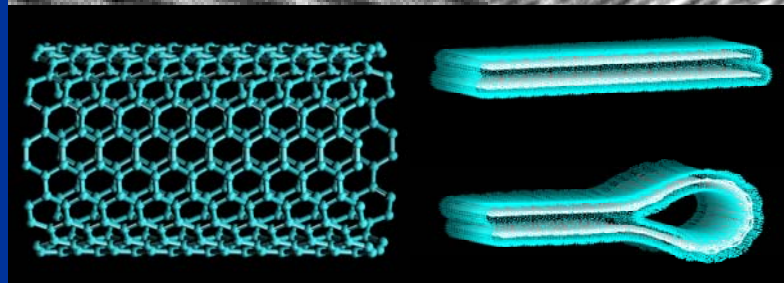
Material properties of the layered lattice of the graphite define an internal nanoscale at which a process of the scrolling happens.

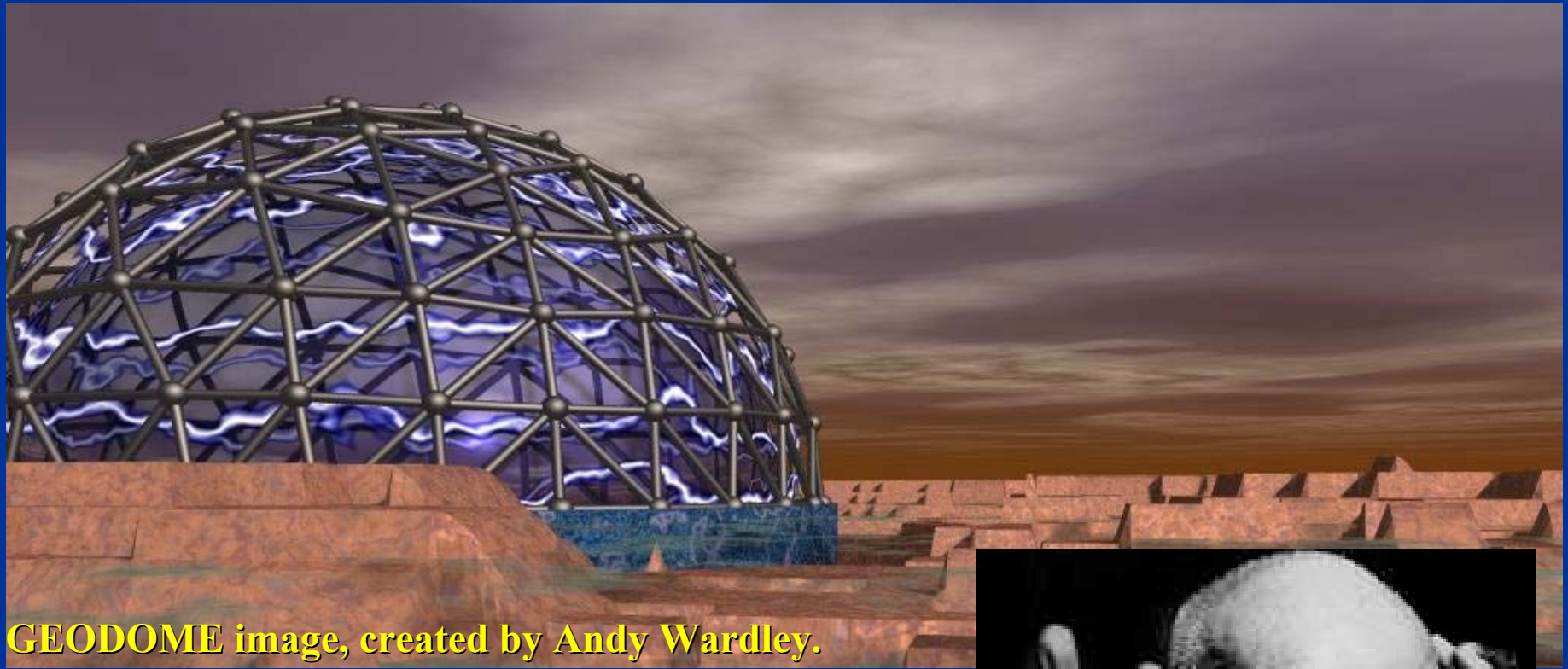


TEM images by Y.Gogotsi

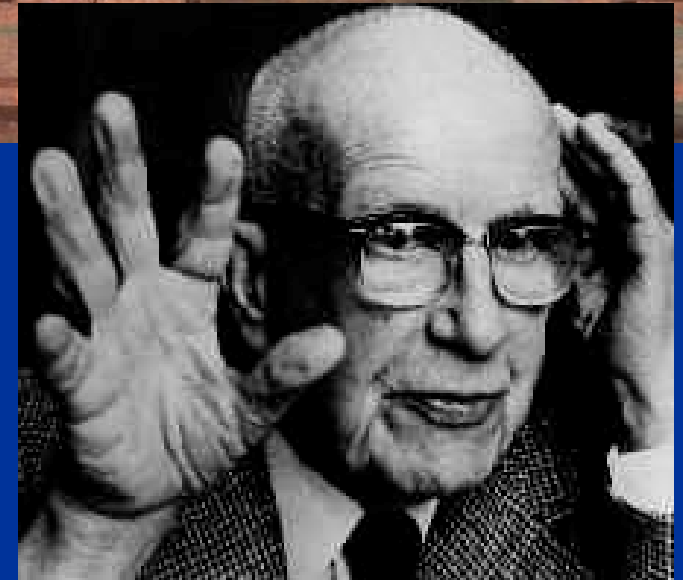


~.34 nm

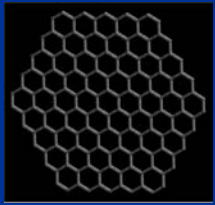




GEODOME image, created by Andy Wardley.

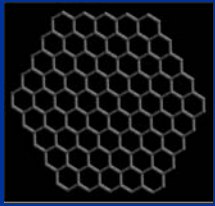


R. Buckminster Fuller
1895 - 1983



Why scrolling

- **Formation of different carbon shell clusters (including nanotubes, nanohorns and fullerenes) has common features: deformations of the planar graphite sheets**
- **The graphite transformations (scrolling) induced by some external influence (mechanical - AFM, chemical - etching, complex - ion bombardment) are also known to produce nanosize objects with a curvature**

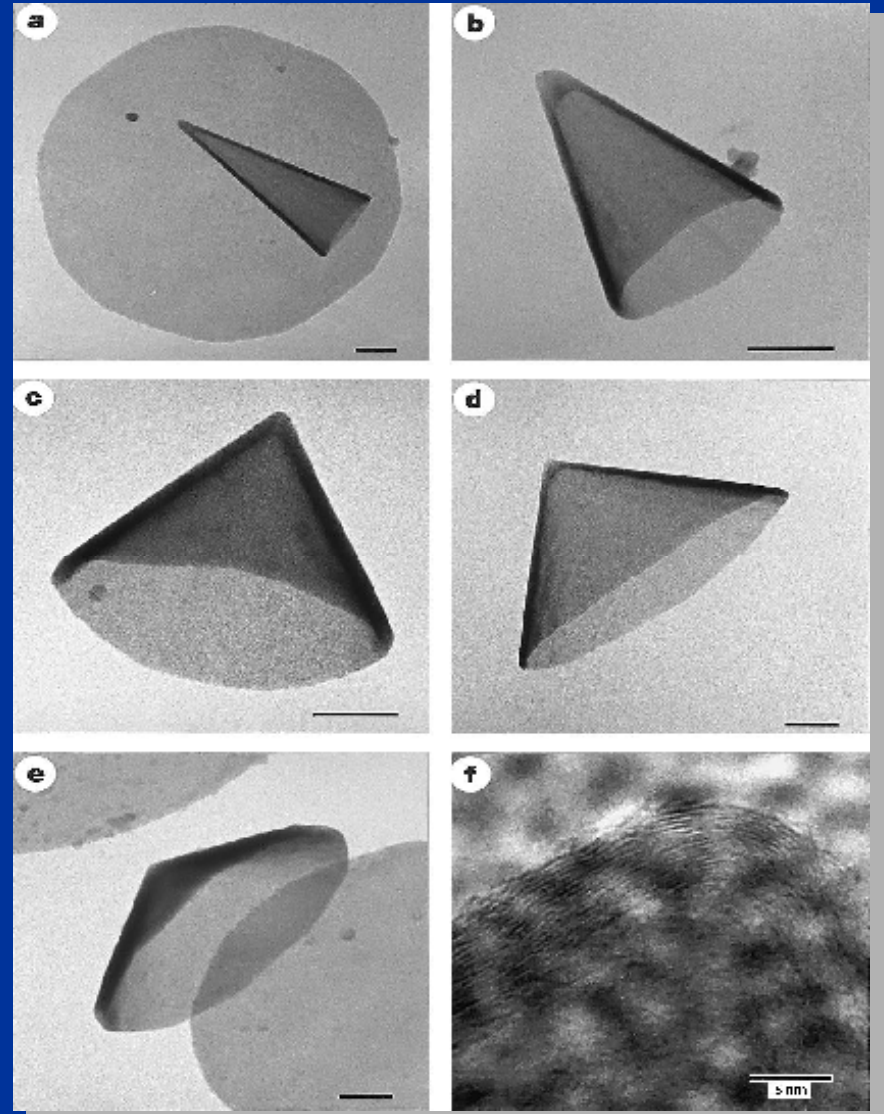


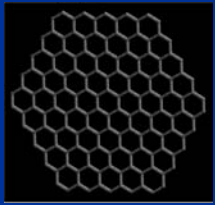
Experimental

SEM images of graphite cone formation

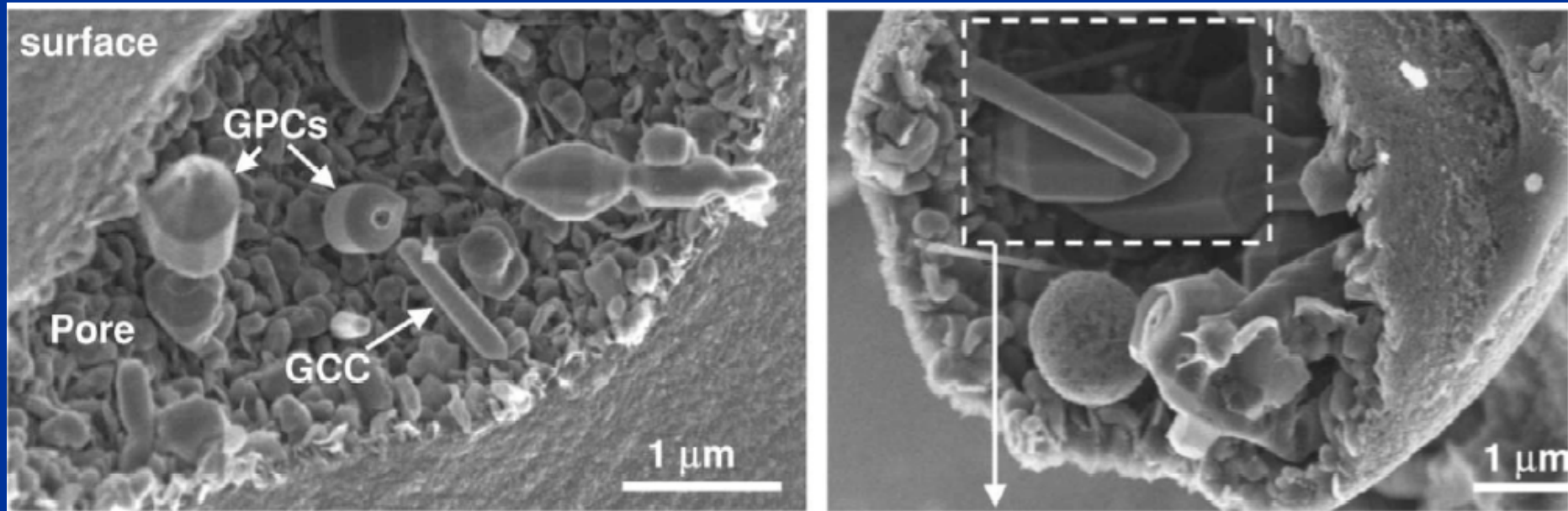
T. W. Ebbesen, Nature

The cones of different shape correspond to structures with different number of pentagons



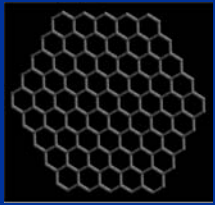


Experimental



SEM images show wide variety of graphite geometries

S. Dimovski et.al., Carbon

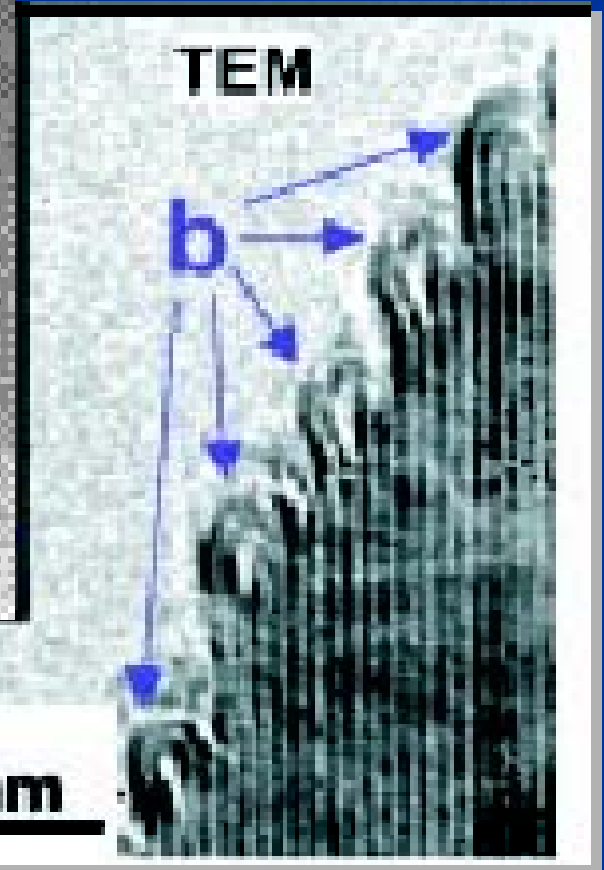


Experimental

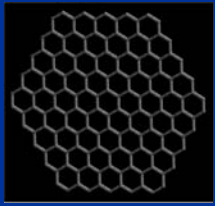
Natural scrolling at the graphite edge



W.K.Hsu et.al., Appl.Phys.A

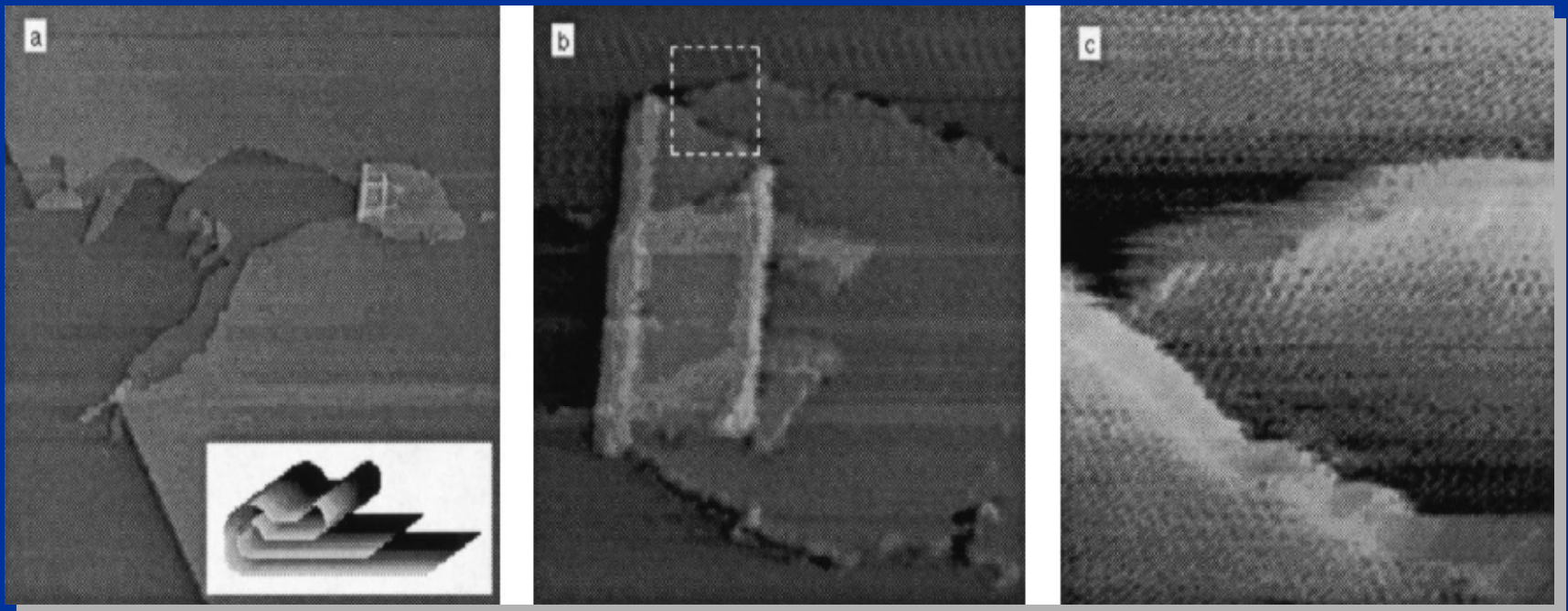


Yu.Gogotsi, Science

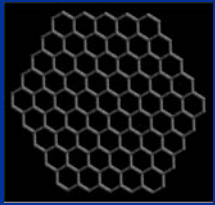


Experimental

AFM and STM manipulation results in graphene scrolling

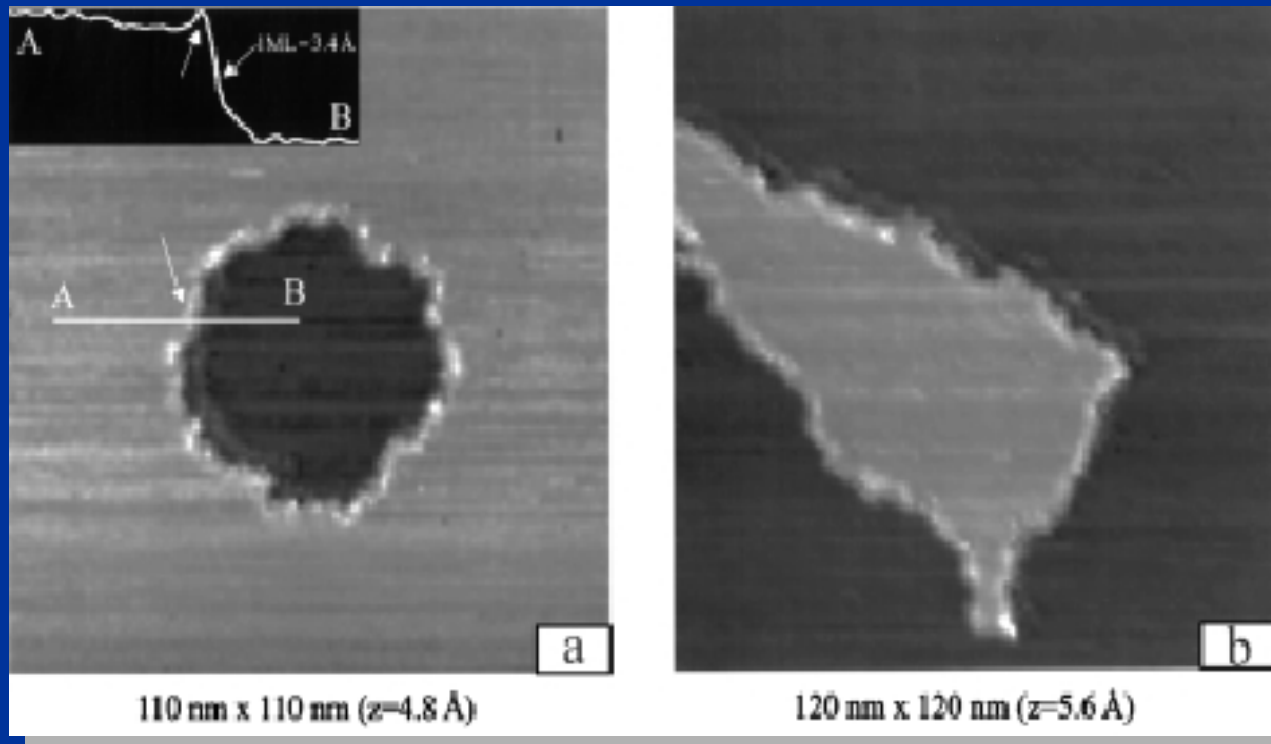


K.Sattler, Surf.Sci.

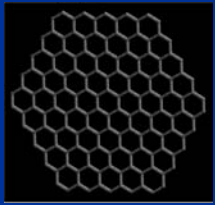


Experimental

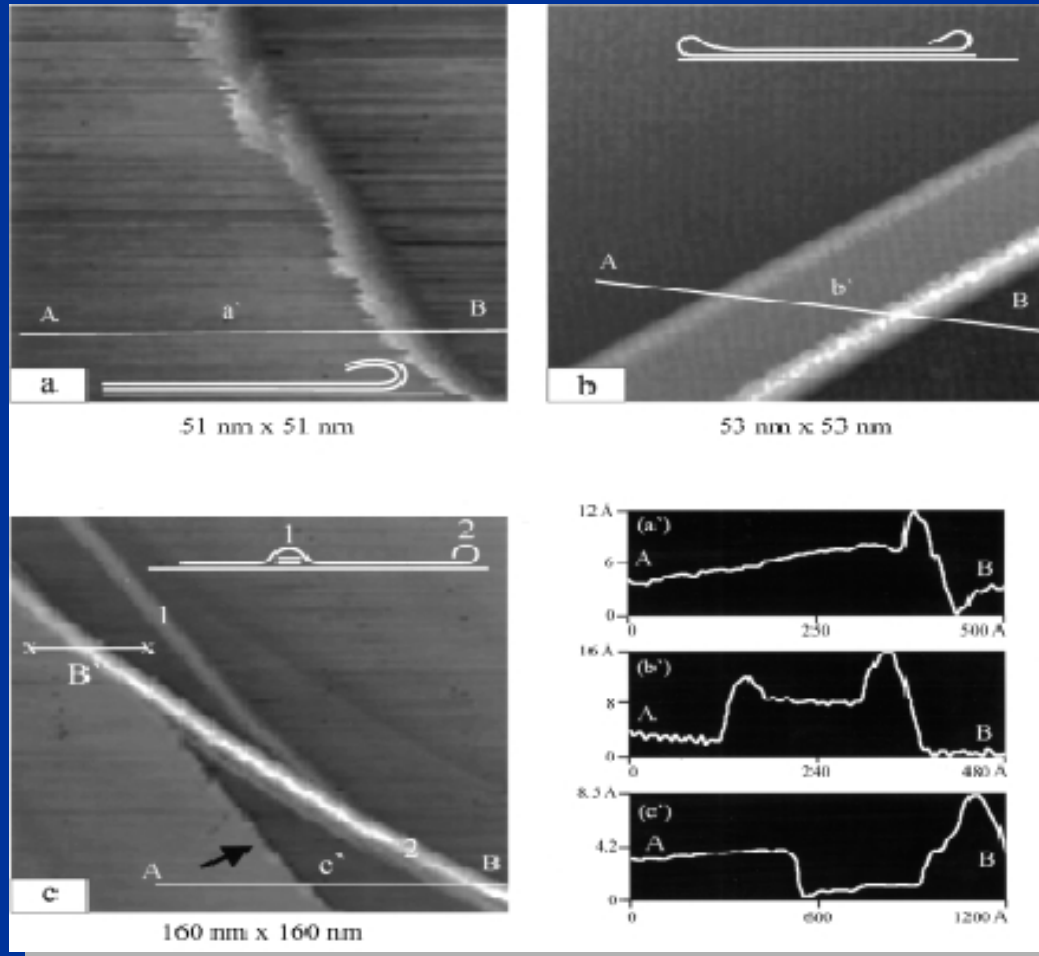
Scrolled structures are formed at an edge of etched pits



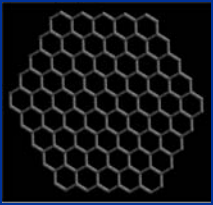
R. Schlögl et.al., Appl.Phys.A



Experimental

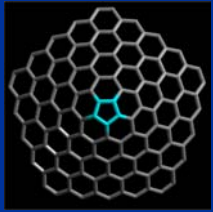


R. Schlögl et.al., Appl.Phys.A



Why scrolling (continued)

- Formation of different carbon shell clusters (including nanotubes, nanohorns and fullerenes) has common features: deformations of the planar graphite sheets
- The graphite transformations (scrolling) induced by some external influence (mechanical - AFM, chemical - etching, complex - ion bombardment) are also known to produce nanosize objects with a curvature
- **Knowledge about the Continuum Energetics of formation of the clusters with the low curvature sheds light on the nucleation of larger ones**
- **Starting with the optimized geometry of a cluster, we may go for electronic properties of the system**



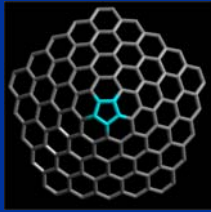
Bases of the model

1. Continuum Energetics of carbon shell formation

- Formation energy can be decomposed into (nearly) independent terms

$$E = \frac{N_{\text{curv}}}{K(R_1, R_2)} E_c + N_5 E_5 + N_b(\mathcal{P}) E_b + N_{\text{neighb}} W(\mathcal{D})$$

- The vdW interaction will be considered later
- Assume clusters to have one shell (the generalization of the model to multishell cluster is straightforward)
- Shells of high symmetry were computed analytically



Bases of the model

- Parameters of the continuum model are well known from atomistic simulation

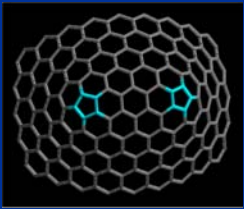
elastic curvature energy $E_c \sim 1.8 \text{ eV } \text{Å}^2$

disclination core (pentagon) energy $E_5 \sim 1.5 \text{ eV}$

dangling bond (surface) energy $E_b \sim 2.4 \text{ eV}$

$$E = \frac{N_{\text{curv}}}{K(R_1, R_2)} E_c + N_5 E_5 + N_b(\mathcal{P}) E_b$$

- The interplay between these terms controls the equilibrium shape of the cluster
- The graphite parameters are that the last term is the most important term (in general)

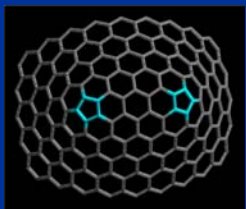


Continuum theory results

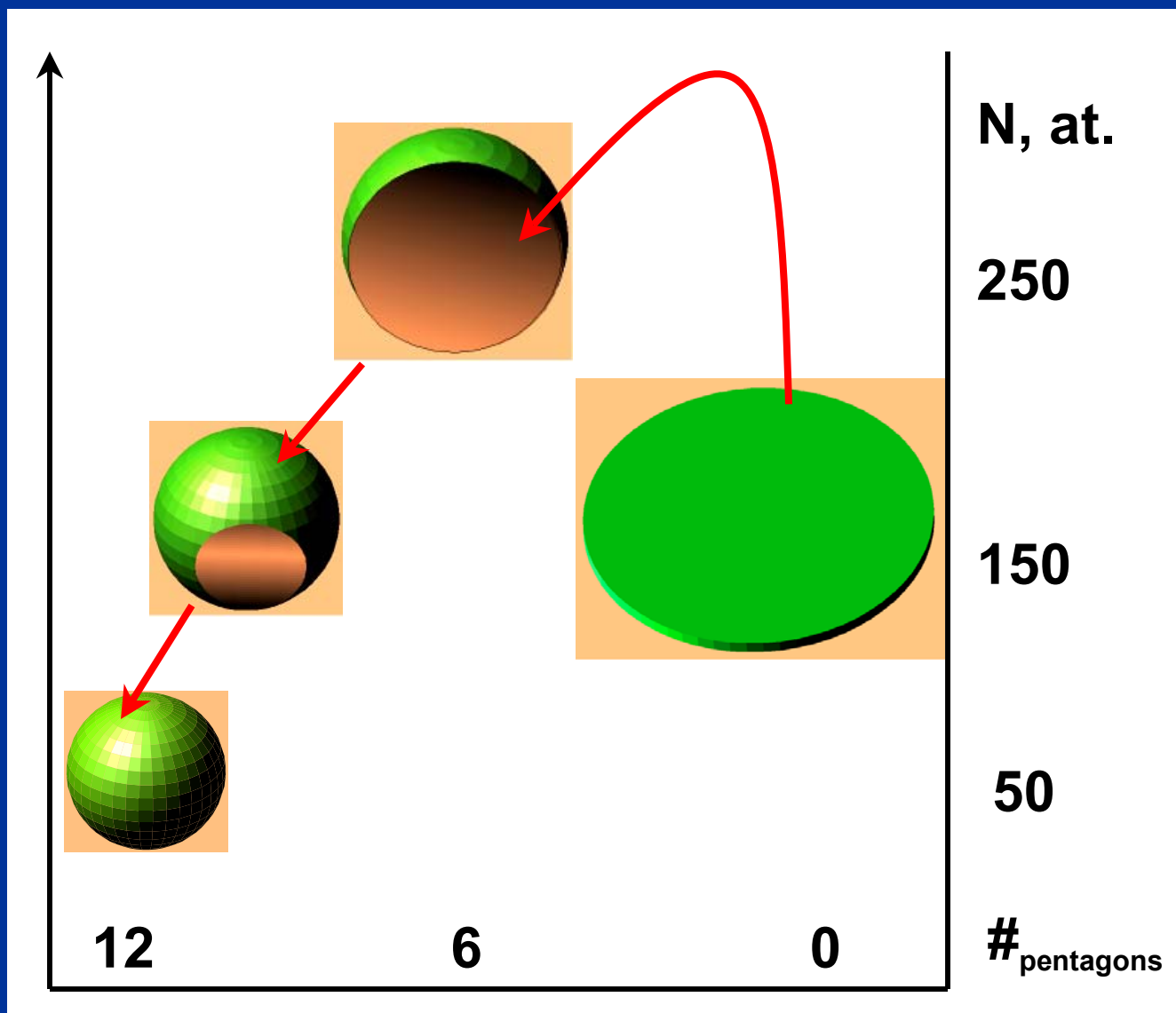
- The curvature radius of the cluster tends to increase (it helps to minimize the elastic energy term)
- The perimeter minimization (surface tension) is the reason for the cluster scrolling

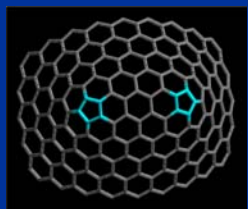
$$E = \frac{N_{\text{curv}}}{K(R_1, R_2)} E_c + N_5 E_5 + N_b(\mathcal{P}) E_b$$

- The prevalent cluster has the minimum (zero) perimeter and the minimal curvature shape (spherical)
- Starting from a planar flake the cluster scrolls up and picks up the proper number of pentagons



Phase diagram of scrolling

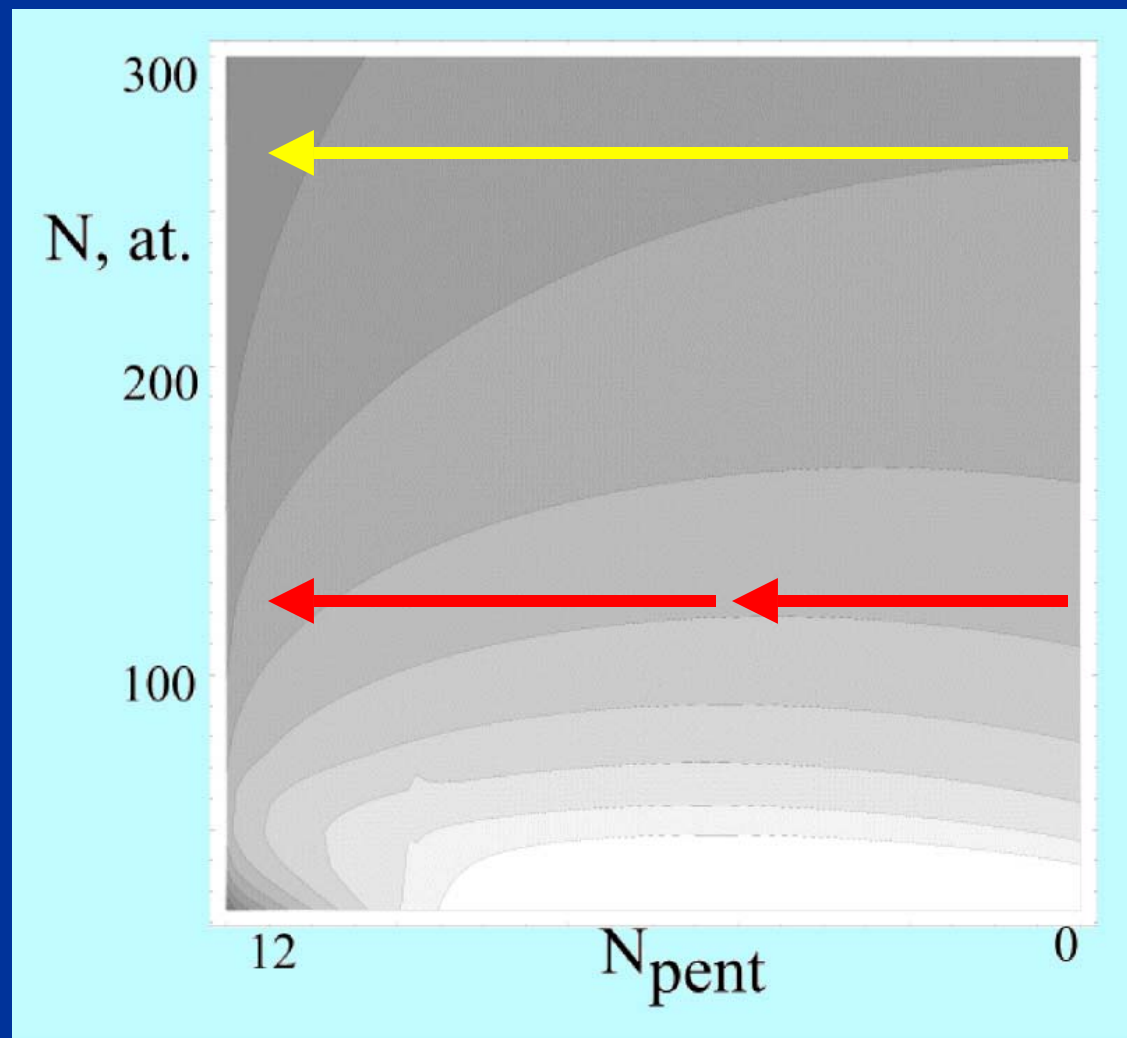


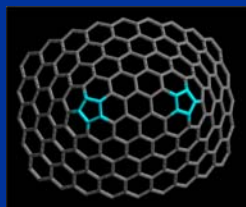


Continuum theory results

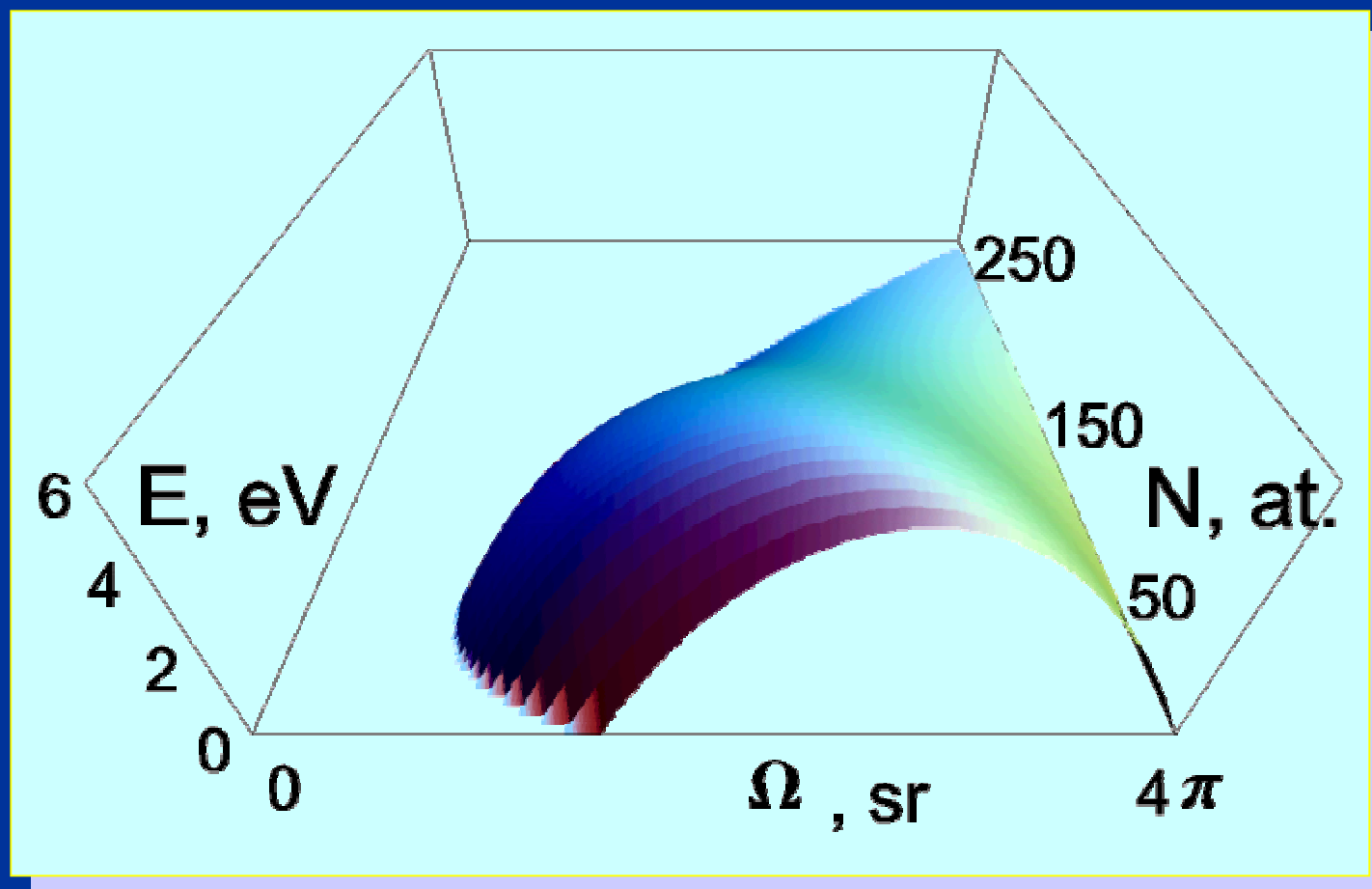
The energy landscape of the scrolling

The darker the color the lower the cluster energy. The scrolling is energetically favored: N_{pent} grows along the gradient lines of the energy landscape.

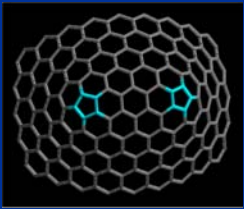




Continuum theory results



- The barrier to the cluster scrolling as the function of the number of atoms and the open solid angle

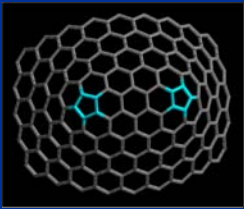


Atomistic Verification

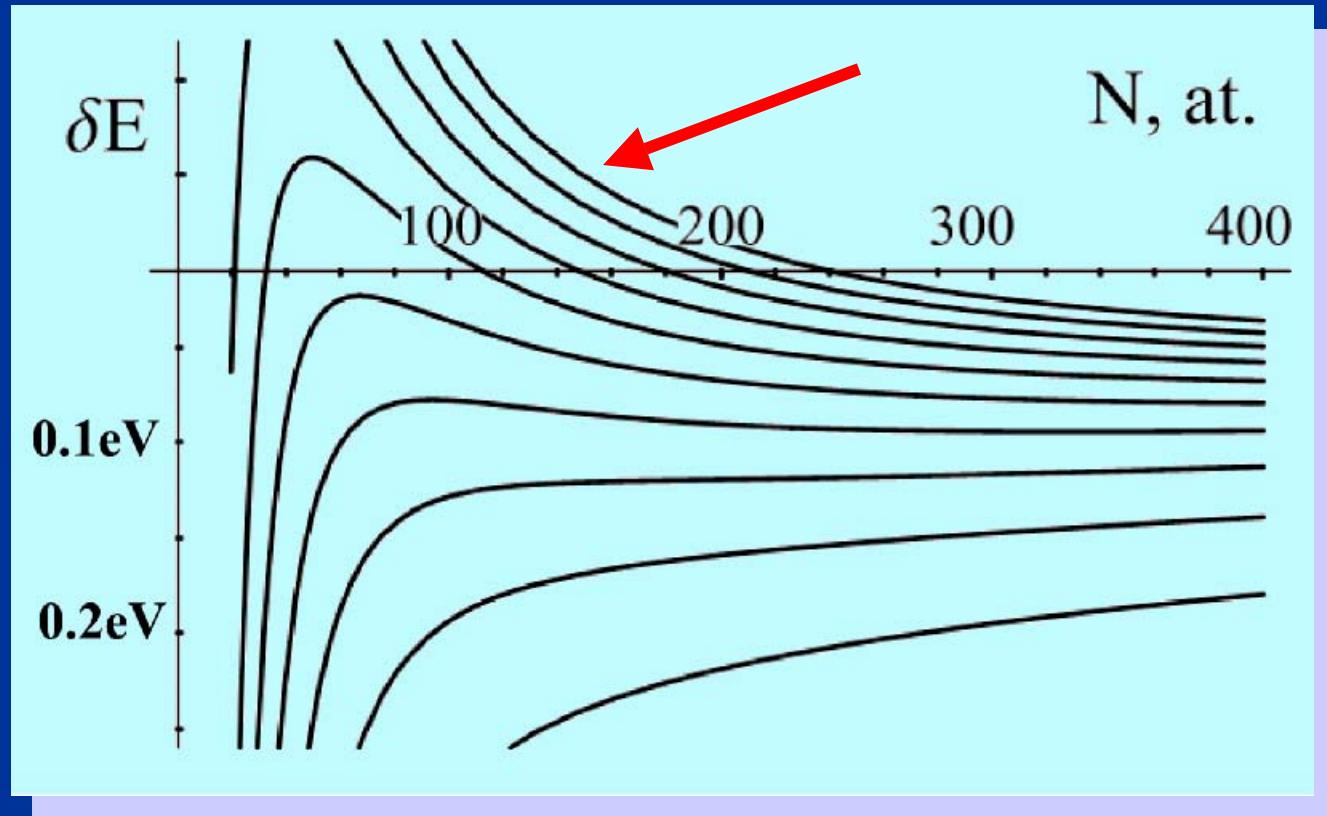
- The Gauss-Bonnet theorem states that for the cluster of given Gaussian curvature the number of defects appear

$$\sum_n f_n (6 - n) = \frac{12}{4\pi} \oint dSG$$

- Although, the defect number is a discrete variable, we treated it as a continuous parameter within shell approximation:
 - the correction to this will be given within continuum model
 - as well as within atomistic simulation

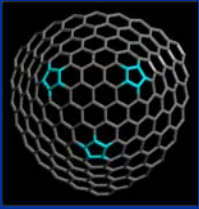


Continuum theory results



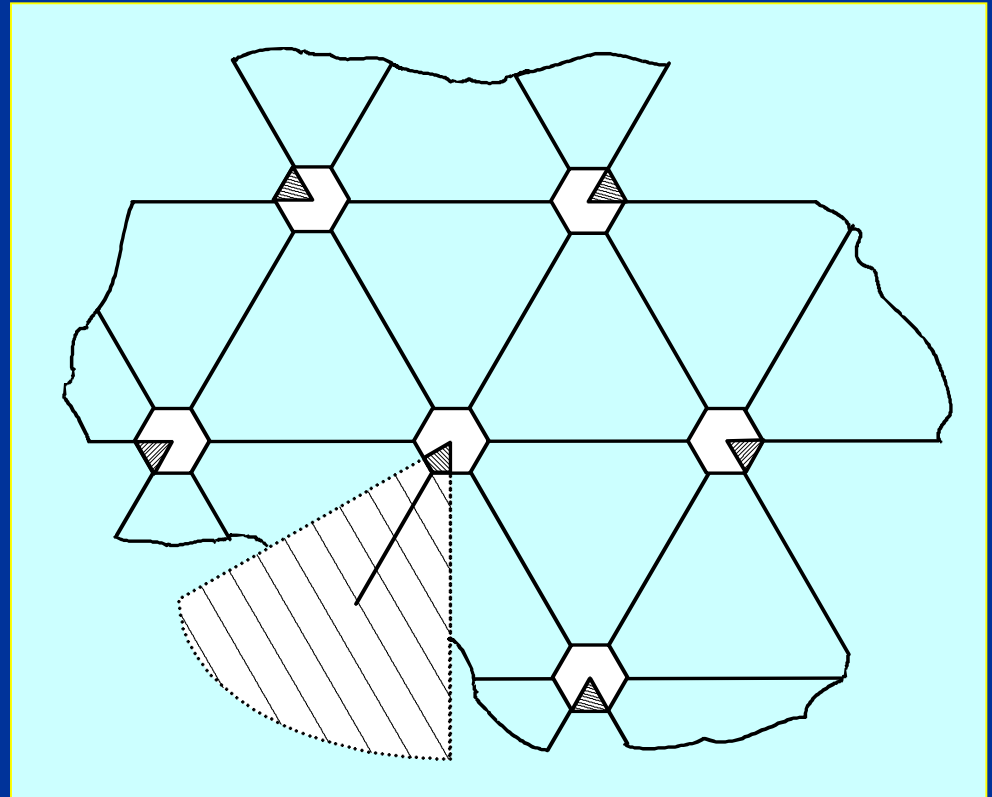
The specific energy difference between states with P and $P+1$ pentagons for $P=0..9$

The $P < 5$ curves go above energy zero that corresponds to the barrier for creation of next pentagon at $N < 250$

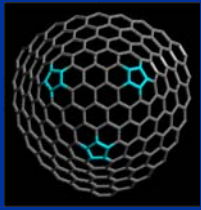


Atomistic Defect Modeling

- We need to check the result with the direct simulation, therefore some structure of the cluster has to be supposed:
 - what are the pentagon positions?

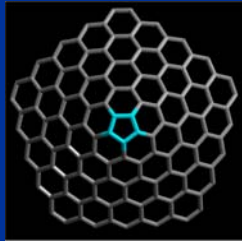


The spheroid has a number of disclinations (pentagons) each of those is a triangular cut from graphene plane

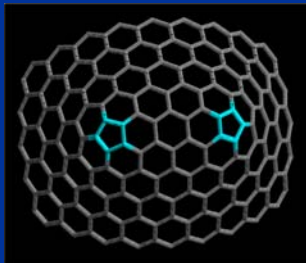


Atomistic Defect Modeling

The single pentagon structure is definitely the cone with the pentagon in the apex.

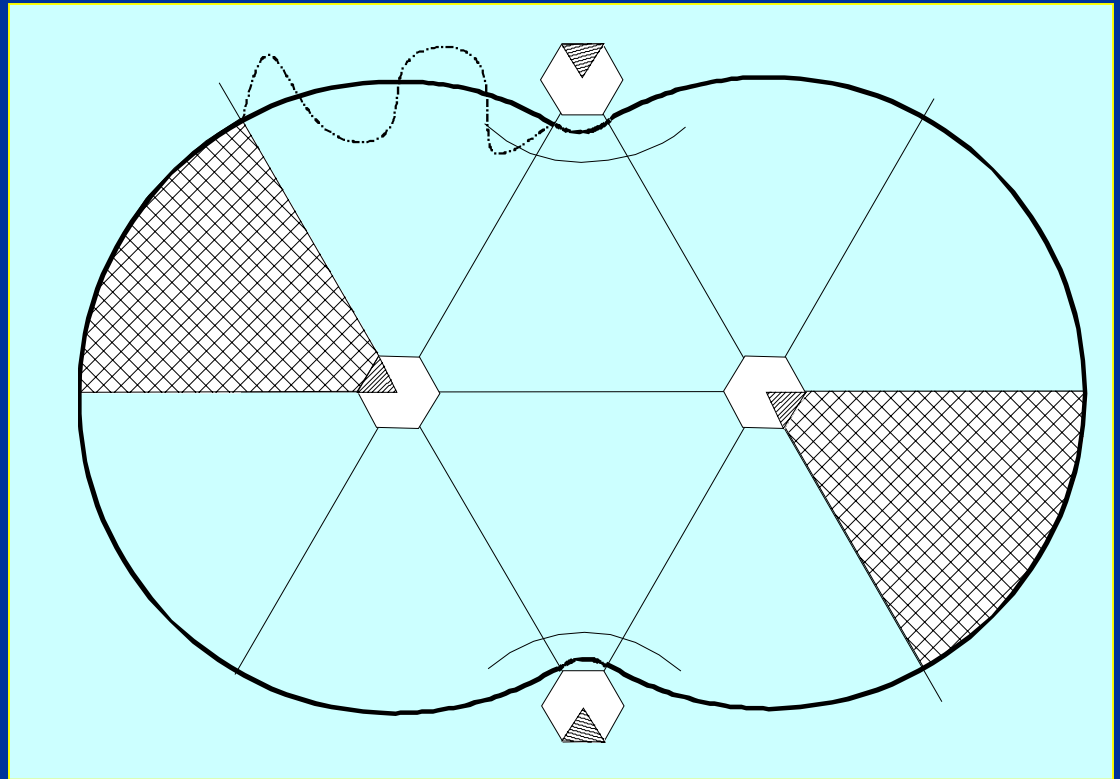


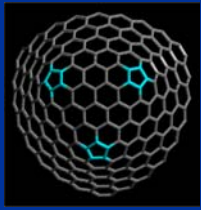
- What about 2PRs?



The optimum shape is a dumb-bell:

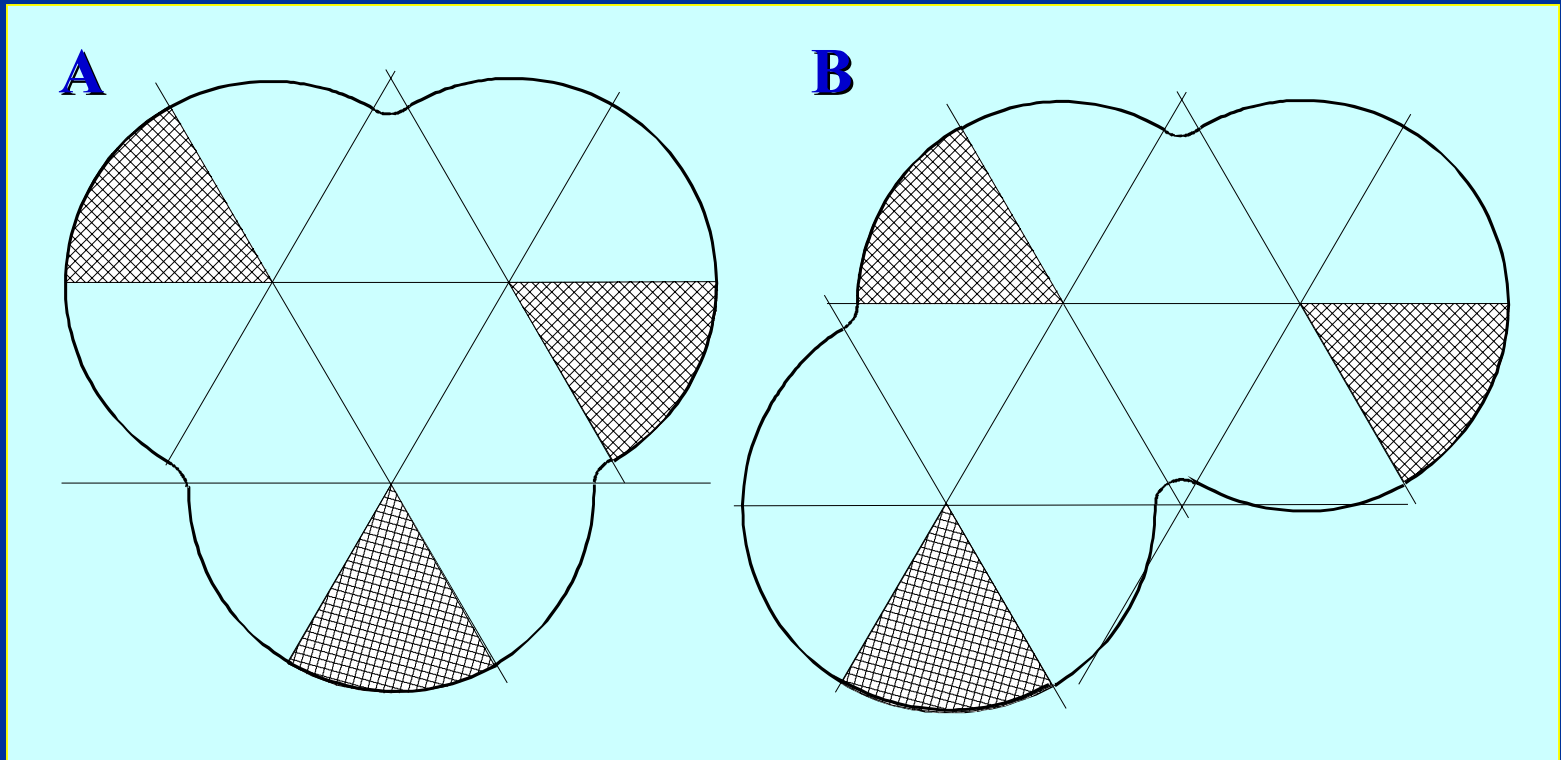
its high symmetry allows to minimize the curvature and the perimeter simultaneously (variational solution)



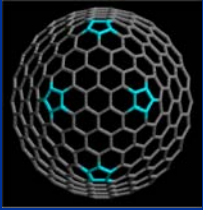


Atomistic Defect Modeling

Three pentagon structures

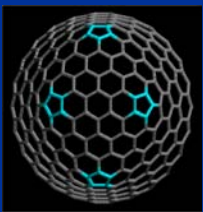


The minimization of perimeter and curvature shows that trefoil (A) structure is preferable versus (B) zigzag structure

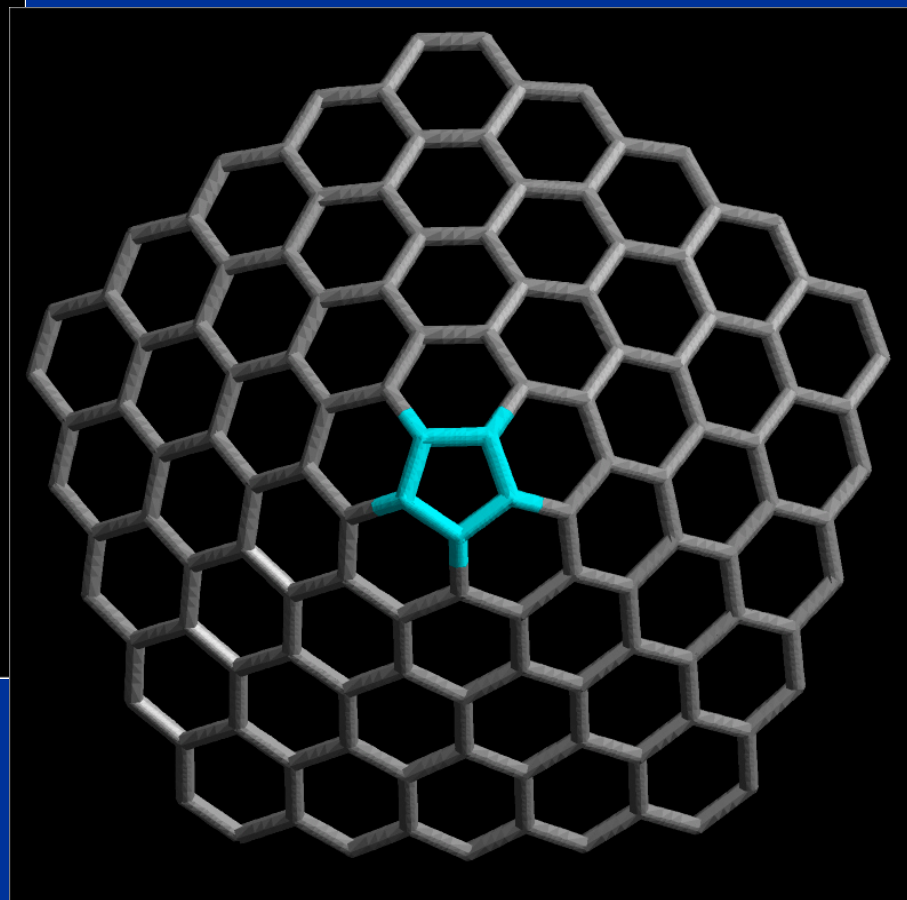
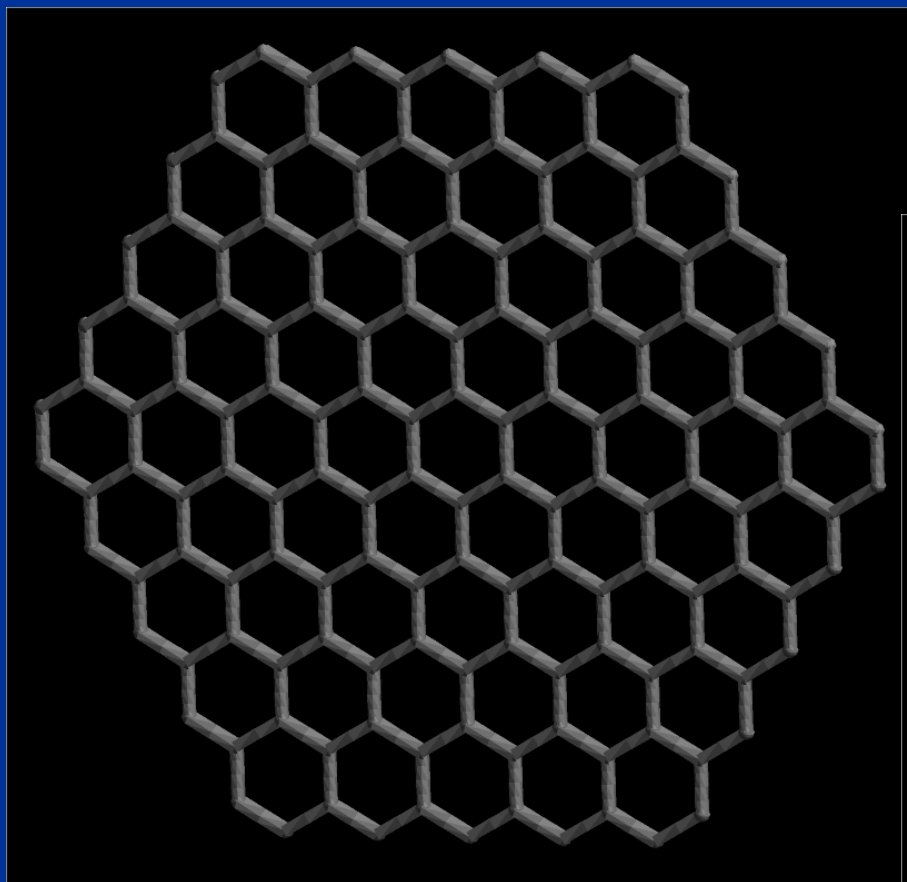


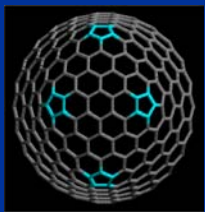
Atomistic modeling details

- **As a verification for the results of the continuum theory the MM simulation was carried out with the use of MSI-package Cerius2 (Universal Force Field)**
- The structures considered were most stable clusters (had a minimum perimeter) with high symmetry (had a minimum elastic energy)
- The number of atoms has not been kept: this computation drawback was corrected by the calculation of the specific energy (instead of total energy of the cluster)
- **The result is in qualitative and quantitative agreement with continual result**
 - the scrolling barrier at ~ 150 atoms disappears at $P > 2$
 - the barrier energy $\sim 50 \text{ meV/atom}$ (at ~ 150 atoms)

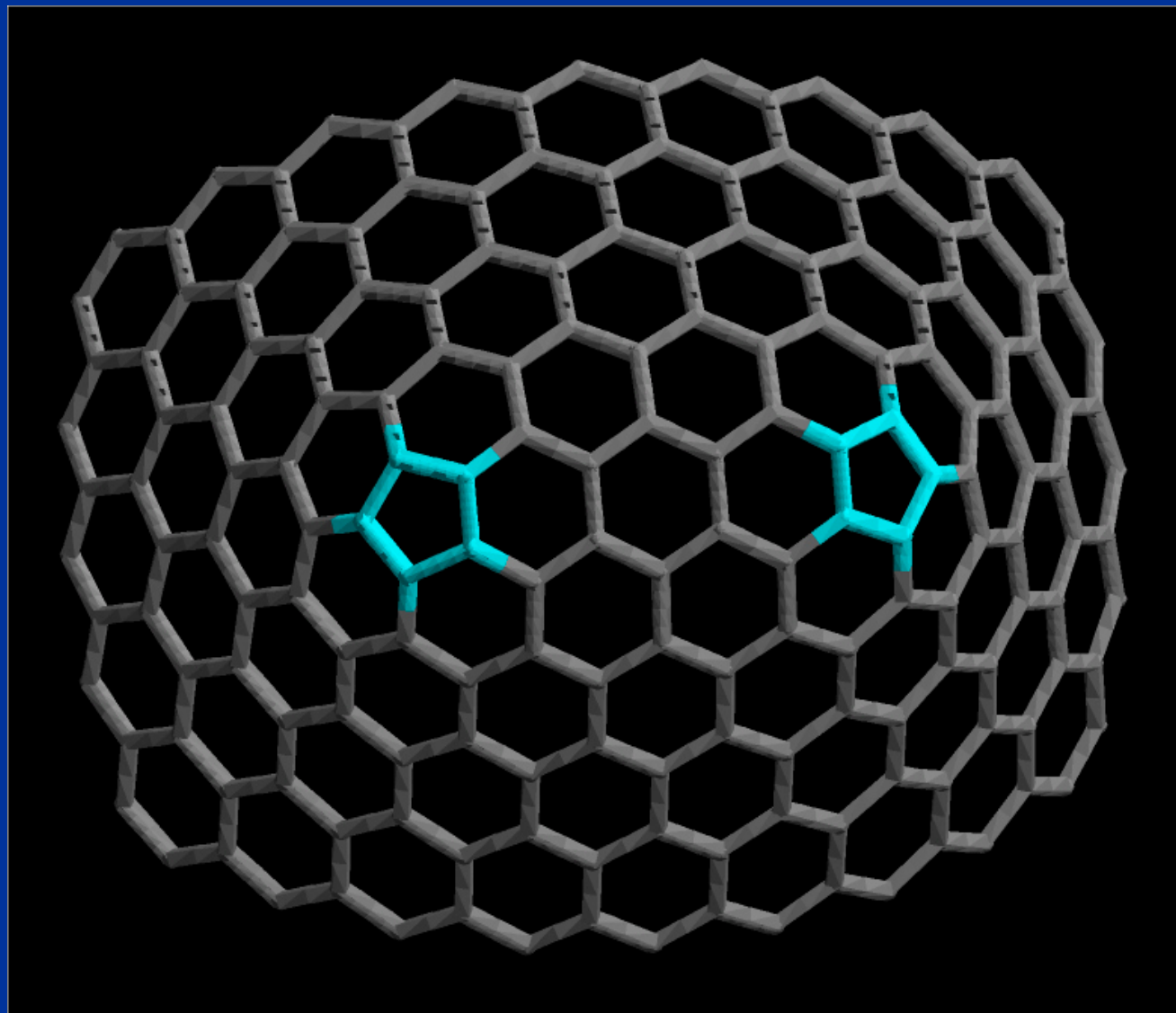


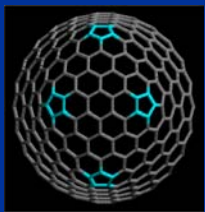
Simulated Shapes



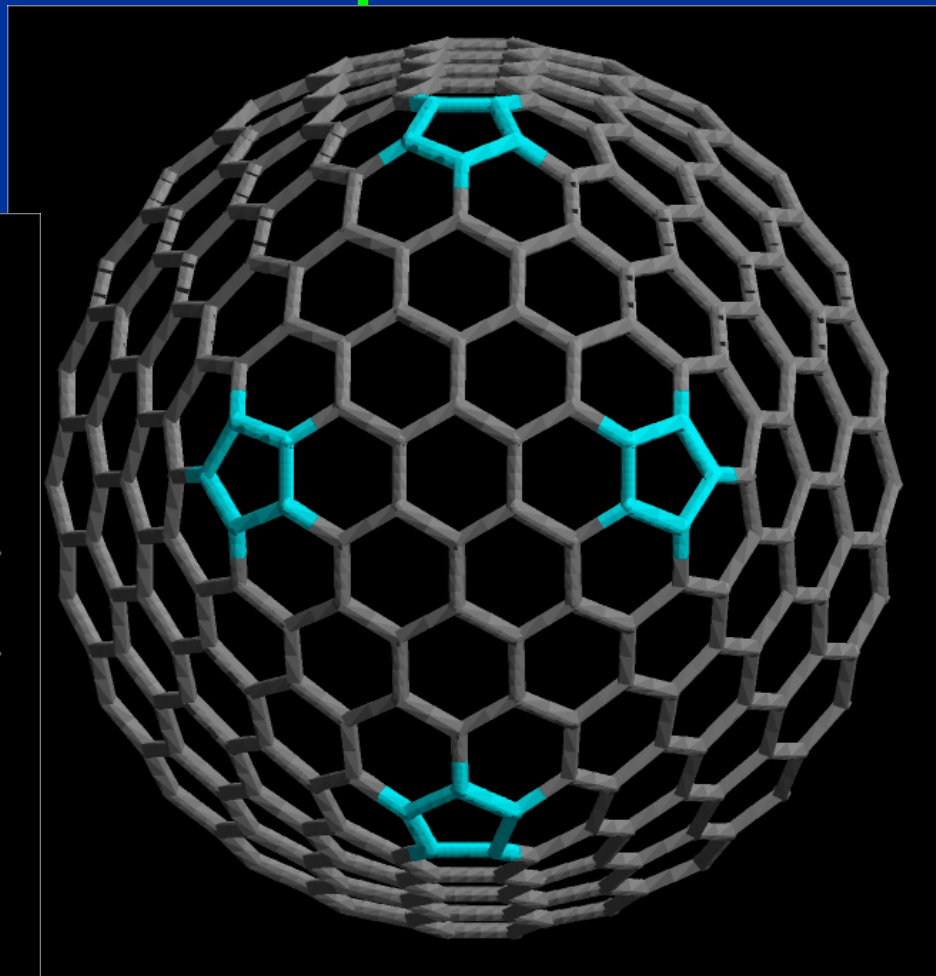
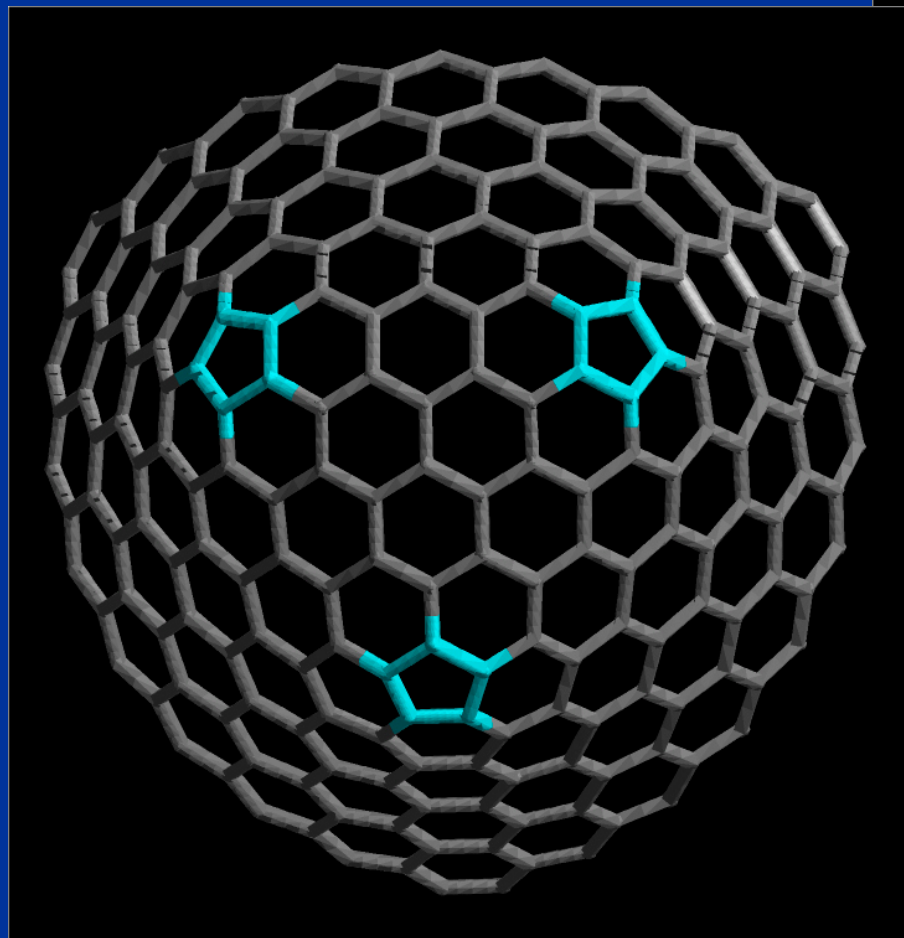


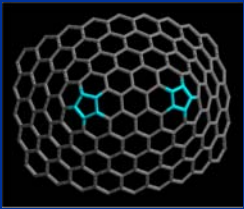
Simulated Shapes



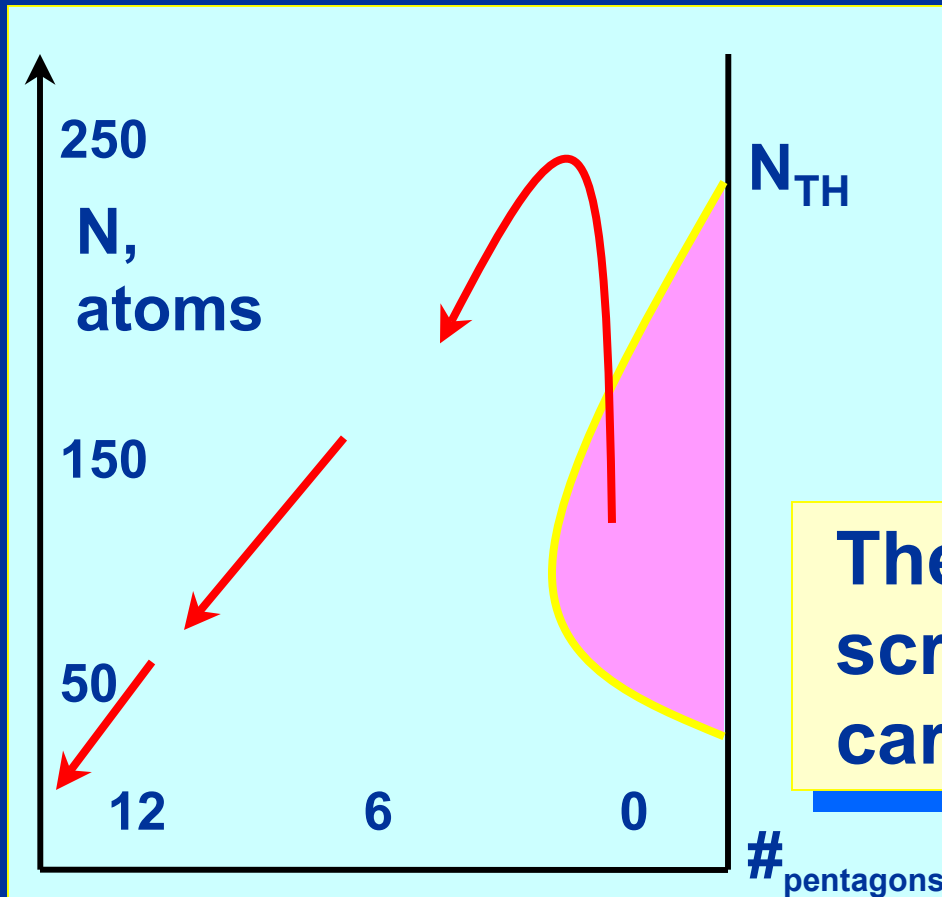
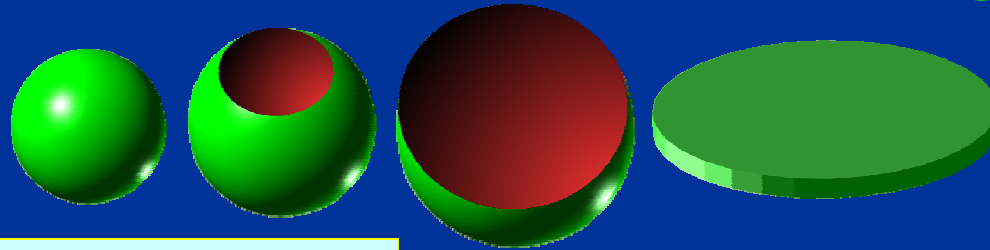


Simulated Shapes

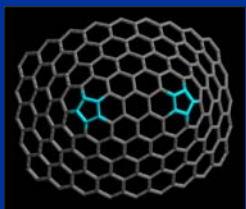




Conclusions on Scrolling

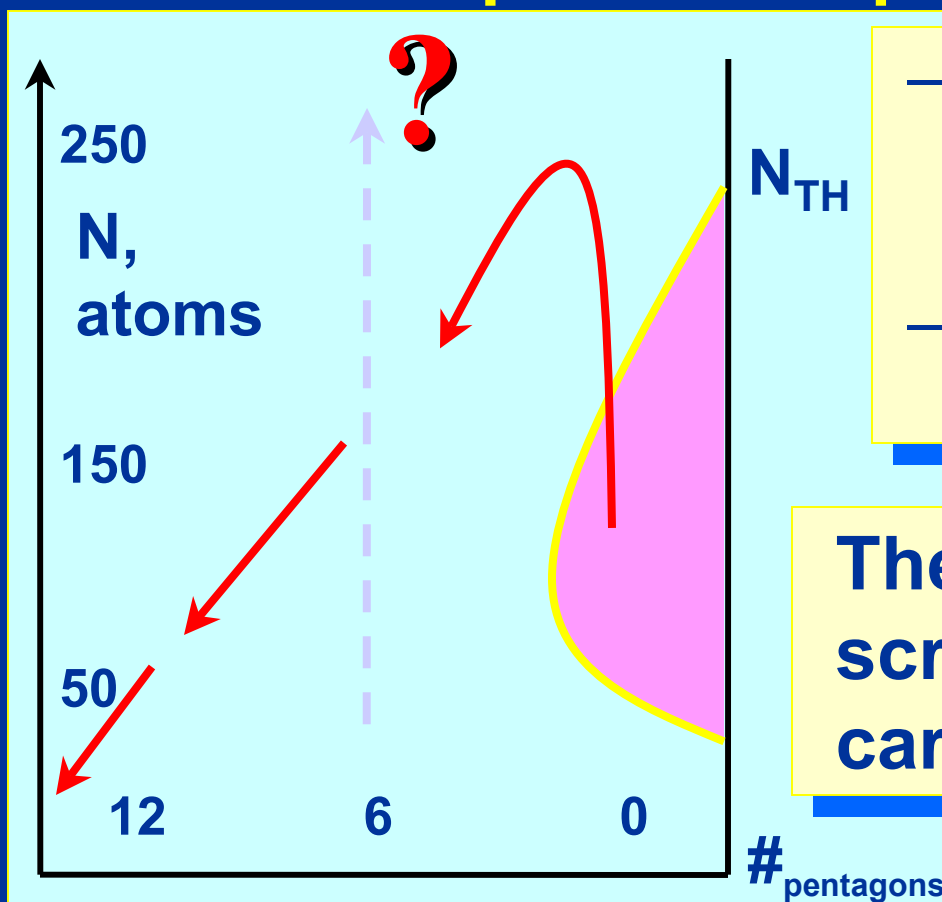


The phase diagram of the scrolling process for the carbon yarmolke cluster



Conclusions on Scrolling

- NT formation can follow to the nucleation of the hemispherical cap but...



- the cap is metastable to the scrolling in the sphere at $N < N_{TH} \sim 260$ atoms
- at $N > N_{TH} \sim 260$ the cap is unstable to the scrolling

The phase diagram of the scrolling process for the carbon yarmolke cluster

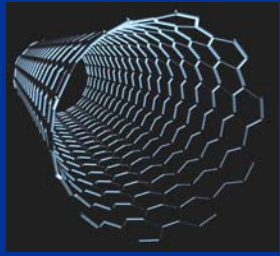
Spherical clusters cannot lead to NT formation

2. Continuum Energetics of Cylinders

Questions to current SWNT formation models:

- the anisotropic growth without preset direction;
- the nucleation;
- the high yeild of SWNTs of given radius and chirality.

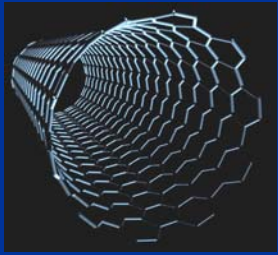
Experimental evidence allows us to consider as a possible route of SWNT formation: solid-state reaction



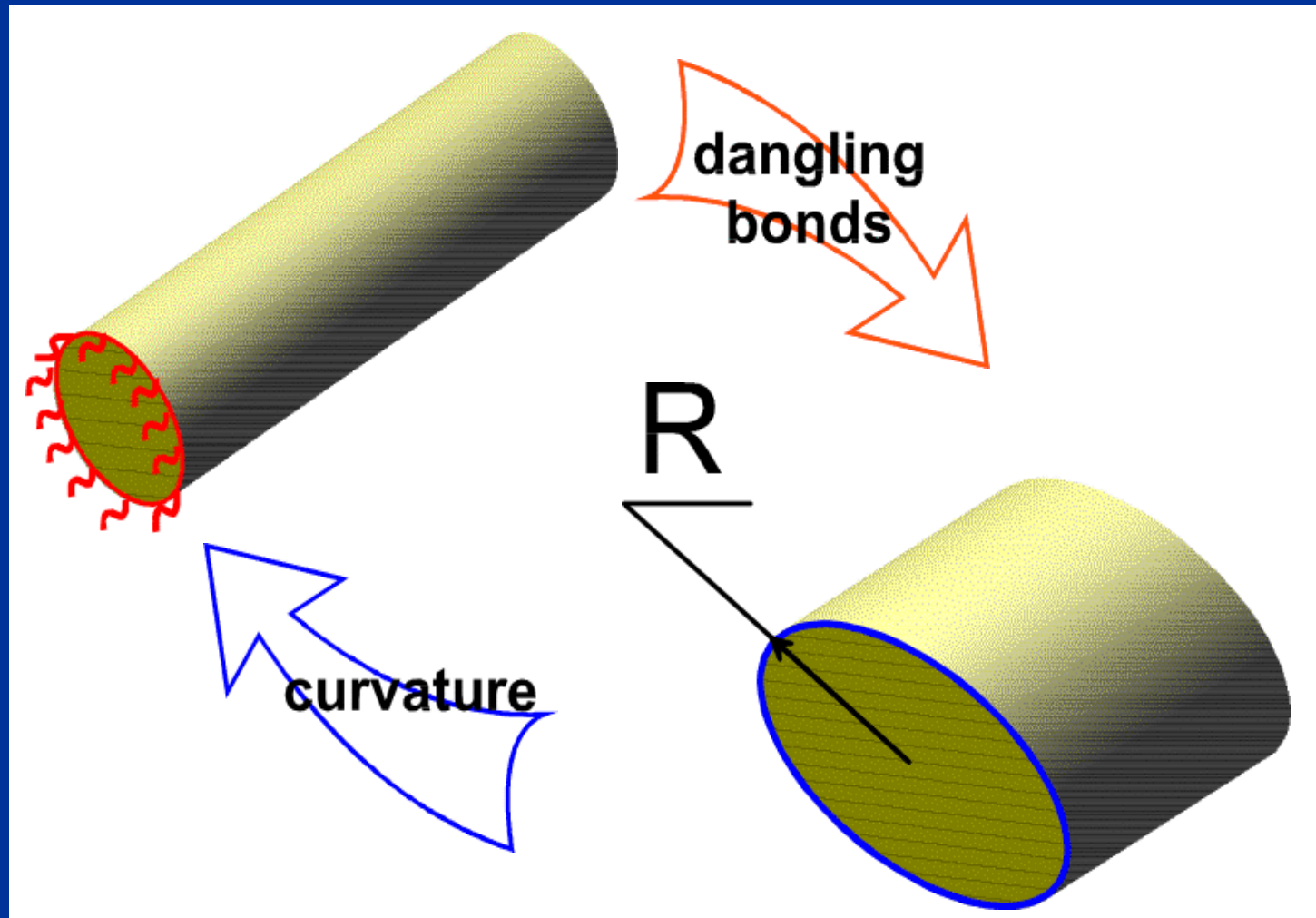
NT Energetics

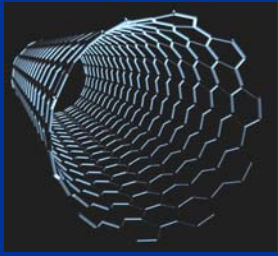
Energetics of a finite SWNT is defined by its radius (except for dangling bonds at the ends)

$$E_{\text{tube}} = \pi \sqrt{3} E_c \frac{H}{R}$$



Energy competition





NT Energetics (cont.)

Energetics of a finite SWNT is defined by its radius (except for dangling bonds at the ends)

$$E_{\text{tube}} = \pi \sqrt{3} E_c \frac{H}{R}$$

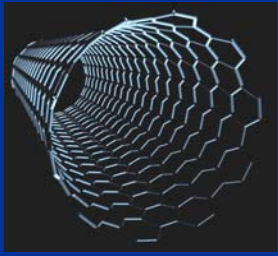
$$E_o = 6 \pi \sqrt{3} E_c \left(\frac{N}{N_\star} \right)^{1/3}$$

Optimal SWNT energy

Optimal SWNT radius (number of atoms) is a universal function of a characteristic radius (number of atoms)

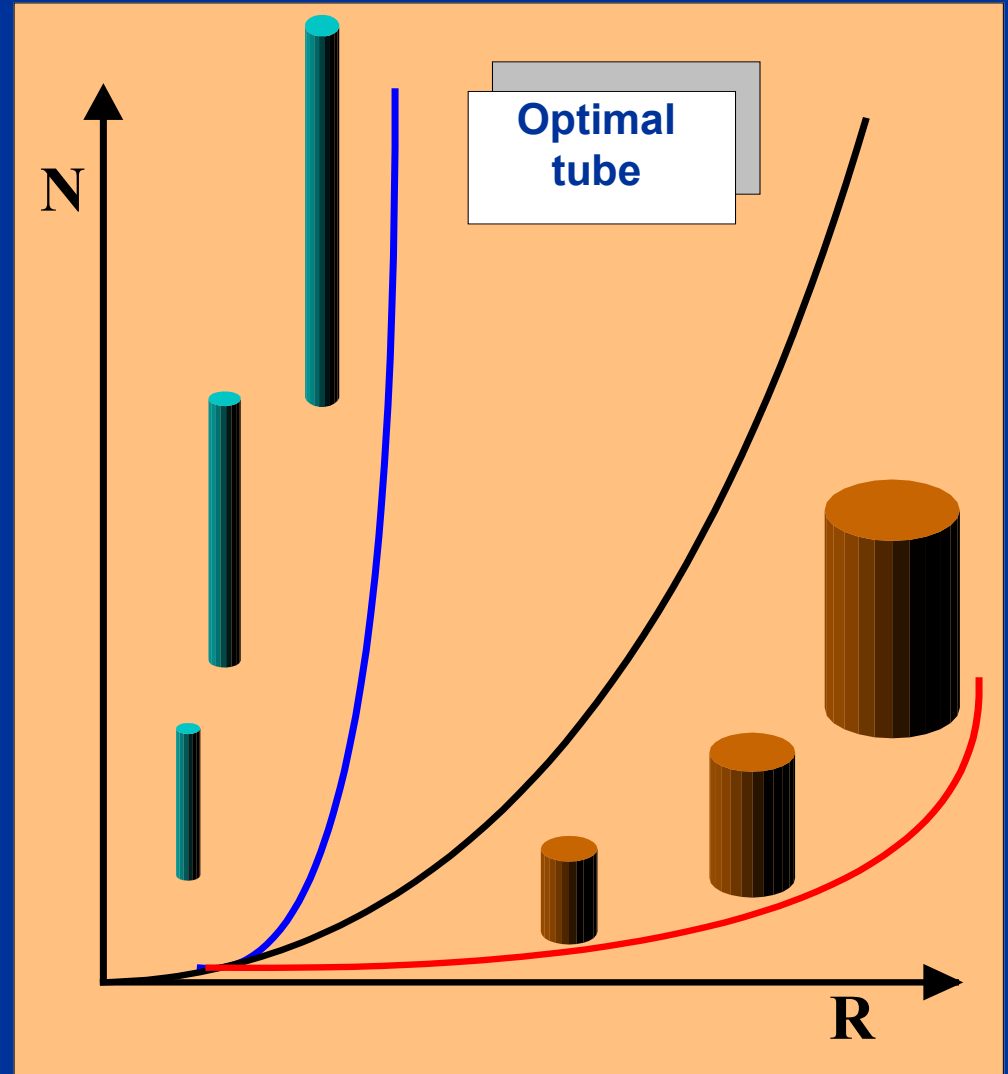
$$R_\star / b = 3 E_c / E_b$$

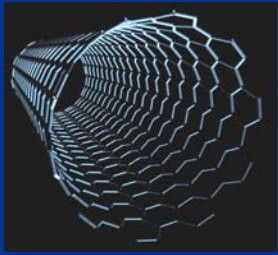
$$N_\star = 16 \sqrt{3} \pi E_c^2 / E_b^2$$



Optimal NT regrowth

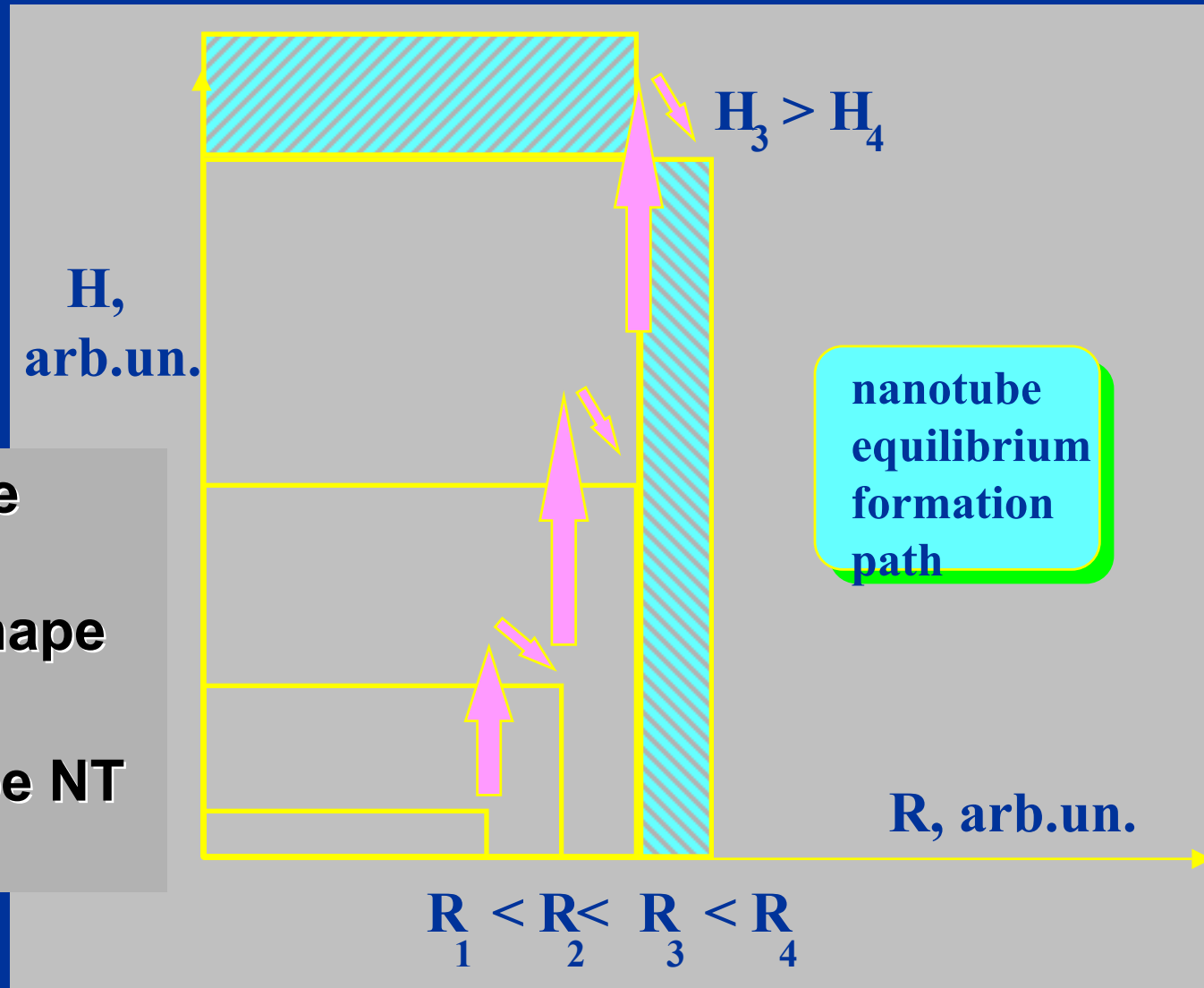
- Phase diagram of coexistence of NTs and planar fragments of graphene

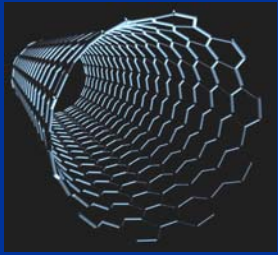




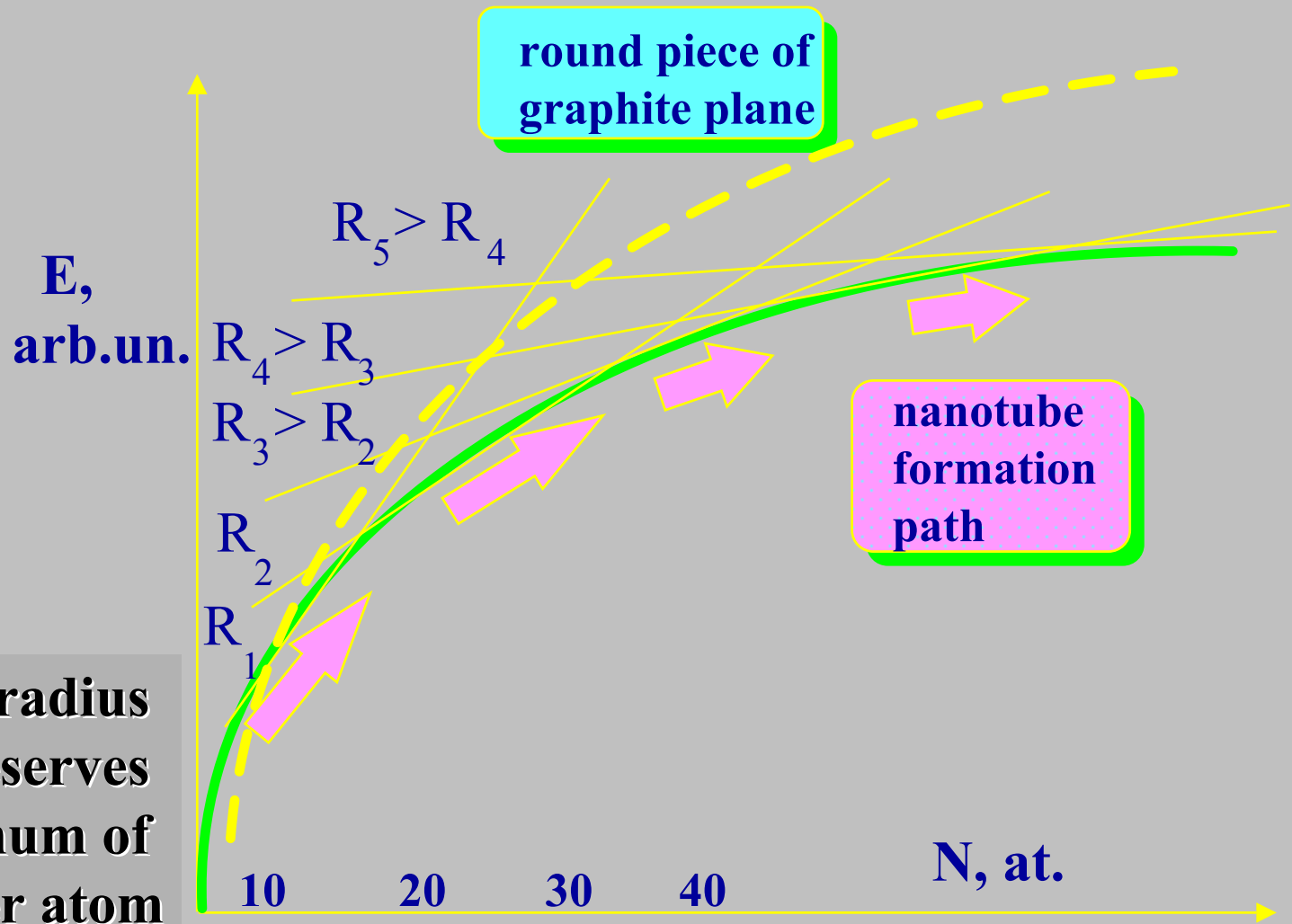
Optimal NT regrowth (2)

- NT during the growth has preferable shape
- to keep the optimal shape NT changes R

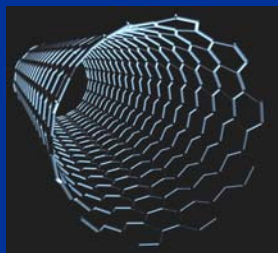




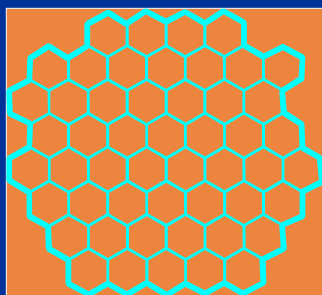
Optimal NT regrowth (3)



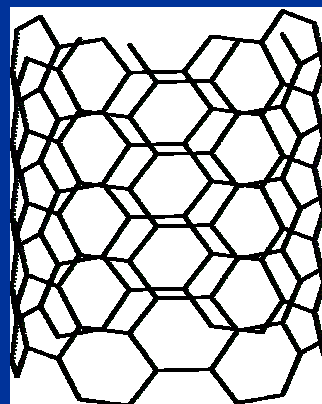
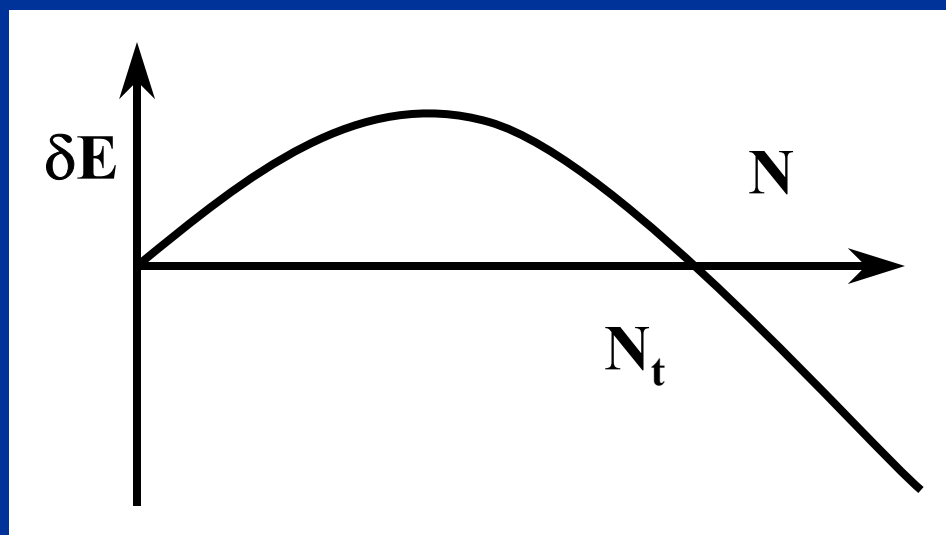
Changing its radius
the NT preserves
the minimum of
the energy per atom

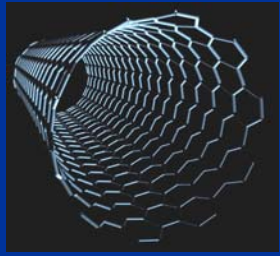


NT Nucleation



- Nucleation is a key stage of the synthesis
- Cylindrical nuclei
 - unstable to transformation to planar flake up to $N_t \sim 148$





NT Critical Size

Energy competition between cylinder and fragment of plane

gives a critical size of a nanotube

$$E_o - E_{pl} = 6\sqrt{3} \pi E_c \left(\frac{N}{N_\star} \right)^{1/3} - \frac{2\pi R}{\sqrt{3}} E_b$$

$$= 12\pi E_c \left(\frac{N}{N_\star} \right)^{1/2} \left[\left(\frac{N_t}{N} \right)^{1/6} - 1 \right]$$

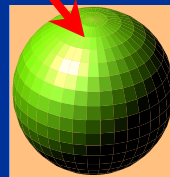
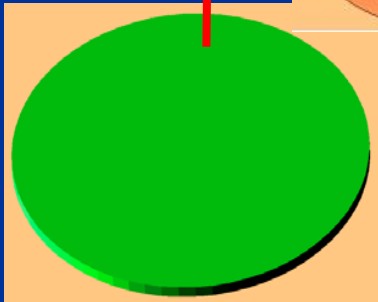
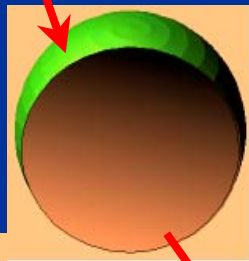
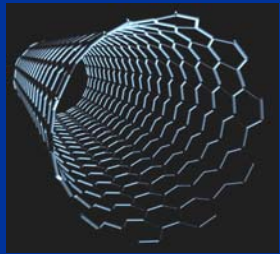
$$N_t = 729 N_\star / 64 \simeq 148$$

Passivation of dangling bonds changes the stability region boundary

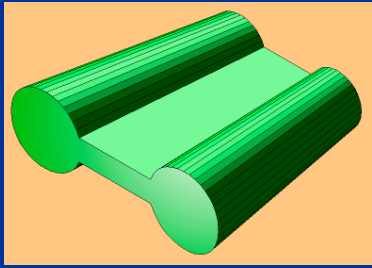
$$E_b \rightarrow \xi E_b$$

$$N_t(\xi) = N_\star \left(1 + \frac{1}{2\xi} \right)^6$$

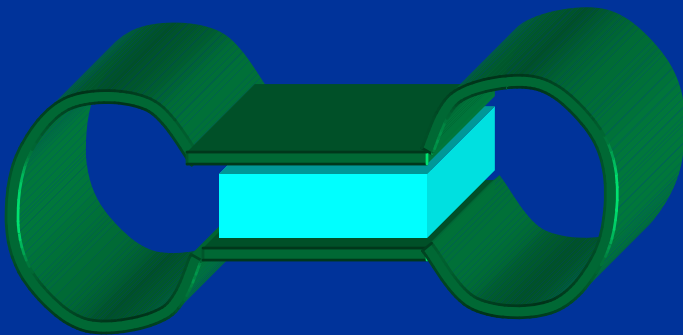
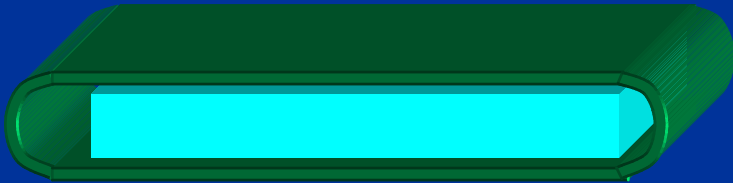
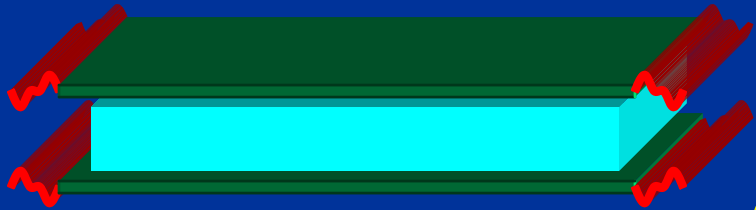
NT Nucleation



- Nucleation is a key stage of the synthesis
- Cylindrical nuclei
 - unstable to transformation to planar flake up to $N_t \sim 148$
- Cap (hemisphere) nuclei
 - cap is metastable to scrolling in sphere at $N < N_{TH}$
 - tube with cap is unstable to scrolling in sphere at $N < N_{TH}$

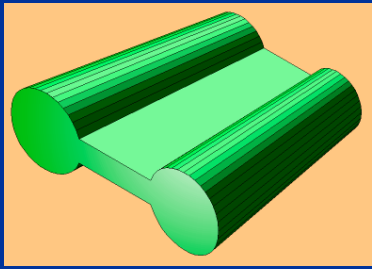


NT formation from stripe



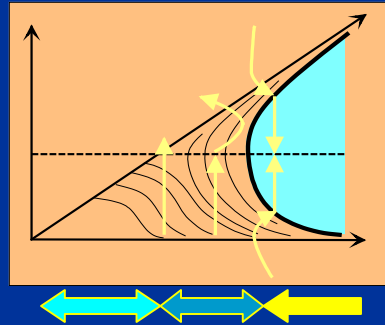
- “stripe - pincenez - tube”
 - interplay between curvature, DBs and VdW energy
 - energy landscape of stripe transformation has minimum
 - optimal pincenez structure has radius of bulbs $R_m \sim 7.5 \text{ \AA}$

P.Zhang et al., first MD simulation of popping up, PRL, 1999

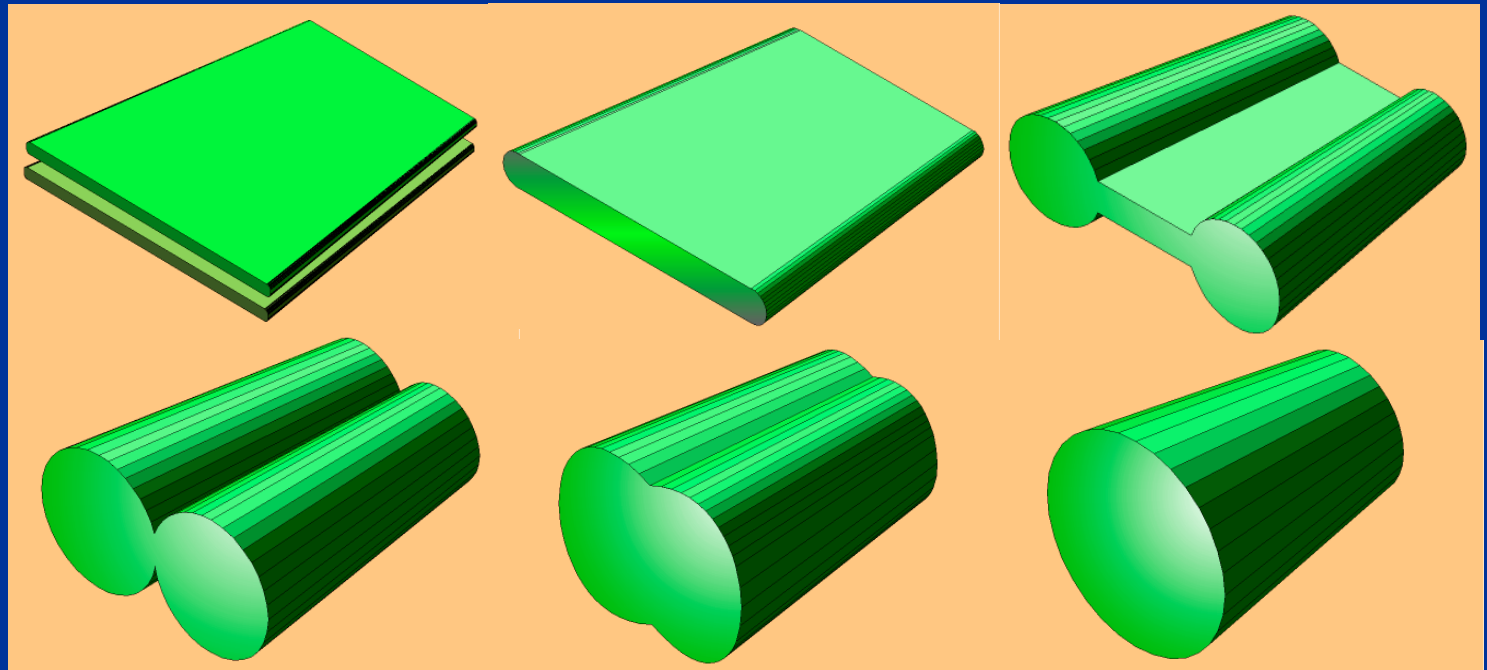


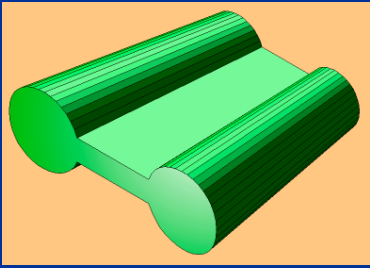
NT formation from stripe

- Energy landscape: 3 regions



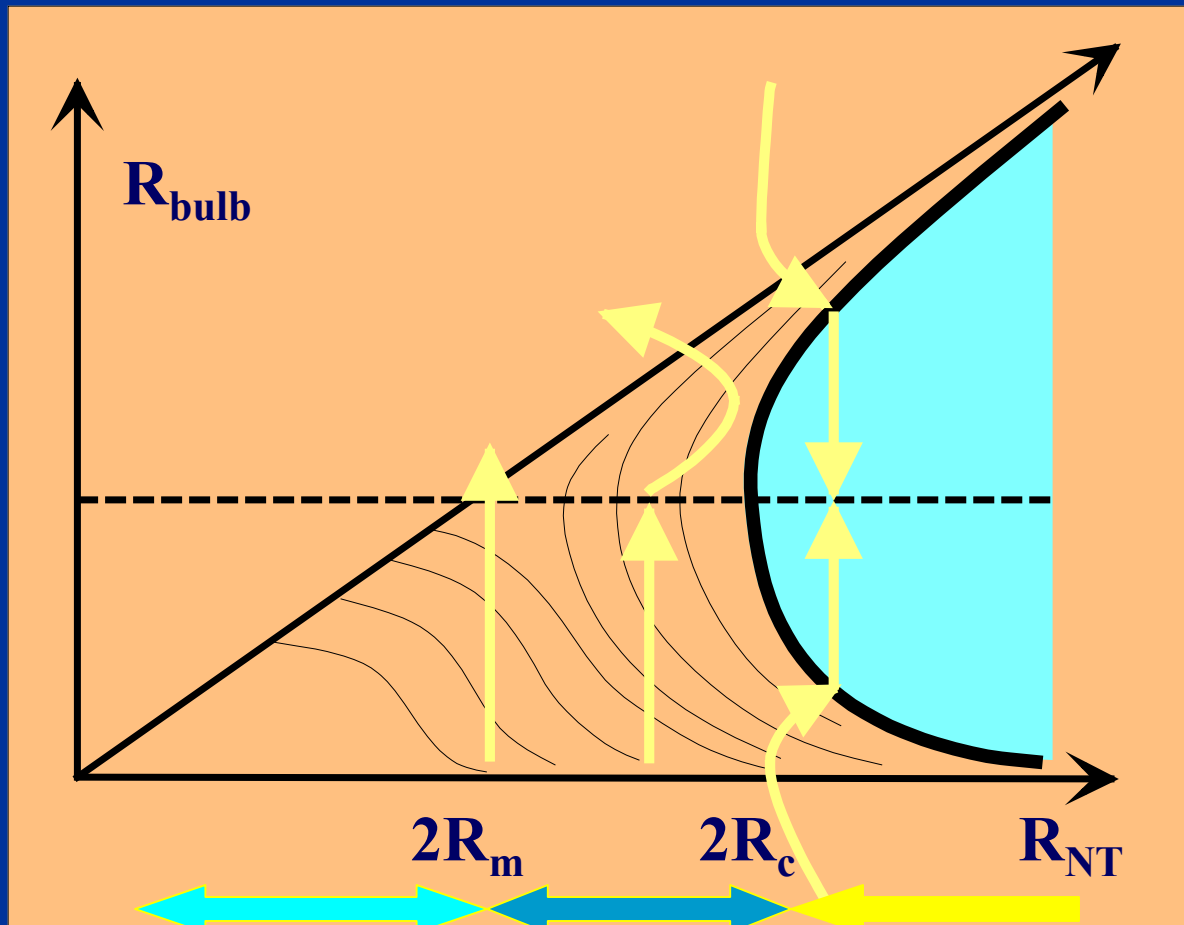
- popping-up
- over-barrier transformation
- collapse (no NTs)





NT formation from stripe

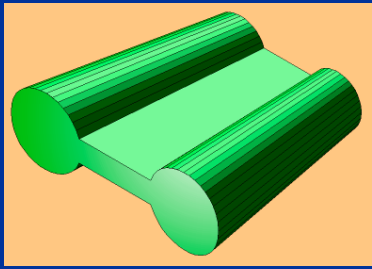
- Energy landscape: 3 regions



- popping-up
- over-barrier transformation
- collapse (no NTs)

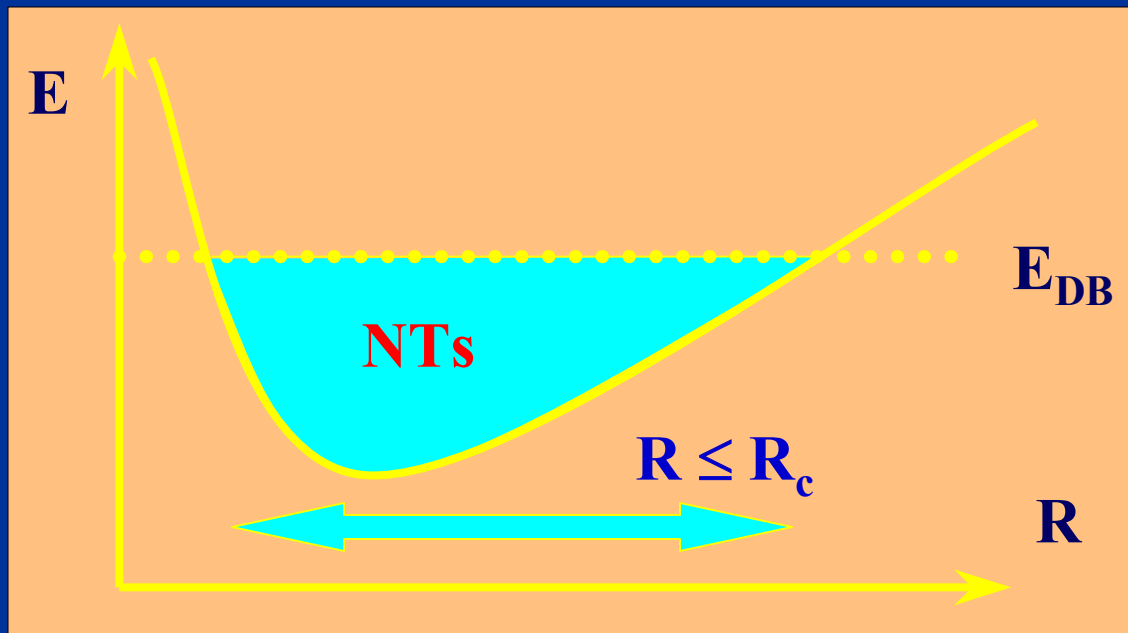
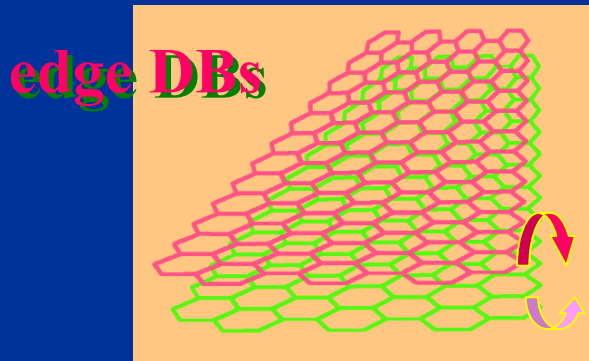
$$2R_m \sim 15 \text{ \AA}$$

$$2R_c \sim 28 \text{ \AA}$$



NT formation from stripe

- Closing of DBs gives initial push to transformation
 - energy of rectangular stripe depends on bulb radius R
 - NT formation occurs at

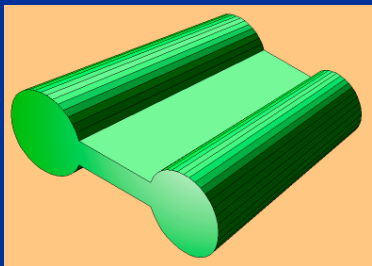


$$R \leq R_c$$

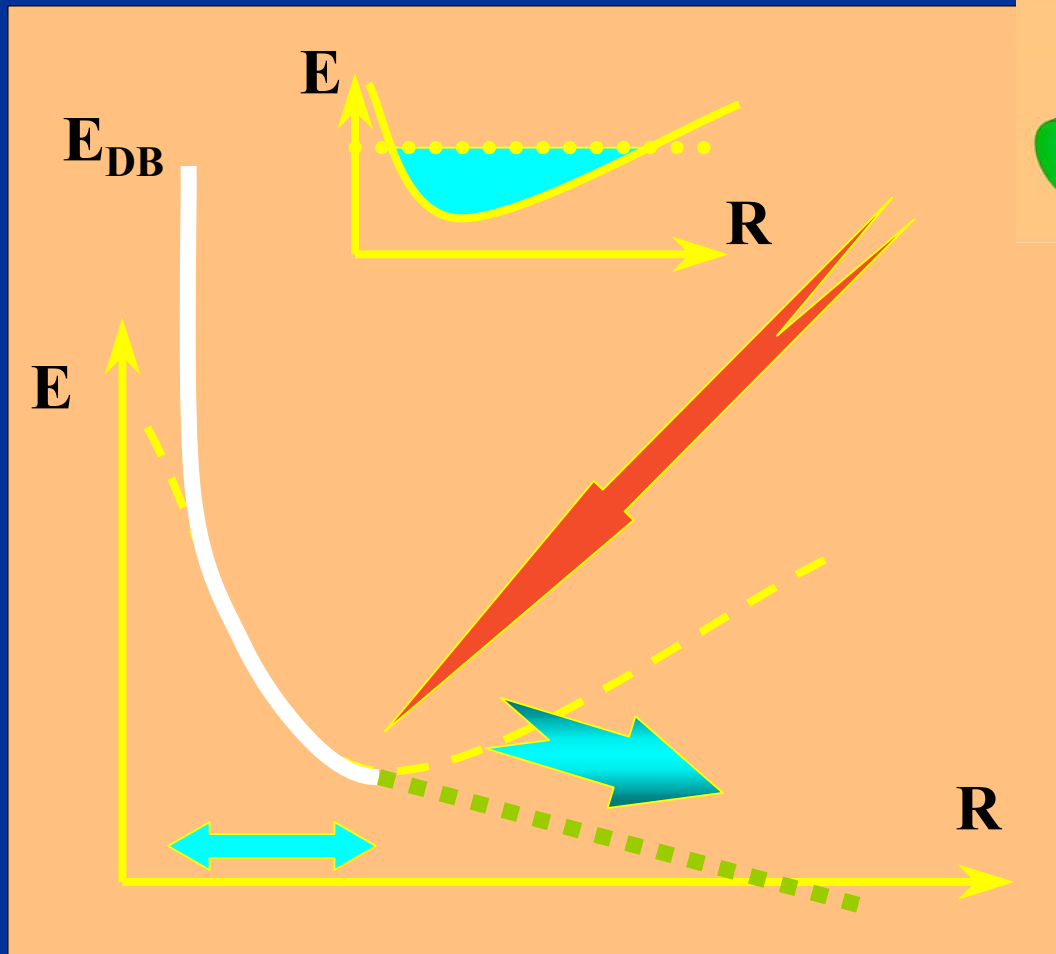
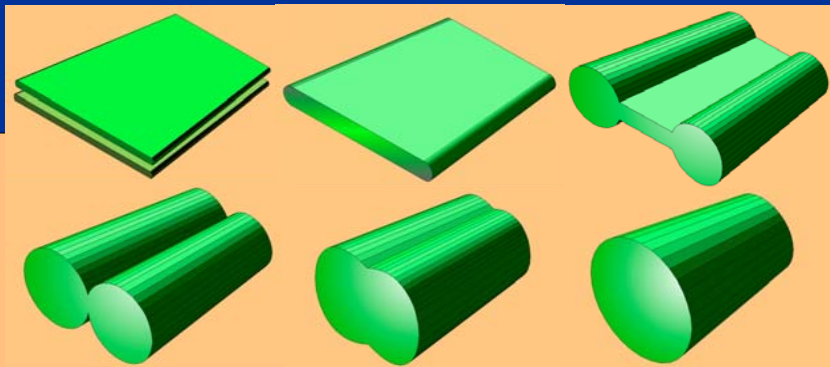
$$R_c \sim 14 \text{ \AA}$$

$$R \leq R_c$$

R



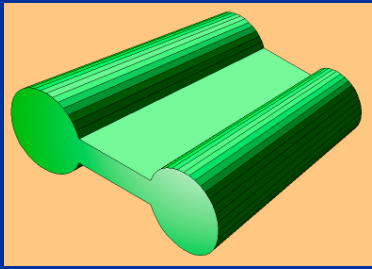
NT formation from stripe



- Path for NT formation depends on stripe width:
- narrow stripe pops up

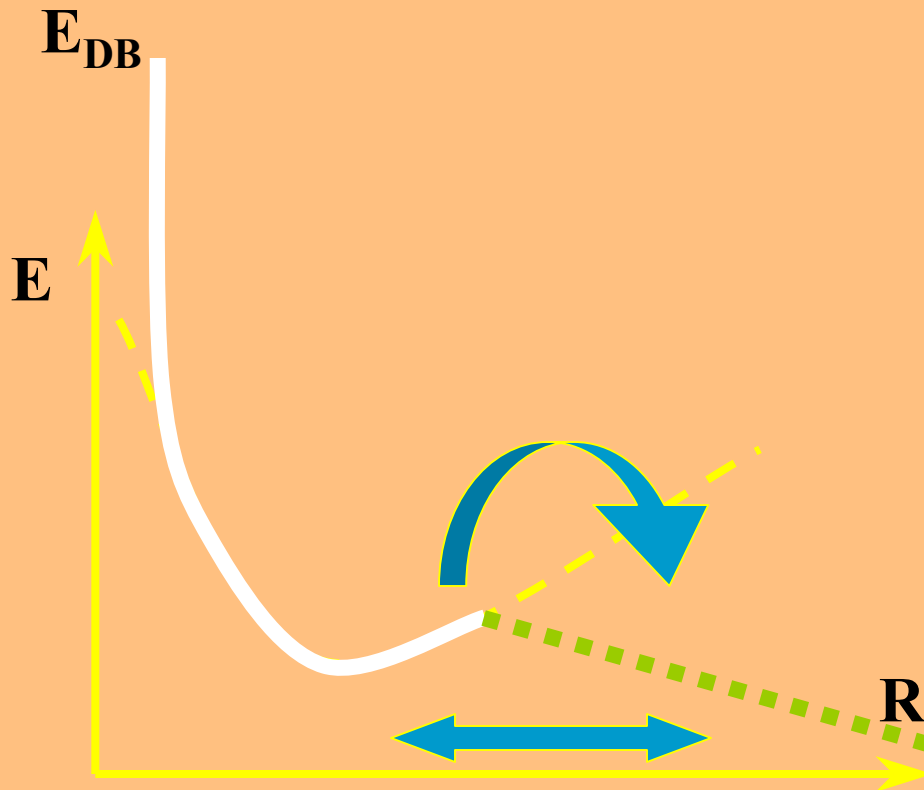
$$R_{NT} \leq 2R_m$$

$$R_m \sim 7.5 \text{ \AA}$$



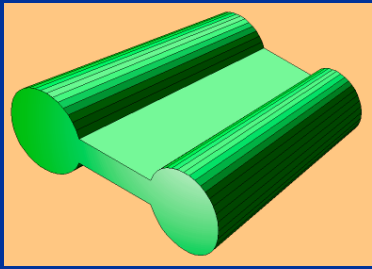
NT formation from stripe

- Path for NT formation depends on stripe width
 - narrow stripe pops-up
 - wider stripe has a barrier



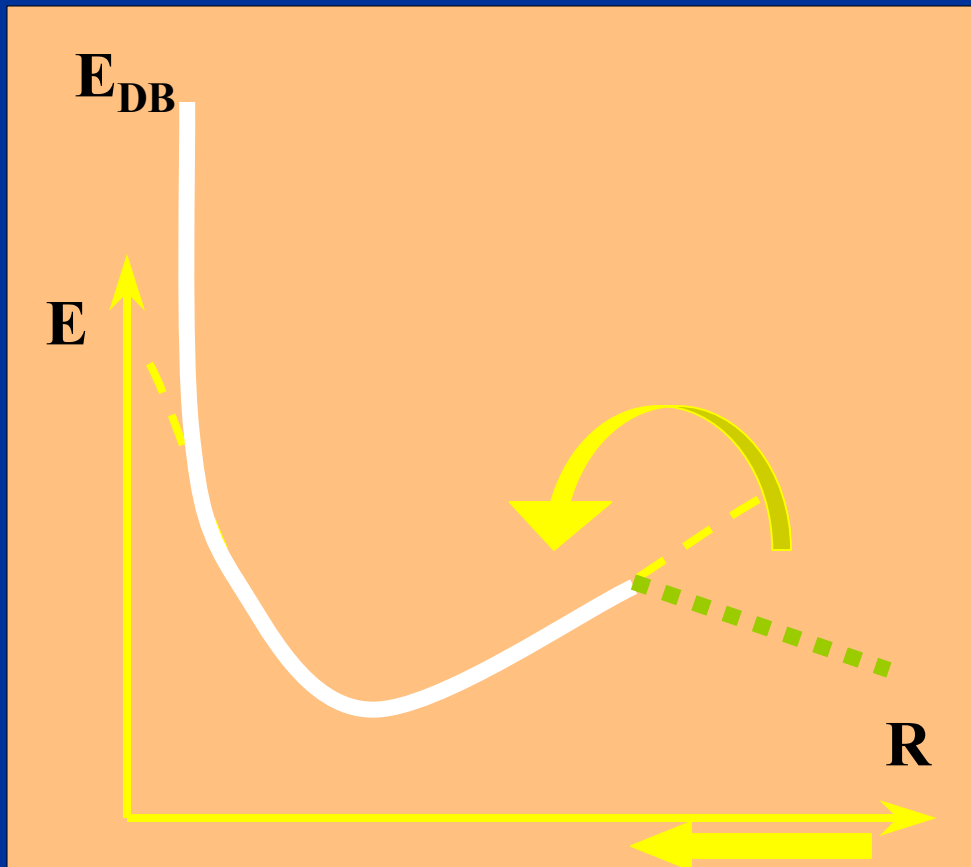
$$2R_m \leq R_{NT} \leq 2R_c$$

$$R_m \sim 7.5 \text{ \AA} \quad R_c \sim 14 \text{ \AA}$$



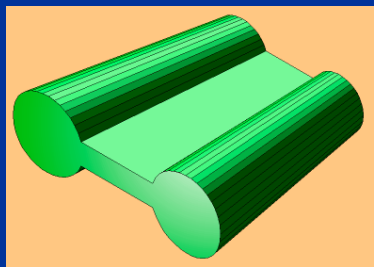
NT formation from stripe

- Path for NT formation depends on stripe width
 - narrow stripe pops-up
 - wider stripe has a barrier
 - **NT of large radius collapses**



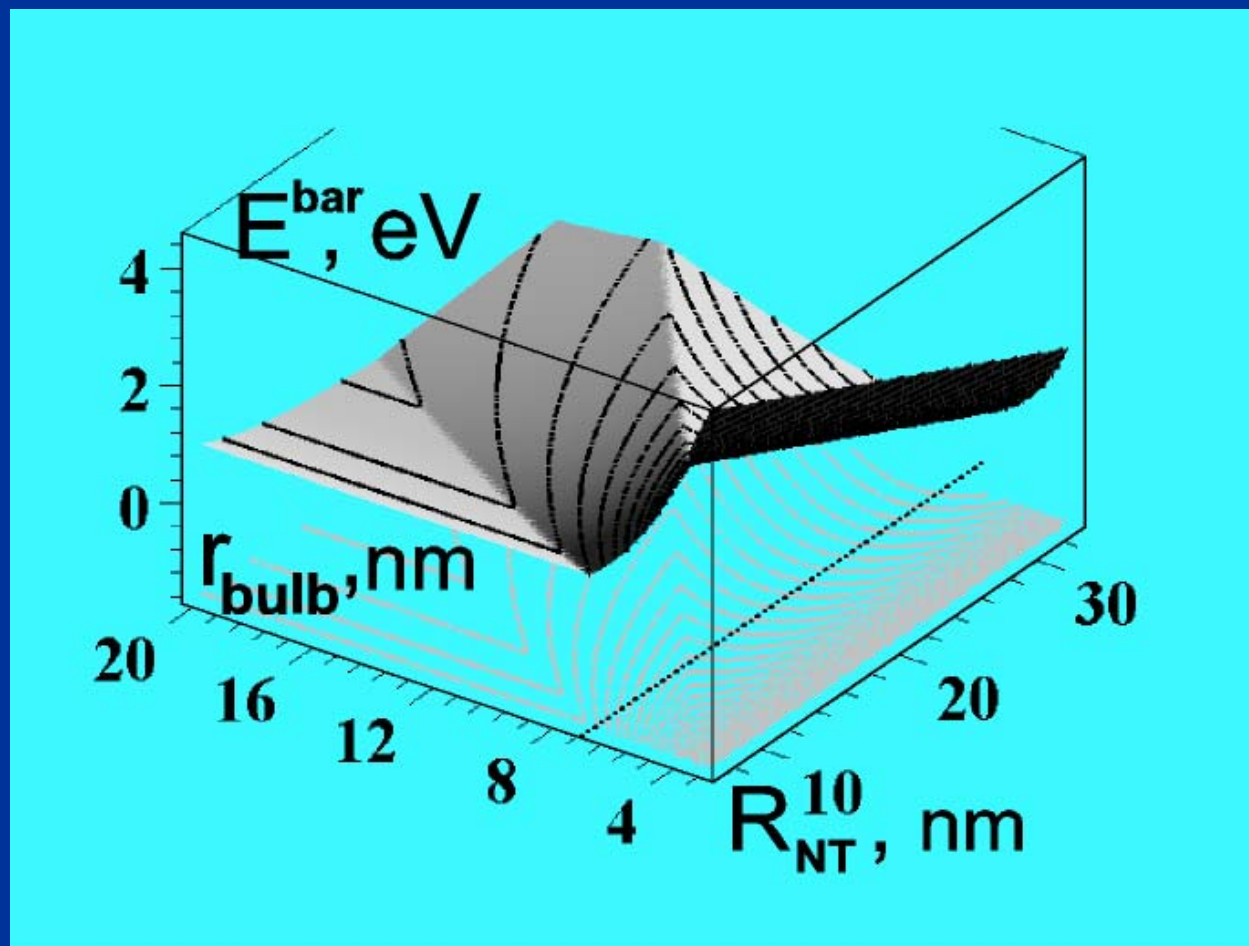
$$2R_c \leq R_{NT}$$

$$R_c \sim 14 \text{ \AA}$$



NT formation from stripe

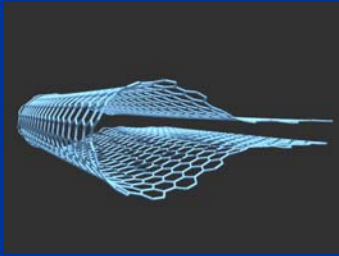
- 3D-view of phase diagram of stripe-to-tube process



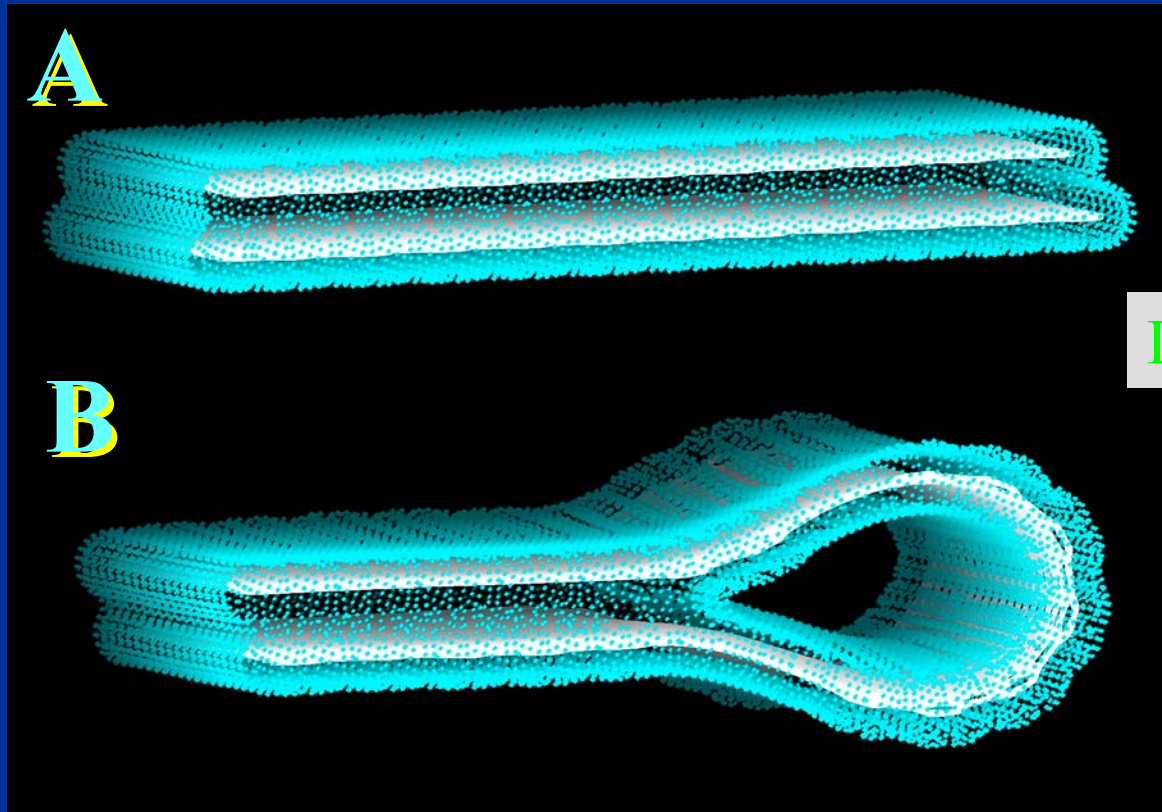
- popping-up
- over-barrier transformation
- collapse (no NTs)

$$2R_m \sim 15 \text{ \AA}$$

$$2R_c \sim 28 \text{ \AA}$$



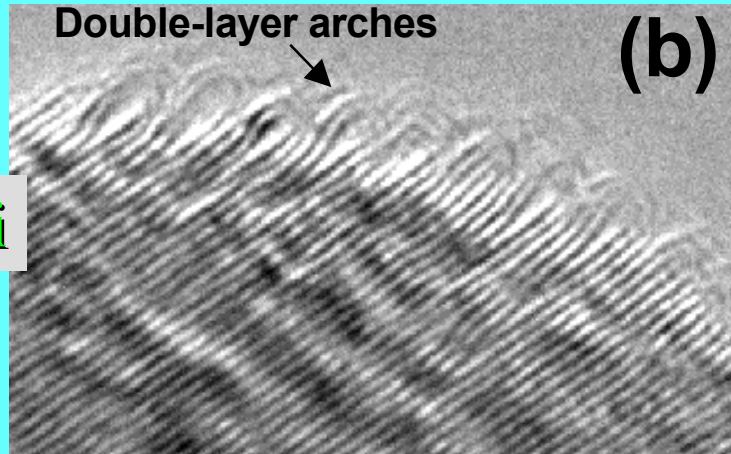
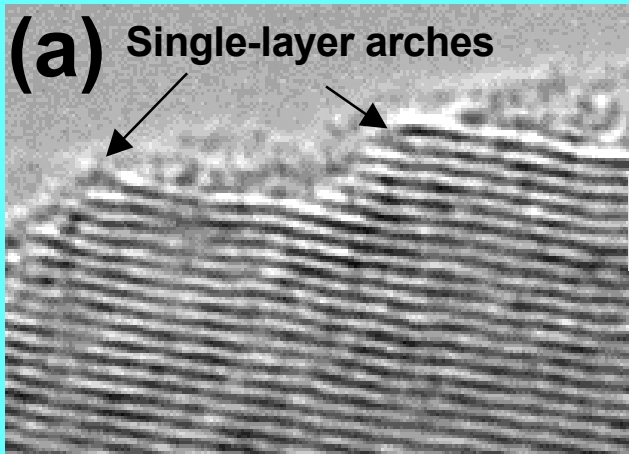
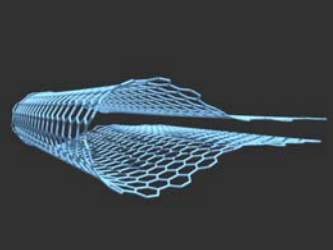
Sleeve Formation



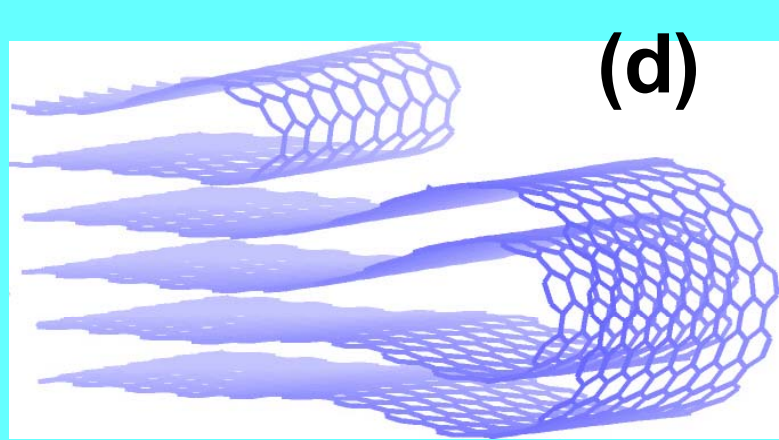
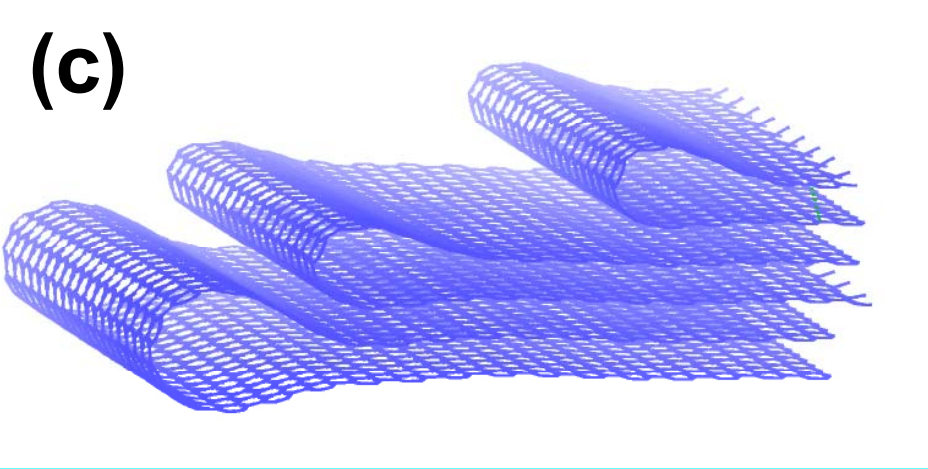
I.Zharov

A: graphite bi-layer; blue represents van der Waals cohesion which keeps layers together. B: after Dangling Bond closing the structure anneals into a cylindric sleeve. The energetics allows to estimate its radius ~ 1.5 nm.

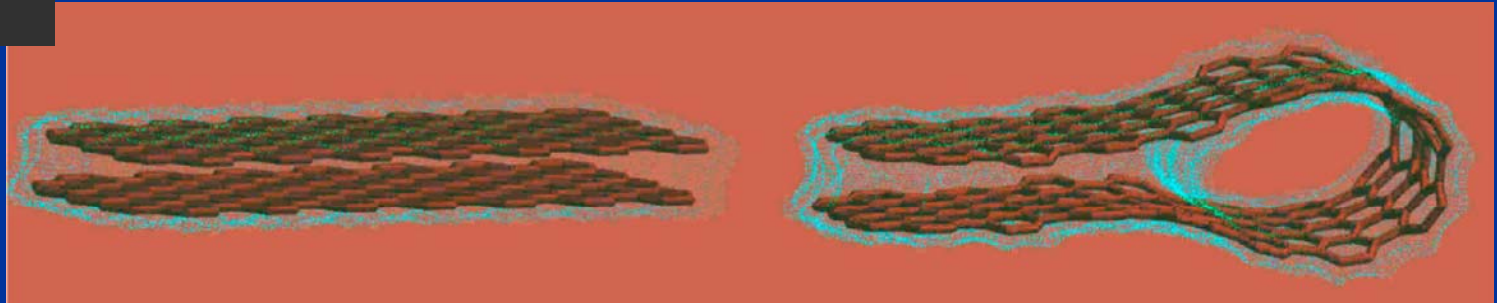
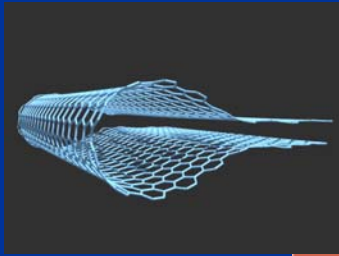
Simulation of Zipping



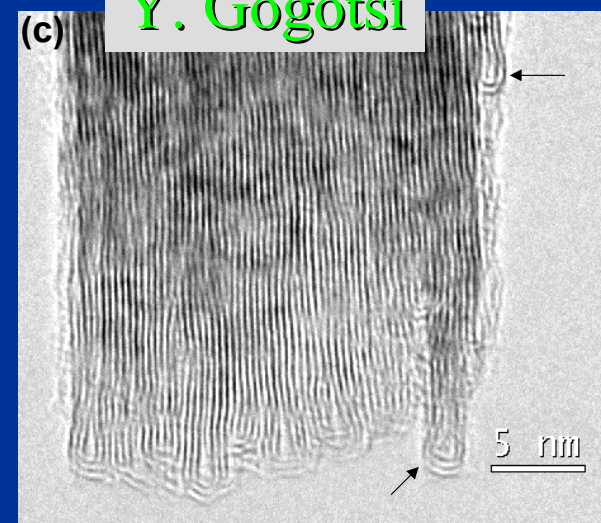
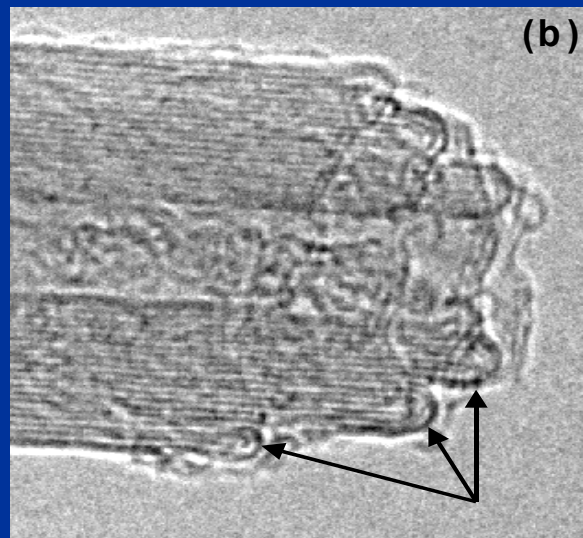
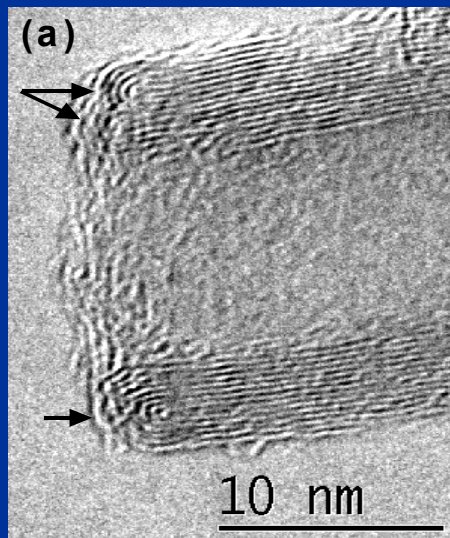
Y. Gogotsi

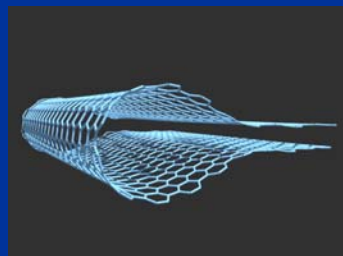


Graphitic Sleeves



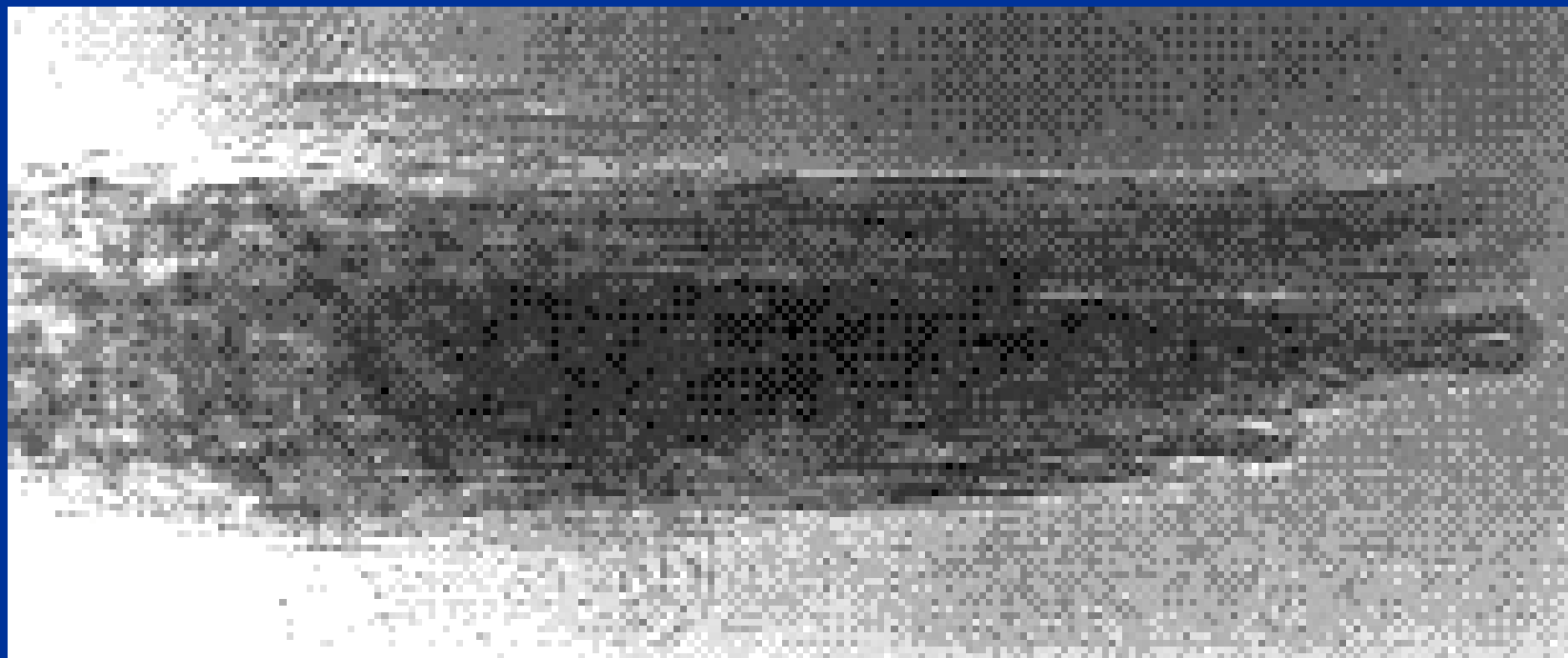
Edge reconstruction: experimental study shows the scrolling of the edge. We studied this effect theoretically for the SWNT nucleation.



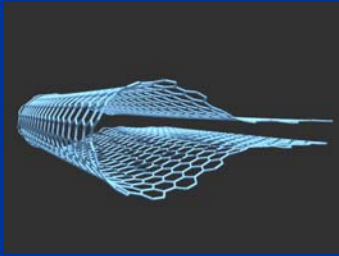


NT zipping-formation

- scrolling of graphite edges



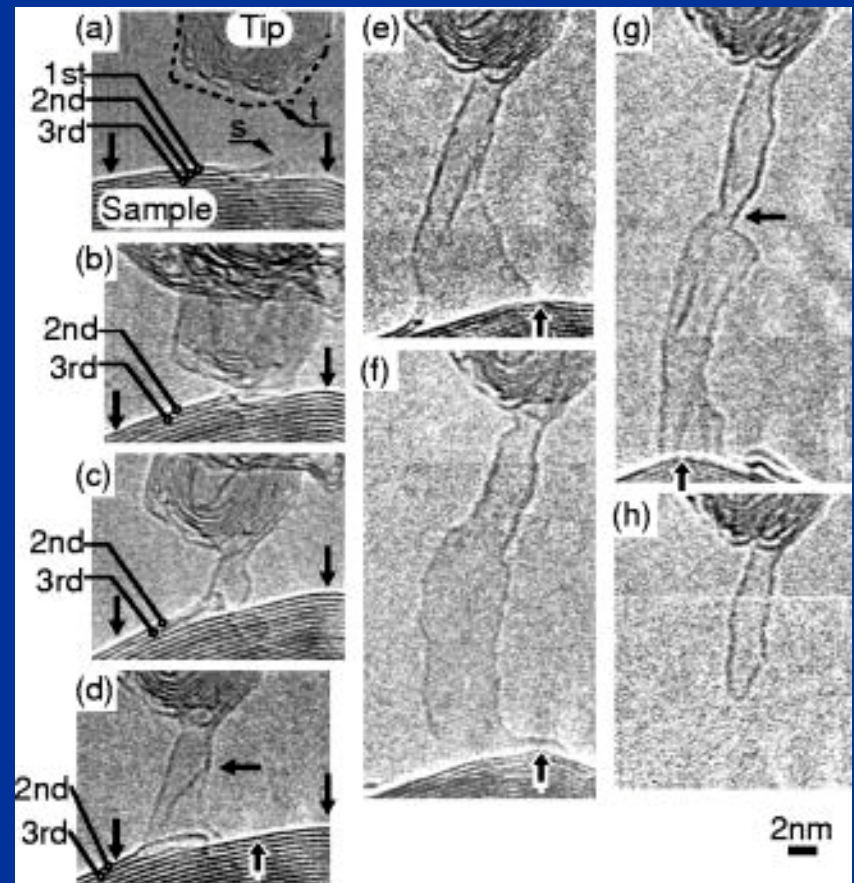
Appl. Phys. A 68, 493–495 (1999) “Solid-phase production of carbon nanotubes”, W.K.Hsu, Y.Q.Zhu, S.Trasobares, H.Terrones, M.Terrones, N.Grobert, H.Takikawa, J.P.Hare, H.W.Kroto, D.R.M.Walton

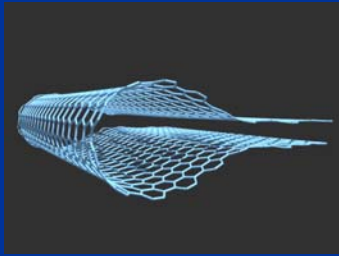


NT zipping-formation

- scrolling of graphite edges
- **NT formation in STM gap**

Applied Physics Letters, Vol. 74,
No. 17, 2450–2452, 26 April 1999,
“Growth of a single-wall carbon
nanotube in the gap of scanning
tunneling microscope”,
J. Yamashita, H. Hirayama, Y.
Ohshima, and K. Takayanagi

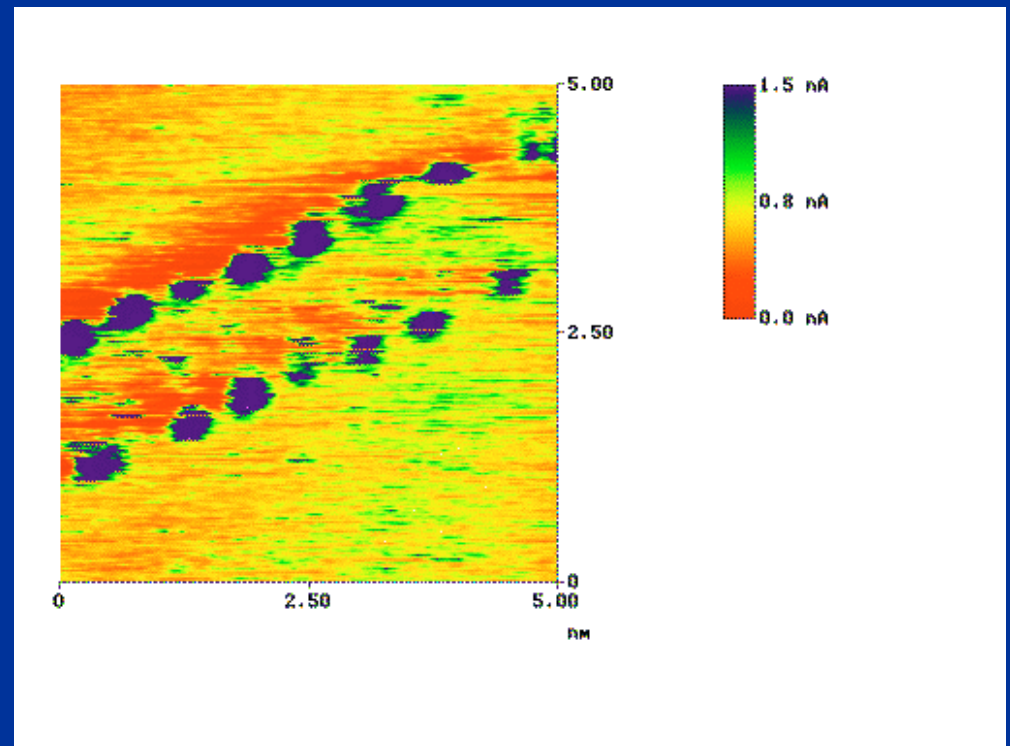




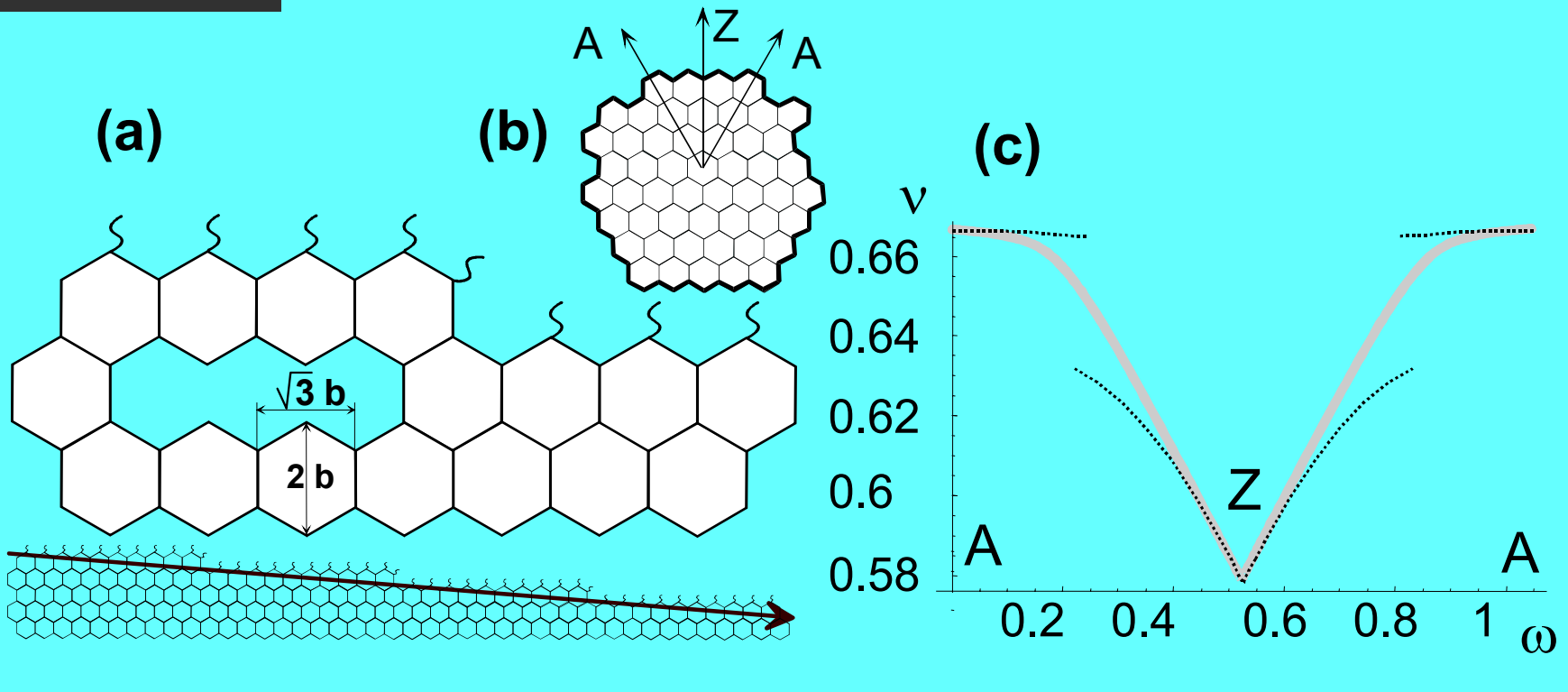
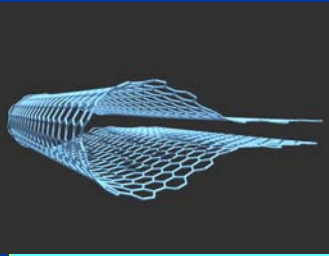
NT zipping-formation

- scrolling of graphite edges
- NT formation in STM gap
- **edge structures observed by**

© David Padowitz ,
Materials Chemistry at
Amherst College, MA, US

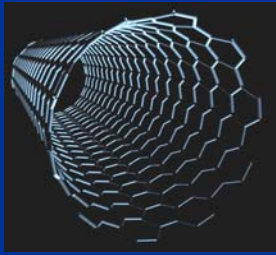


Edge Orientation



The optimal graphene edge orientation is Zigzag. Near the minimum point the energy can be expanded in series.

The first non-zero contribution in the energy is linear in ω .

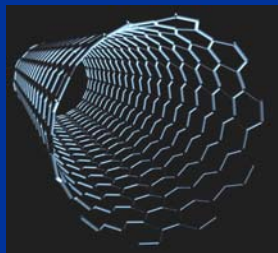


Edge Zipping of NT nuclei

Graphite edge energetics: stable Zigzag orientation of [110] graphite edge is consistent with the Armchair **chirality** of the prevalent SWNT.

The formation energy can be expanded in the series on the chirality at the extremum points (Z&A).

$$\delta E(\omega) = N_{\text{layers}} \delta \nu(\omega) E_b L \simeq 2 \frac{1}{6b} \omega E_b D$$

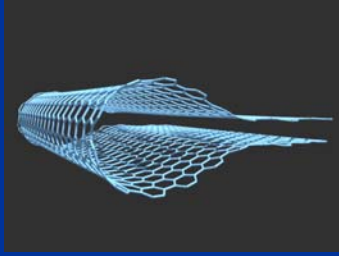


Nucleation Rates

The corresponding probability of the nucleation depends on ω exponentially. The characteristic of the exponent (critical chirality) ω_c is temperature dependent. It depends also on the distribution function of the defects facilitating the zipping: $f(D)$.

$$w \sim w_0 \exp\left[-\frac{1}{T} \frac{\omega D}{3b} E_b\right] = w_0 e^{-\frac{\omega}{\omega_c}}$$

$$\omega_c = \frac{3b}{D} \frac{T}{E_b}$$



Edge Zipping

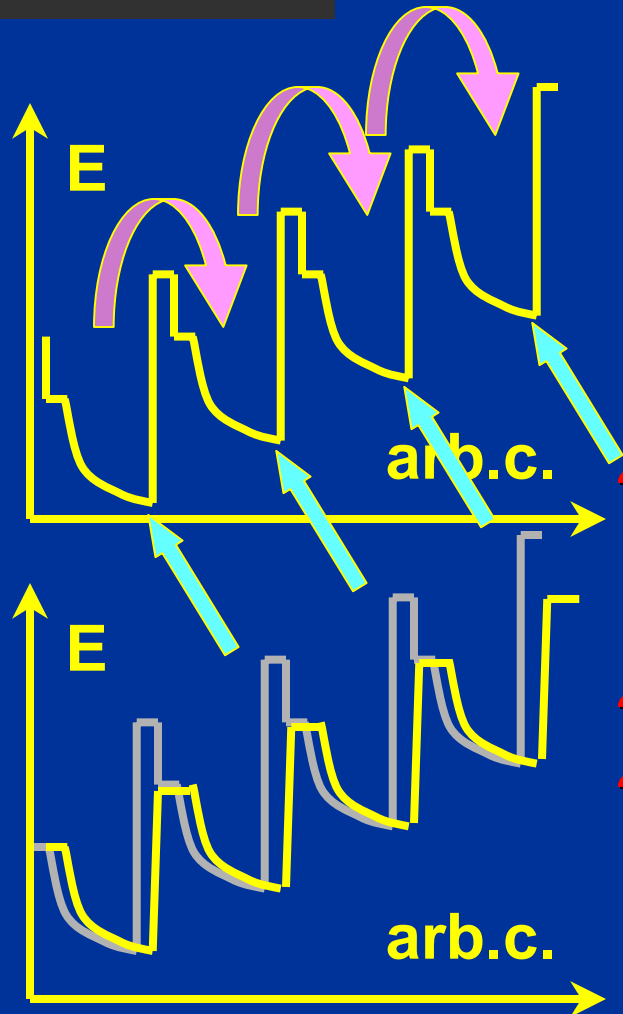
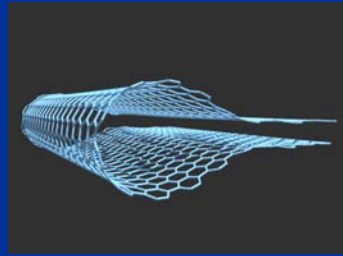
Graphene stripe Zipping will work if

- 1) the radius is less than $R_c \sim 1.4$ nm
- 2) the edge is oriented along the graphite high-symmetry direction and
- 3) no pentagon sources exist

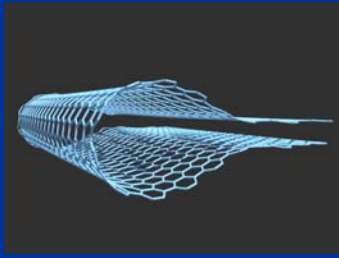
Continuum approach gives analytic formula for the optimum sleeve radius R_m as a ratio of the elastic curvature energy and vdW cohesion

$$R_m = \sqrt{\frac{9 E_c}{8 W}}$$

NT zipping-formation

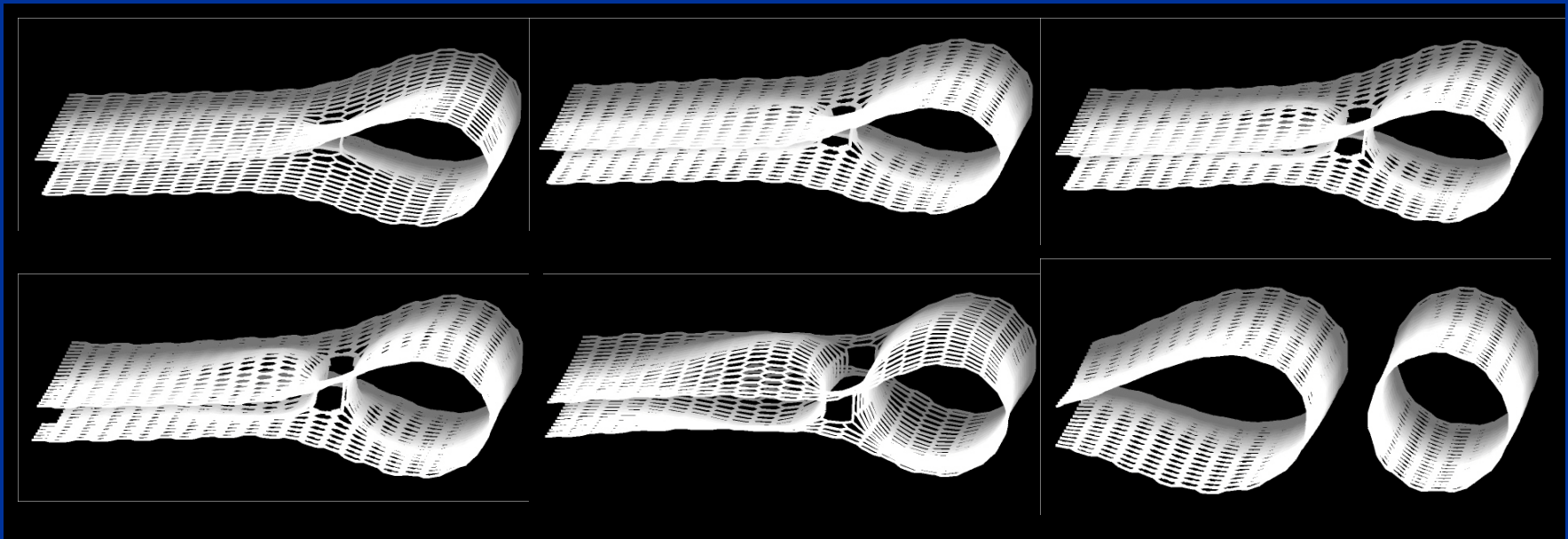


- Zipping of graphite double-layer
 - ! – anisotropic growth follows to an edge
 - ! – chirality relates to edge free energy
 - ! – the better edge, the less # of defects
- Energy landscape of zipping
 - ? – over-barrier transformation
 - ! – the fixed radius of NT as a result of deep minimum for pince-nez structure
 - ? – large barrier for cut-off of NTs
 - ? – passivation of DBs and/or catalysis have to change the zipping path



Molecular Mechanics Simulation

MM + MD was used to verify the result of phenomenological calculations. The main prediction is confirmed - the optimal sleeve radius is about 1.5 nm.



Conclusions

Continuum models provide valuable support to the simulation at the nanoscale.

A new physics appears in the model and parameters for continuum simulation have to be modified because of standard bulk models are no longer valid at nanoscale. Result of Continuum Modeling has to be verified by an atomistic simulation.

Conclusions

The scrolling mechanism for graphene clusters was studied. A rich structure of the equilibrium nanographites is found. The modeling revealed the specific length scale for graphite rolling transformation. A nano-curvature $\sim 2-3$ nm is common feature which displays at nano-, micro- and macroscale.

The model provides an explanation why layered systems (isostructural to graphite) form nanotubes and nanoarches at edges.