The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

International Atomic Energy Agency

SMR/1758-5

"Workshop on Ion Beam Studies of Nanomaterials: Synthesis, Modification and Characterization"

26 June - 1 July 2006

Using energetic ion beams to modify properties of carbon nanotubes

Kai Nordlund
Accelerator Laboratory
Dept. of Physical Sciences
University of Helsinki
Finland

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

CMS

Using energetic ion beams to modify properties of carbon nanotubes

A. V. Krasheninnikov, J. Kotakoski and Kai Nordlund

Accelerator Laboratory, Department of Physical Sciences

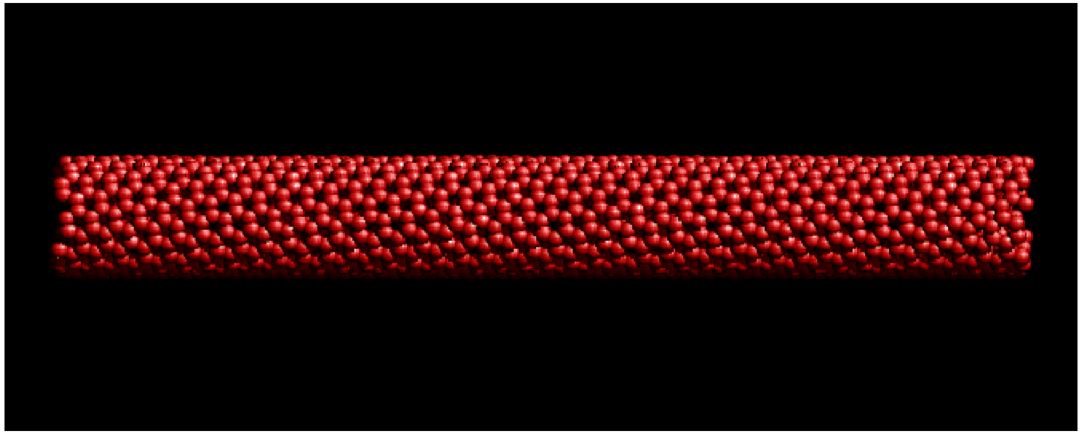
University of Helsinki, Finland

Contents

- Background: carbon nanotubes
- Basics of irradiation effects in nanotubes
- KMC model of irradiation of nanotubes
- Modifying electrical properties
- Welding of carbon nanotubes
- Using nanotubes as a high-pressure vessel

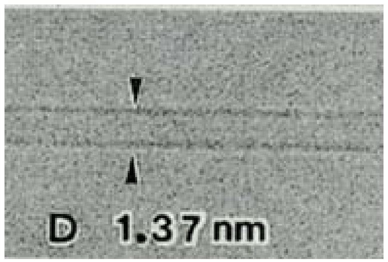
Background:
Carbon Nanotubes - What are they?

- Hollow tubes of pure carbon
  - "A graphene sheet rolled up to a cylinder"
  - Found in 1991 by Sumio Iijima

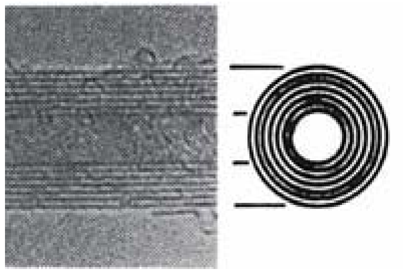


- Can be:

Single-walled

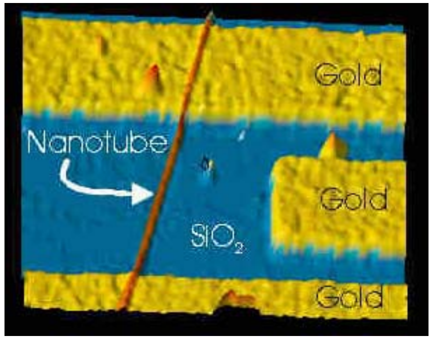


Multi-walled

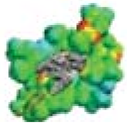


Background:
Carbon Nanotubes - Why are they interesting?

- They have outstanding properties:
  - Tensile strength and Youngs modulus unprecedented
  - Electronic properties intriguing: 1D conductor
  - Either metallic or semiconducting: can be used as electronic circuit components
  - Great light emission
  - Functionalizers for polymers
- Already have a wide range of applications
  - E.g. mechanical reinforcement of epoxies:



[Montreal sports Ltd, Finland]



Ion irradiation of carbon nanotubes

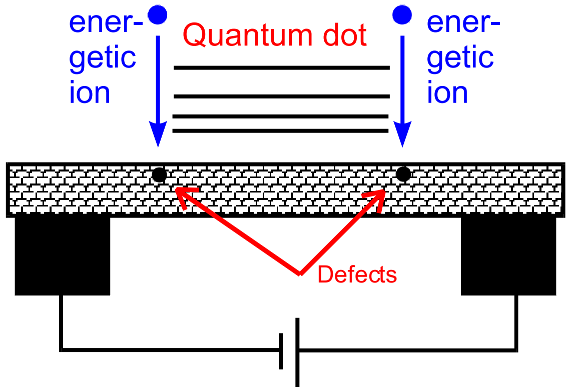
- Ion irradiation can also be used to modify nanostructures such as carbon nanotubes
- The potential benefits are the same as in usual materials:
  - Not limited by thermodynamics
  - Amount of material implanted can be well controlled
  - Penetration depth can be well controlled

- Since 2001 we have theoretically and now also experimentally studied how ion irradiation can be used to modify nanotubes in beneficial ways

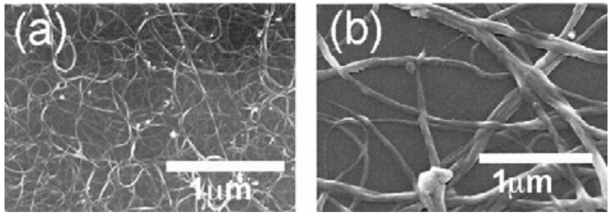
Literature examples of irradiating nanotubes

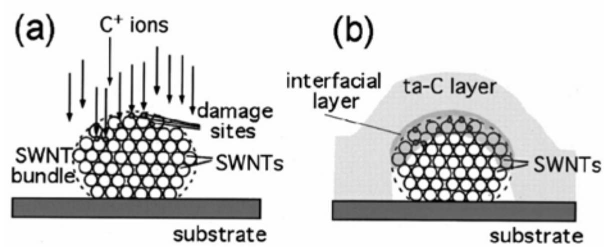
- Electronic transport in quasi-one-dimensional systems; irradiation defects work as tunneling barriers;

[M. Bockrath et al, Science 291 (2001) 283;
M. Suzuki *et al.,* Appl. Phys. Lett. 81 (2002), 2273]



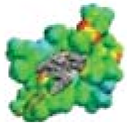
- Self-irradiation with 100 eV C^+ ions: nanotube-amorphous diamond composites;





[H. Schittenhelm, *et al.,* Appl. Phys. Lett. 81 (2002), 2097].

Main method: Molecular dynamics simulation algorithm



- Simulating atom motion:

Give atoms initial $\boldsymbol{r}^{(t=0)}$ and $\boldsymbol{v}^{(0)}$, choose short Δt

↓

Get forces $\boldsymbol{F} = -\nabla\, V(\boldsymbol{r}^{(i)})$ *or* $\boldsymbol{F} = \boldsymbol{F}(\Psi)$ and $\boldsymbol{a} = \boldsymbol{F}/m$

↓

Move atoms: $\boldsymbol{r}^{(i+1)} = \boldsymbol{r}^{(i)} + \boldsymbol{v}^{(i)}\Delta t + {}^{1}/_{2}\,\boldsymbol{a}\,\Delta t^{2}$ + correction terms

Update velocities: $\boldsymbol{v}^{(i+1)} = \boldsymbol{v}^{(i)} + \boldsymbol{a}\Delta t$ + correction terms

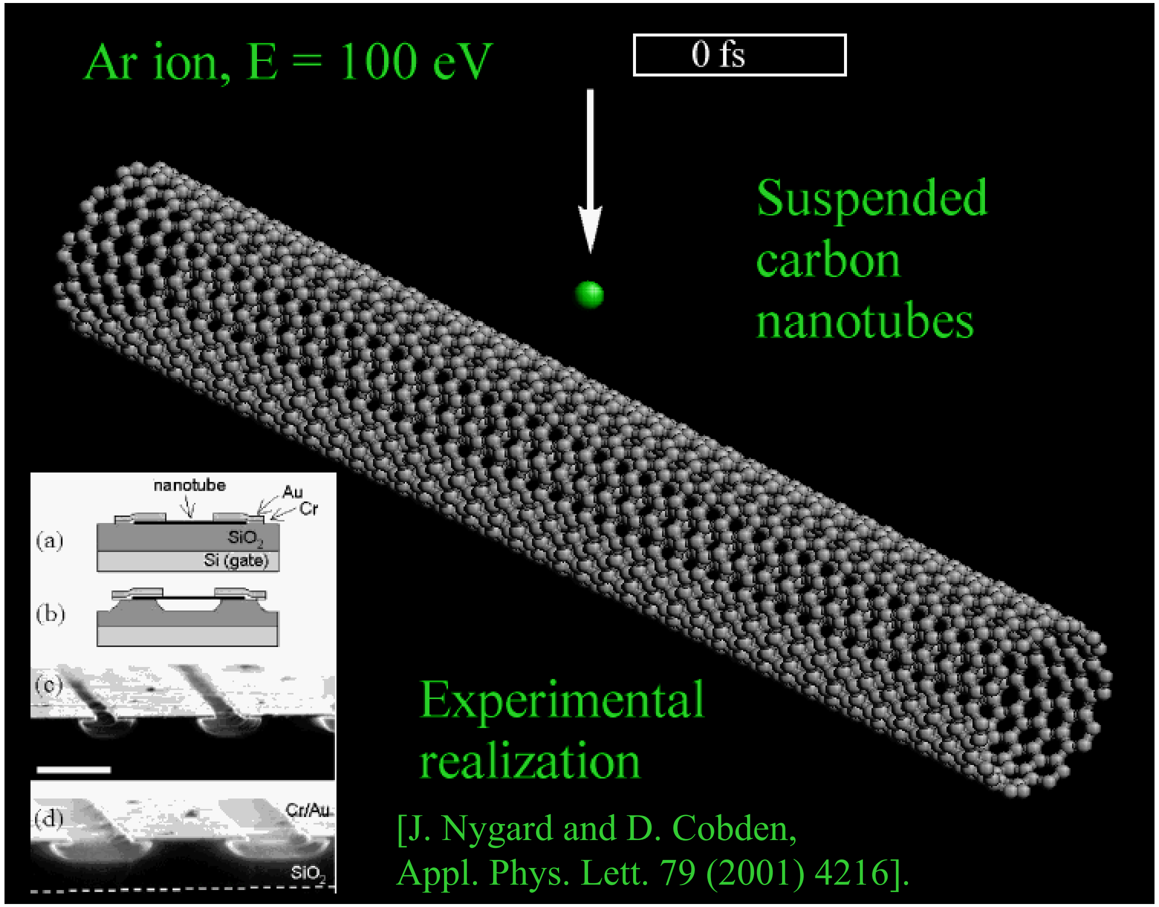
↓

Move time forward: $t = t + \Delta t$

↓

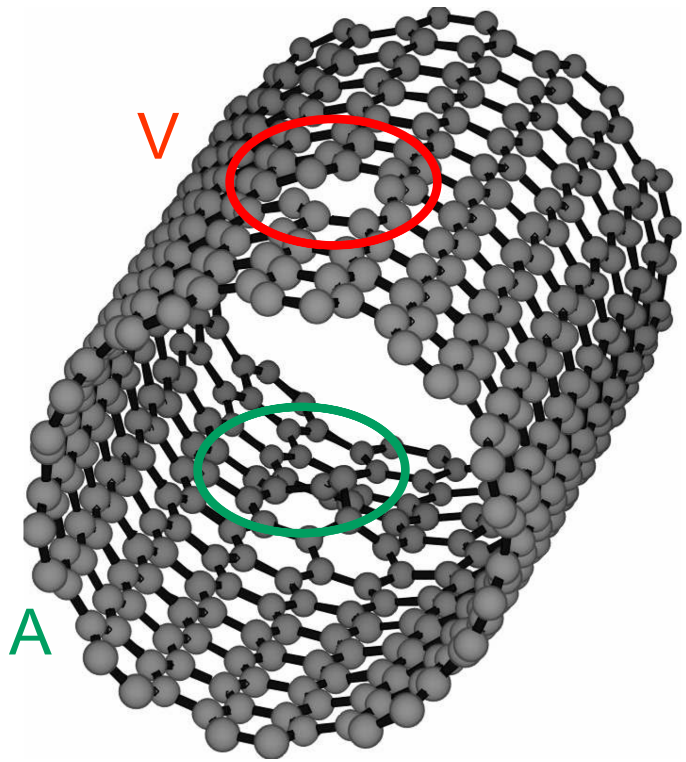
Repeat as long as you need (loop back to "Get forces")

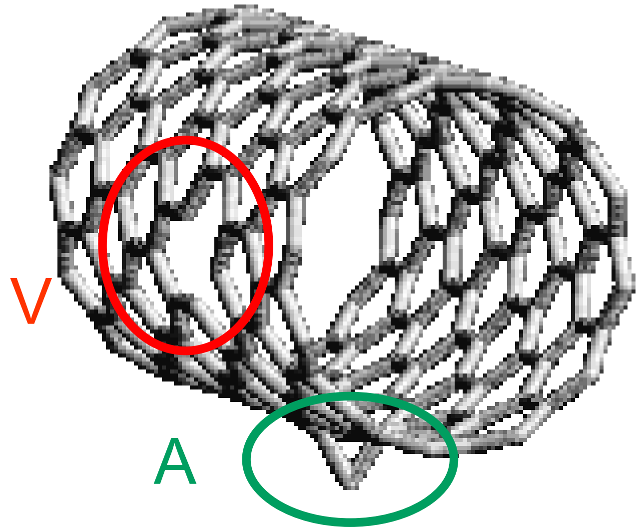
Ion irradiation of a single nanotube



[A. V. Krasheninnikov *et al*., Phys. Rev. B 63 (2001) 245405]

Ion irradiation-induced defects in nanotubes

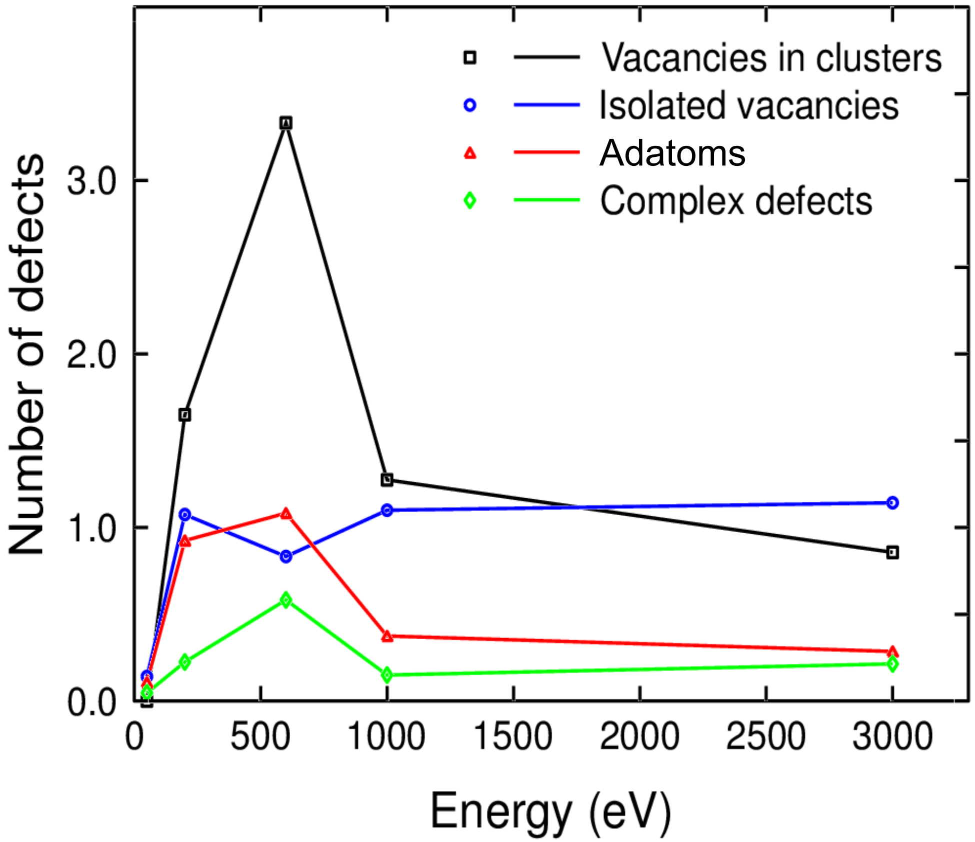




- The most abundant defects in SWNTs are vacancies.

- Carbon atoms absorbed on nanotube walls (adatoms) play the role of interstitials.

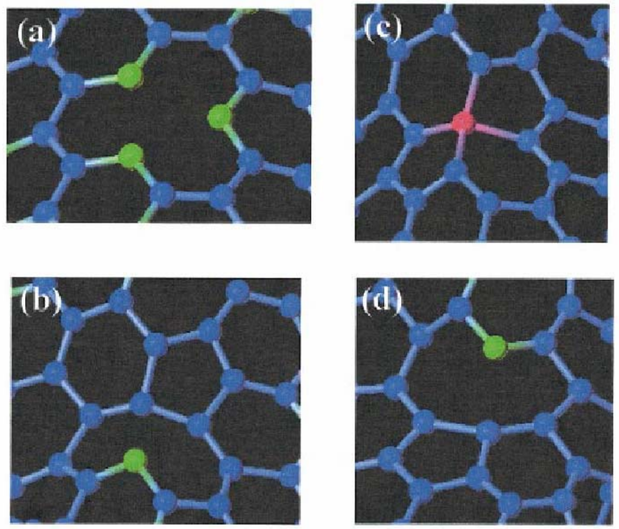
Defect production in single nanotubes



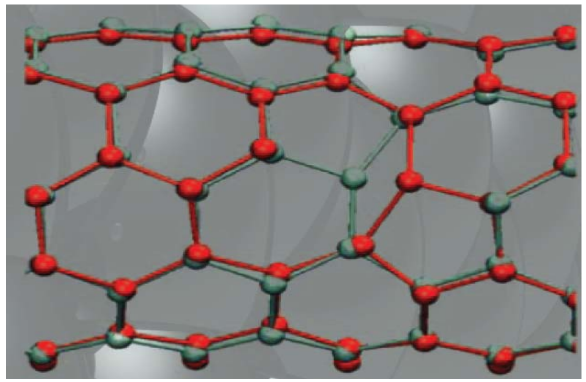
[Krasheninnikov *et al.,* PRB **63**, 245405 (2001)]

Defect migration: vacancy

- (a) is the 'normal' vacancy configuration obtained by removing an atom
- Configuration (b) is the ground-state configuration
- (c) is a metastable state with no dangling bonds but high strain energy
- The vacancy can migrate by switching between states (b) and (c)
- Migration energy fairly high, >= 1 eV
  - But low enough for room T mobility

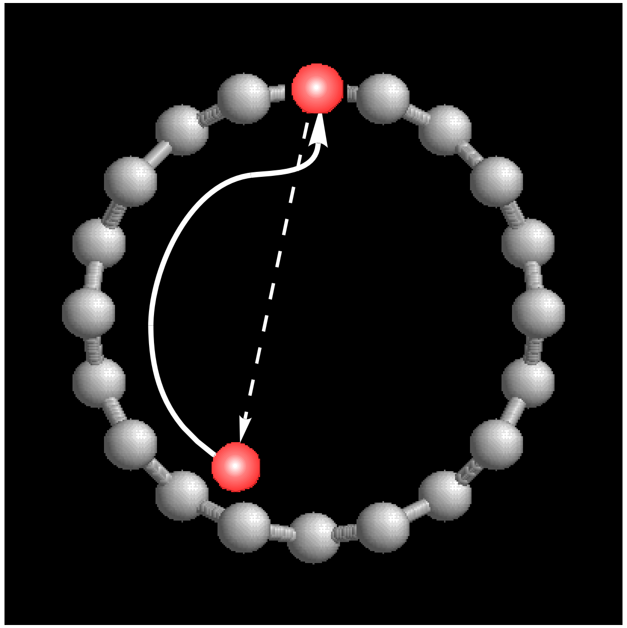


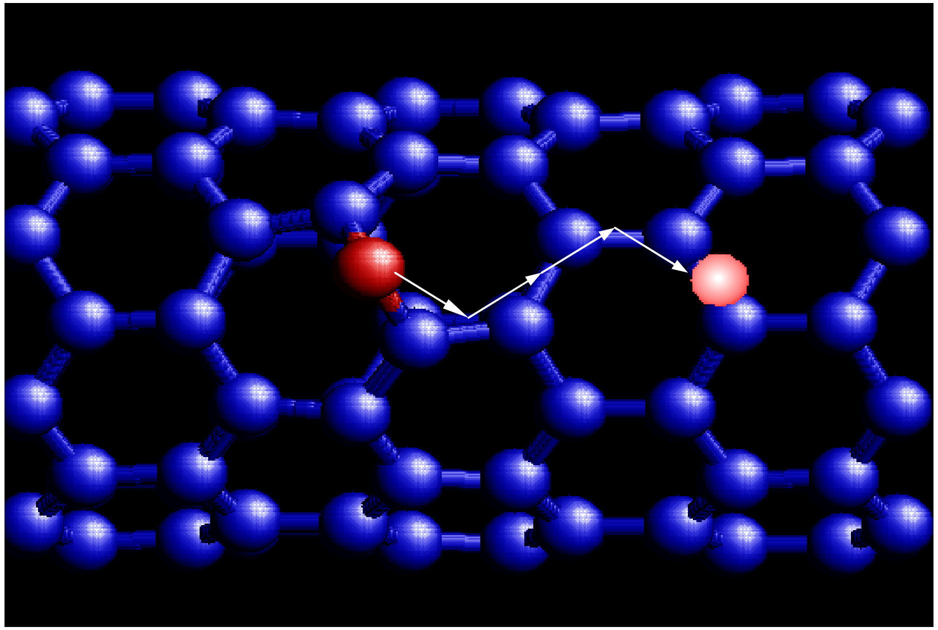
[P.M. Ajayan_*et al.*, Phys. Rev. Lett. 81 (1998) 1437]



[Krasheninnikov et al, Chem. Phys. Lett 418, 132-138 (2006)]

Interstitial/adatom migration

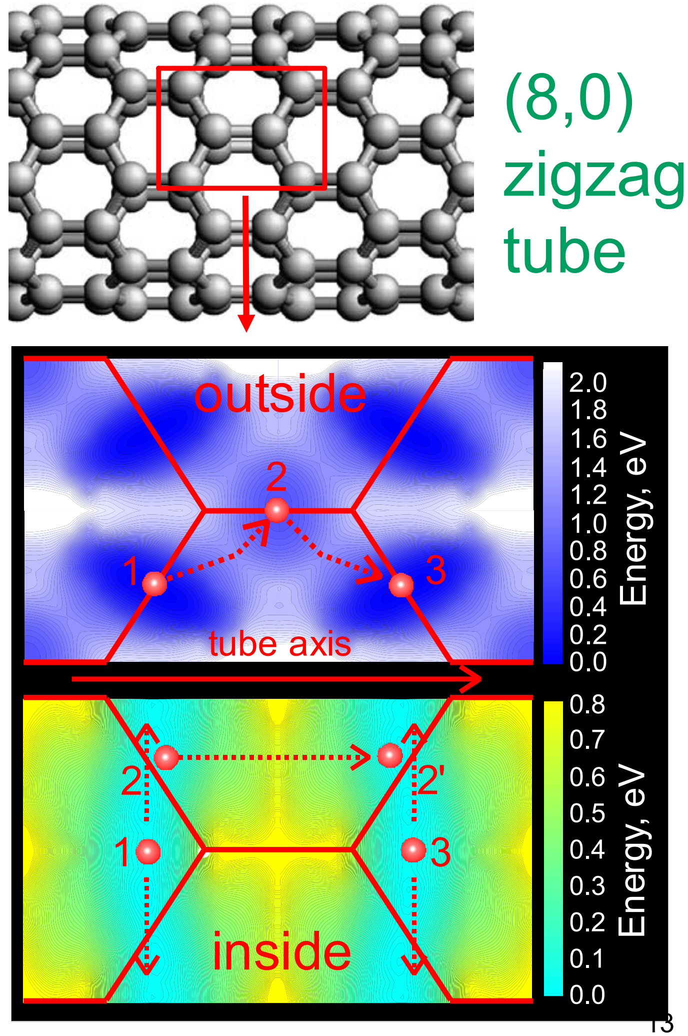




- Knowing adatom migration mechanisms is vitally important for understanding damage annealing!

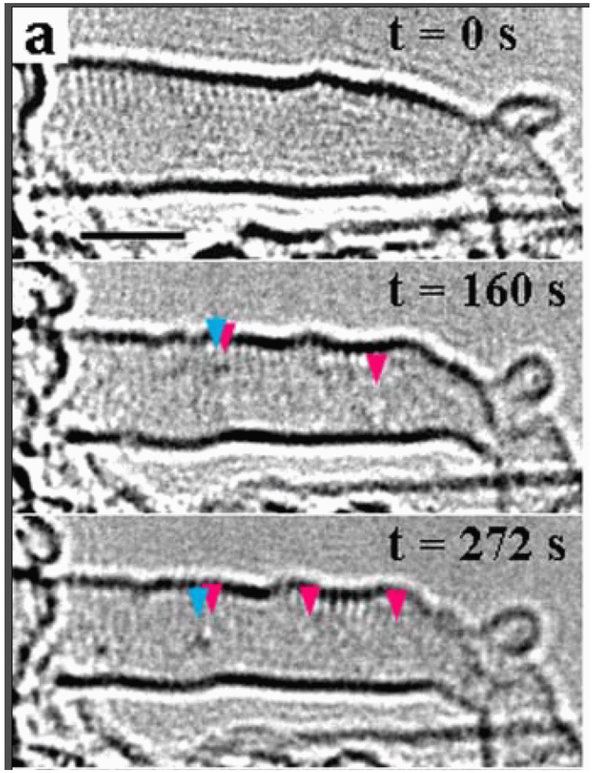
Interstitial (adatom) migration

- We have simulated adatom (interstitial) migration using TB and DFT methods
- It turns out that both the migration mechanism and activation energy is strongly dependent on the nanotube diameter and chirality
- For instance in a (8,0) zigzag tube:
  - E_m outside tube 0.8 eV
  - E_m inside tube 0.1(!) eV (⊥ to tube axis)
  - E_m inside tube 0.4 eV (|| to tube axis)



Experimental confirmation!?

- Our results on defect production and migration can be summarized as:
  - Interstitials migrate very fast
  - Vacancies migrate at room T, and form larger vacancy complexes which are immobile
- This has been confirmed experimentally!?
  - Sumio Iijimas group observed single adatoms and small vacancy clusters in electron-irradiated nanotube-like graphene sheets and *said that* they saw directly that adatoms move rapidly at room T, while the vacancy clusters are immobile



[Kimura-Hashimoto *et al*, Nature **430** (2004) 870]

Kinetic Monte Carlo model for defects in carbon nanotubes

- But how about the long-term migration (like that seen in the experiments of Iijima)
  - Molecular dynamics can be only used on nanosecond time scales
  - One would want to simulate the defect behaviour for macroscopic times

- Method of choice: Kinetic Monte Carlo
- Requires as input rates of defect migration
  - But these can be determined from tight-binding or density-functional theory calculations!

Method to simulate defect migration: Kinetic Monte Carlo algorithm

- Simulates time evolution of a set of processes i with known rates r_i
  - Rates can be anything, but typically diffusion-like: $r = r_0 e^{-\Delta E/kT}$

Form a list of all N possible transitions i in the system with rates r_i

↓

Calculate the cumulative function $R_i = \sum_{j=i}^{i} r_j$ for all $i=0,\ldots,N$

↓

Find a random number u_1 in the interval [0,1]

Carry out the event for which $R_{i-1} < uR < R_i$

↓

Move time forward: $t = t - \log u_2/R_N$ where u_2 random in [0,1]

↓

Figure out possible changes in r_i and N, then repeat

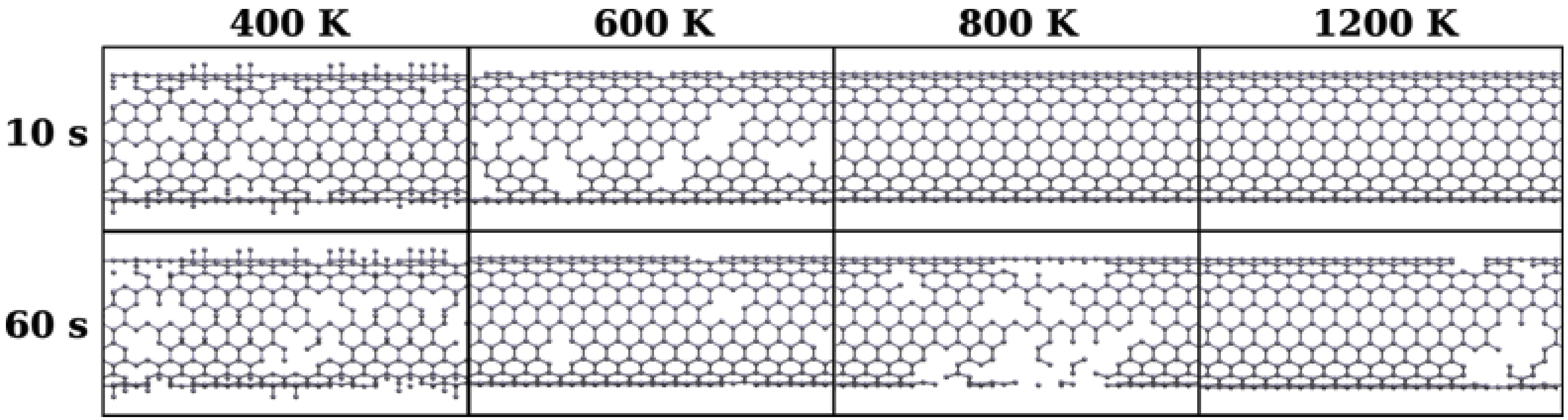
(→ back to the first step)

Determining rates for defects in nanotubes

- The migration barriers and hence rates can be determined from the DFT and TB calculations described above
- However, to obtain a full picture one needs data for all relevant migration mechanisms and defects
- We are collecting data systematically for
  - Vacancies: V, V_2, V_3, $V_{4,}$ …
  - Interstitials: I, I_2, I_3, $I_{4,}$ …
  - In- and out-of-plane migration mechanisms
  - Coalescence reactions of like defects
  - Annihilation reactions for unlike defects

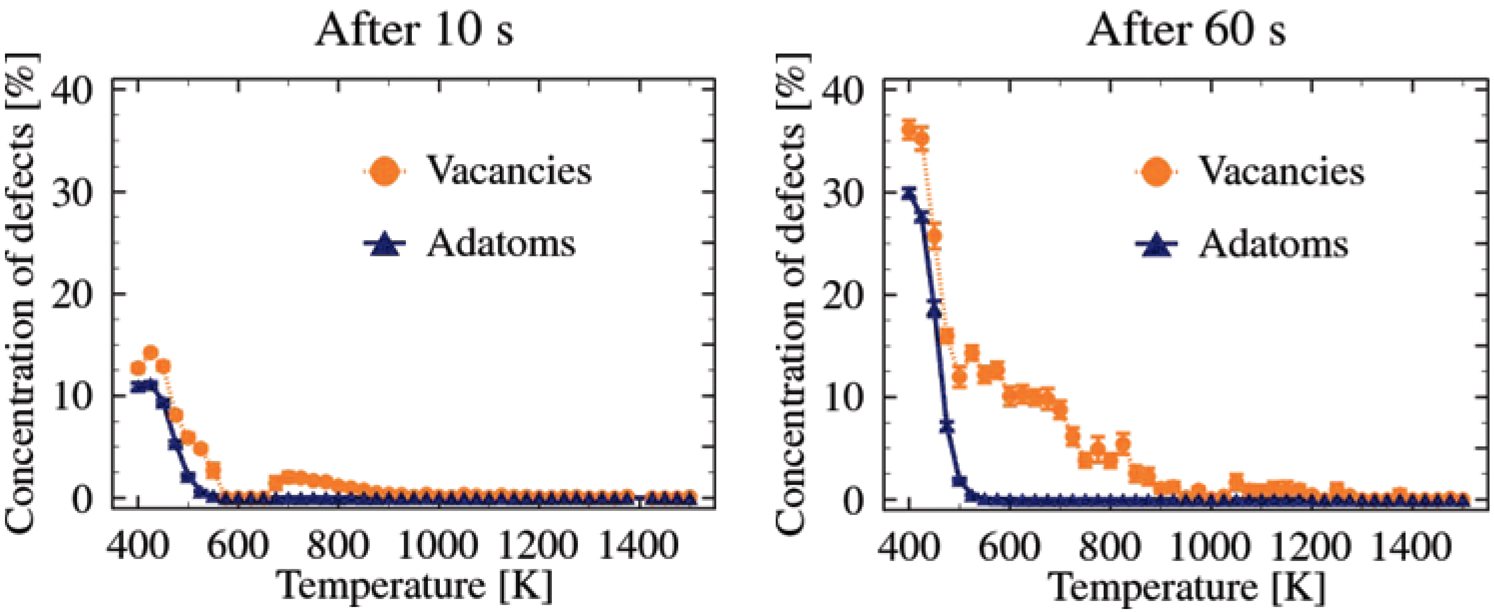
Results from KMC simulations

- Snapshots of a (10,10) SWCNT after 10 s and 60s of electron irradiation at temperatures of 400 K, 600 K, 800 K and 1200 K.



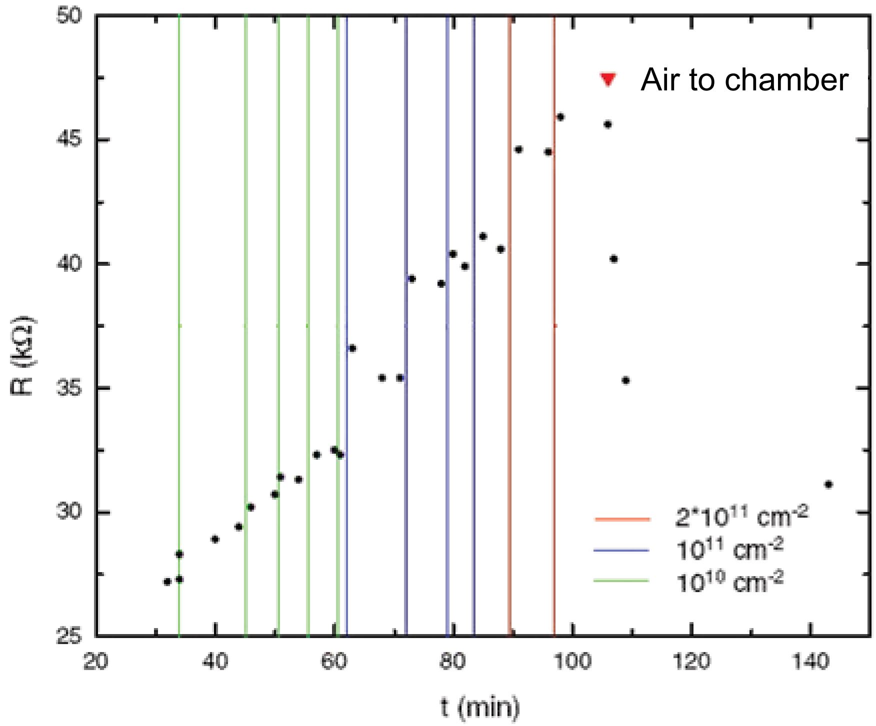
Quantitative results from KMC simulations

- Defect concentrations after 10 s and 60 s of electron irradiation as a function of the temperature:



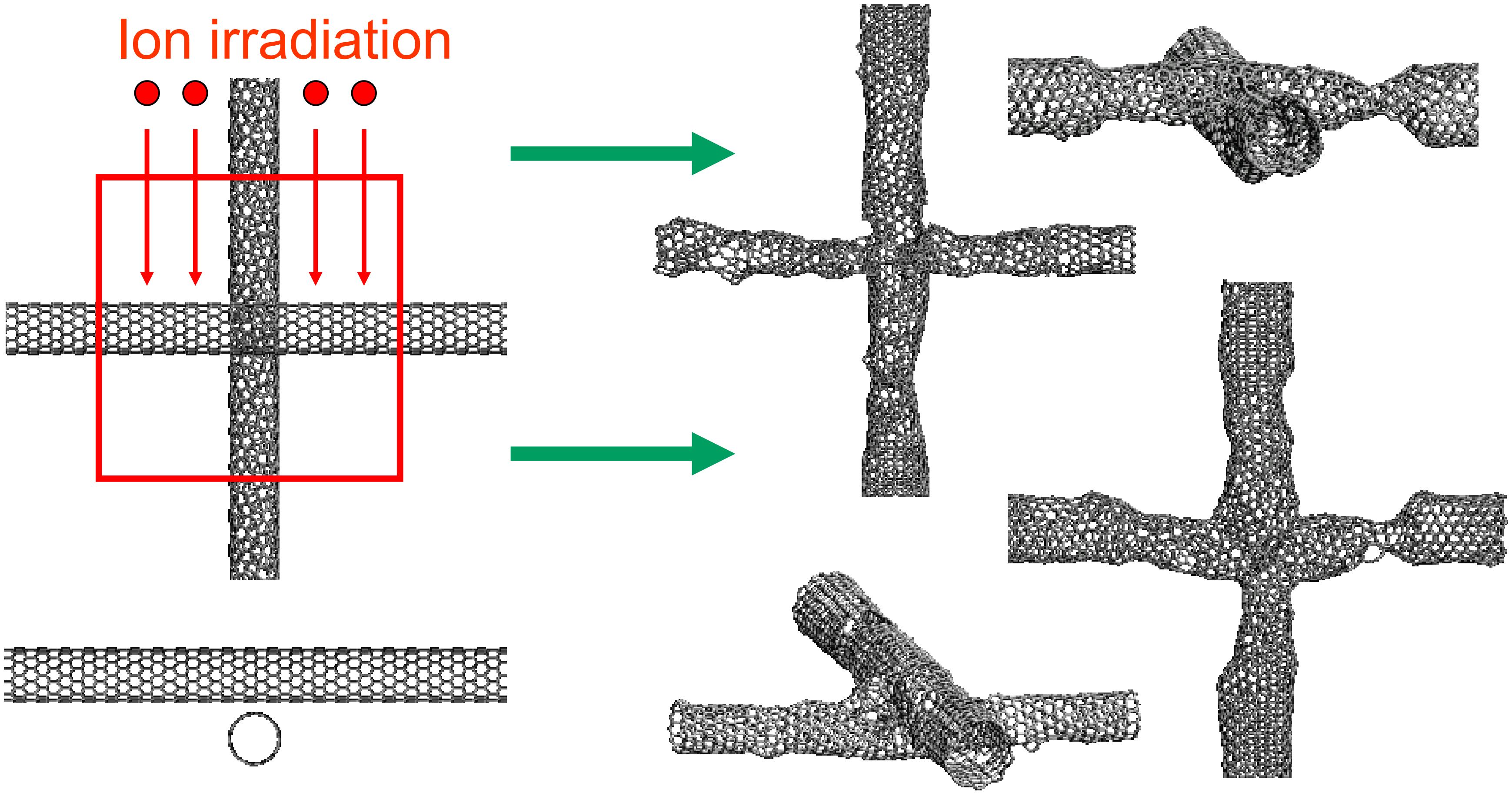
Electrical effects of ion irradiation

- We are now looking at the effects of the irradiation of single multiwalled tubes on the electrical conductivity
- Green lines: on average one ion hits the tube
  - Note that between some doses no effect => no hit
- Single-ion effects!!



[R. Tarkiainen, F. Wu, P. Hakonen, K. Arstila, K. Nordlund, J. Keinonen, to be published]

Applications: welding of nanotubes

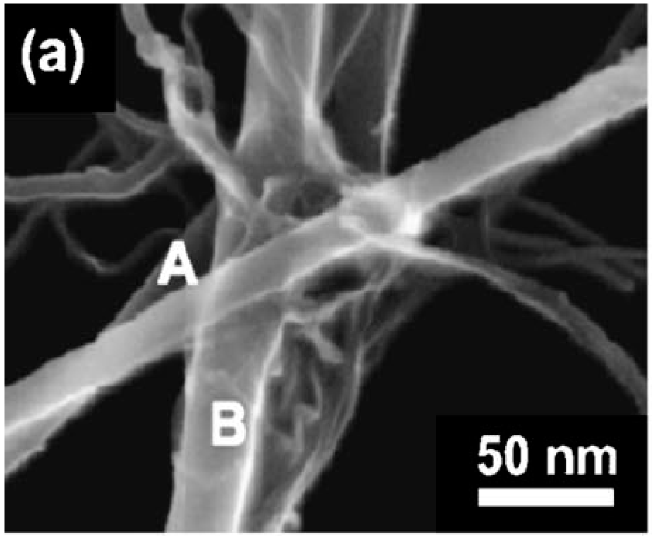


[Krasheninnikov *et al.* Phys. Rev. B 66 (2002) 245403.]

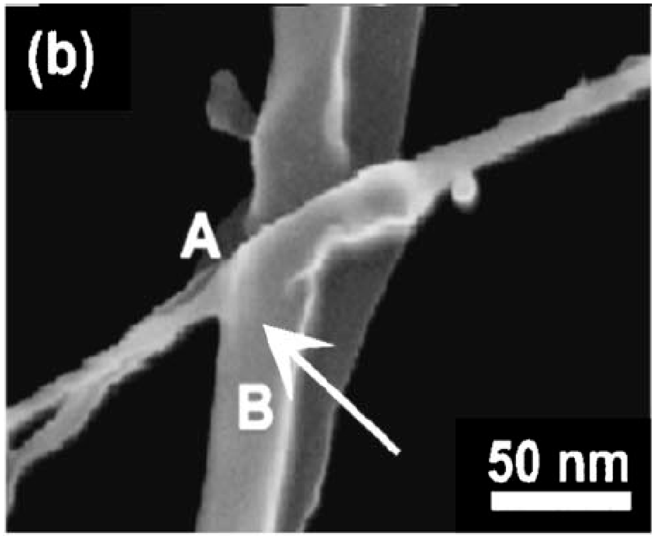
Experimental confirmation of welding

- Raghuveer et al [APL 84 (2004) 4484] have done this experimentally:

Before irradiation

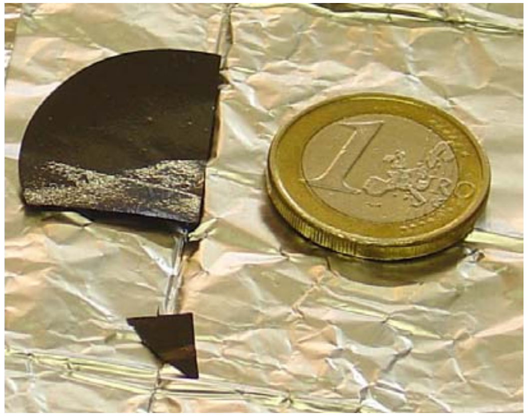


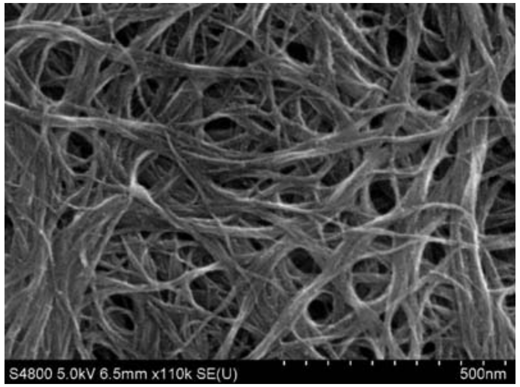
After 10^{16} Ga^{+} ions/cm^2



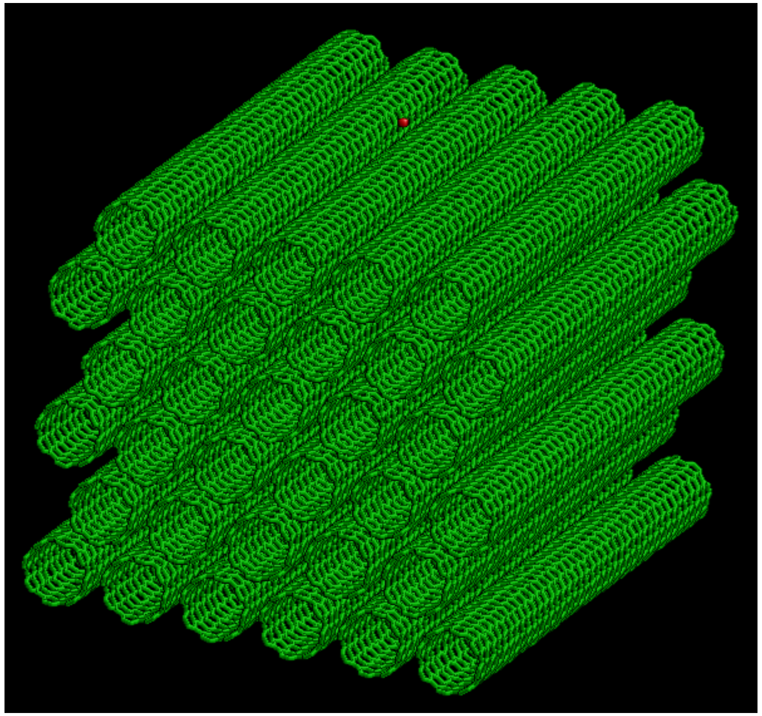
Strengthening nanotube paper

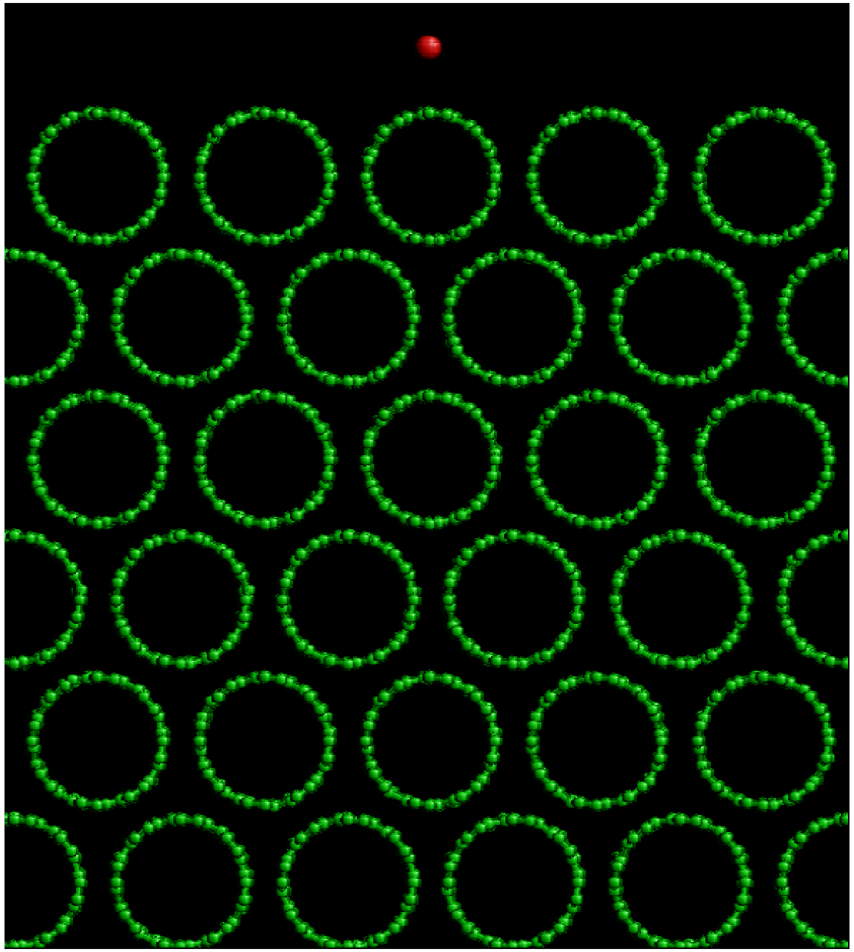
- Ordinary paper consists of fibers in a mat-like configuration
- It is possible to manufacture paper using nanotubes as the fibers
  - This product is sold commercially:
- It consists of bundles of nanotubes in a fiber network
  - But their stiffness is not very high
- We examined whether irradiation can be used to strengthen it





Strengthening of nanotube paper, 1.



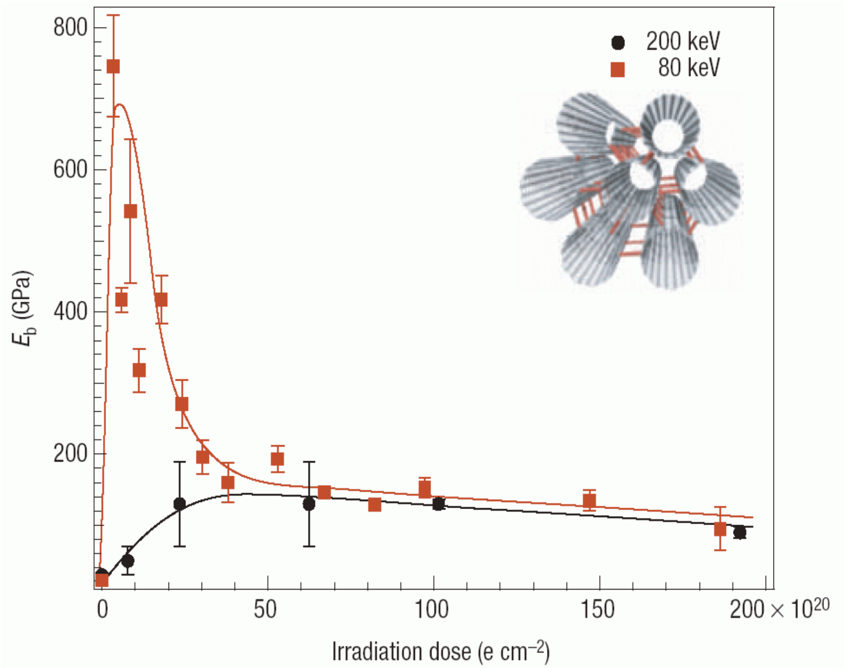


- Irradiation can introduce bonds between nanotubes

[Salonen et al, NIMB 193 (2002) 608]

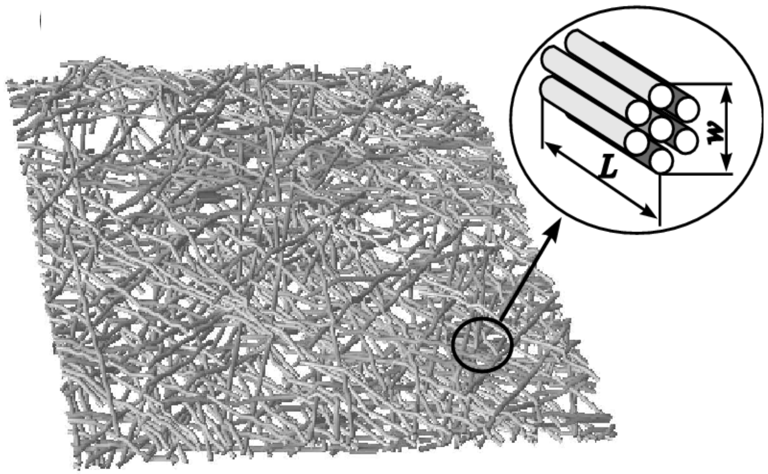
Experimental confirmation

- A similar effect has been observed for electron irradiation, and shown to strengthen the nanotube paper [Kis et al, Nature Materials 3 (2004) 153]



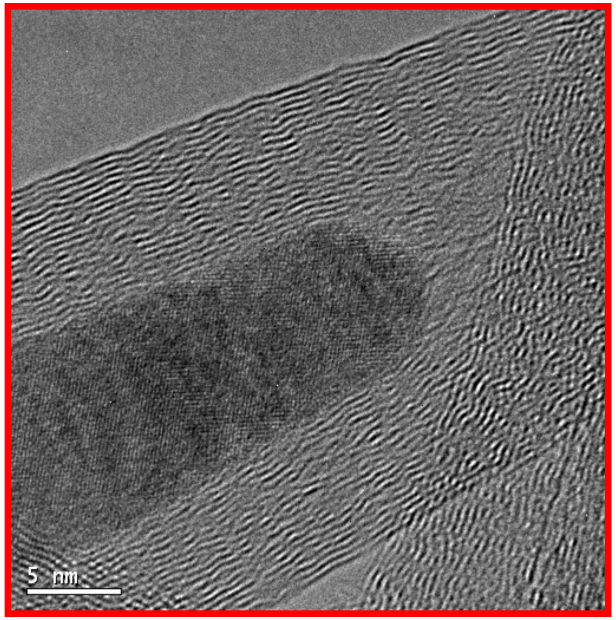
Strengthening of nanotube paper, 2.

- We constructed a fiber network effective medium theory model of nanotube paper
- The model has a parameter which corresponds to the strength of intertube links
- With van der Waals interactions only:
  - Stiffness ~ 1 Gpa
- With irradiation-induced covalent bonds
  - Stiffness ~ 100 GPa!



Irradiation-induced structural transformations in carbon nanotubes encapsulated with metals

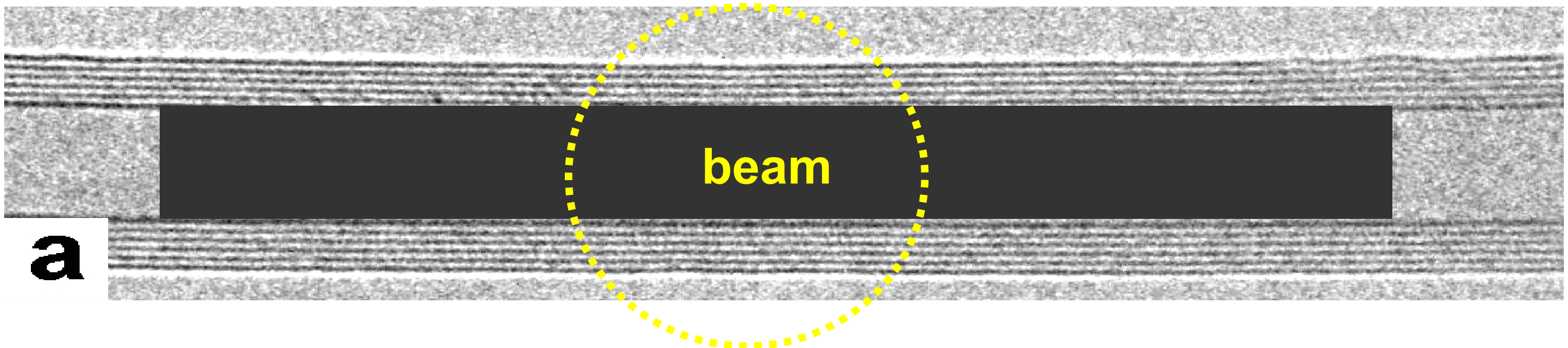
- Experimental co-workers:
  - Florian Banhart, Universität Mainz, Germany (experiment)
  - Pulikel Ajayan, Rensselaer Polytechnic Institute, USA (experiment)
  - Mauricio Terrones, IPYCT, Mexico (experiment)



[L. Sun, F. Banhart, A. V. Krasheninnikov et al, Science 312 (2006) 1199]

Nanotubes encapsulated with metals

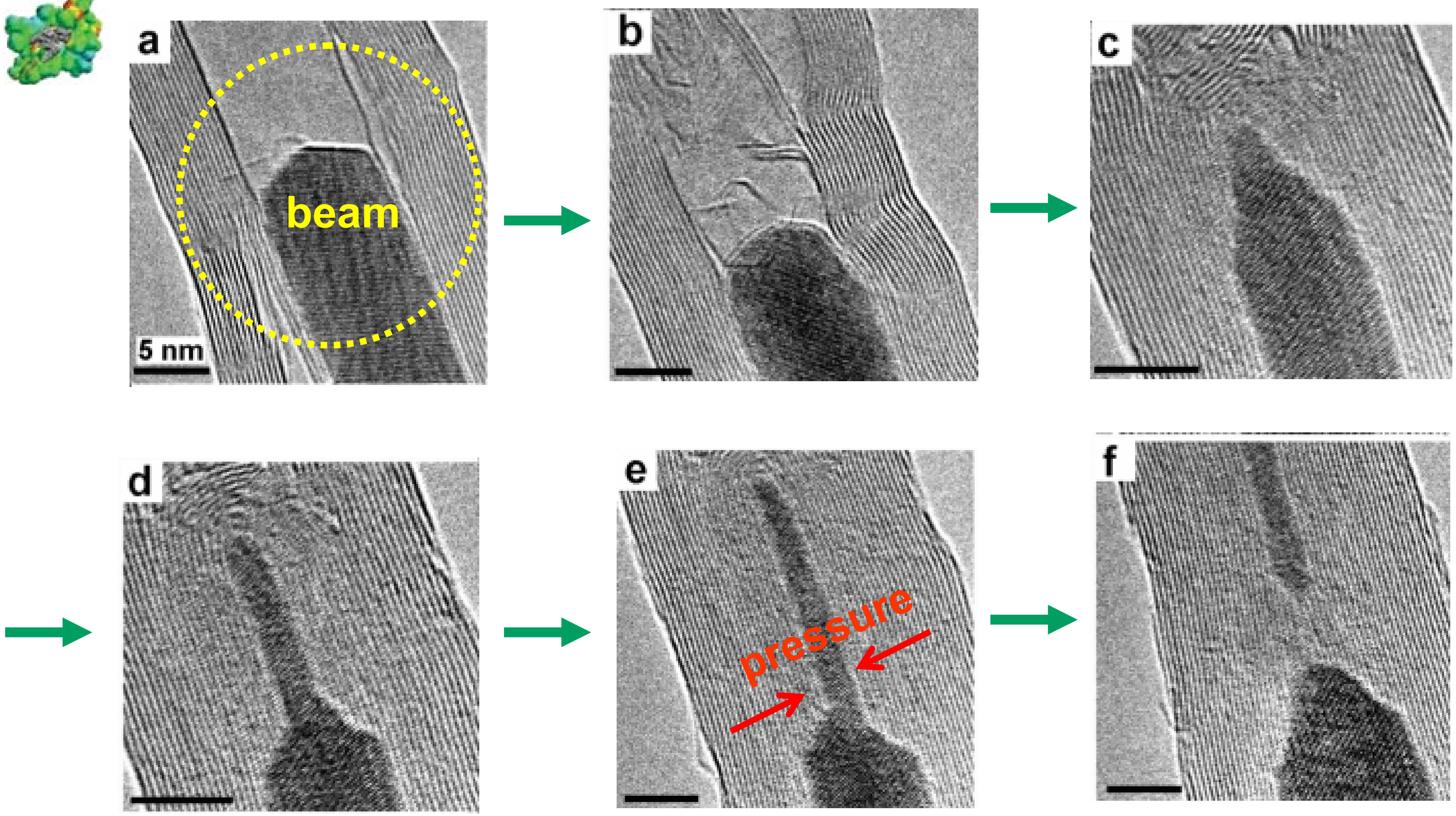
- If we have something (metal) inside nanotubes,



E = 300 keV
j = 450 A/cm^2
T = 600ºC

... and we electron irradiate the system at high temperature, what happens?

Answer: irradiation of nanotubes filled with Fe_3C [experiments by F. Banhart]

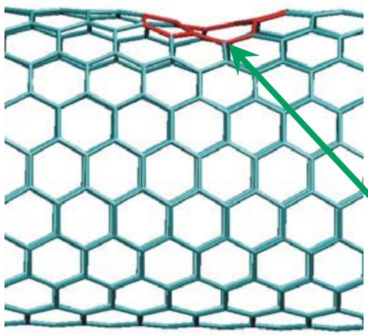


Contracting shells exert pressure on the tube interior!

Origin of the pressure: Nanotube atomic network with double vacancies

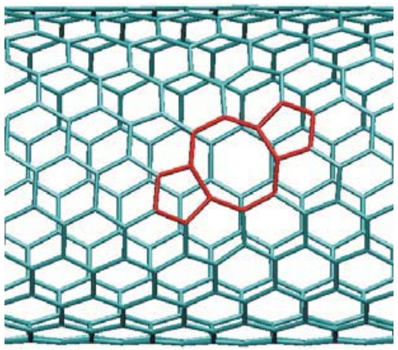
<u>Individual divacancy</u>

Side view



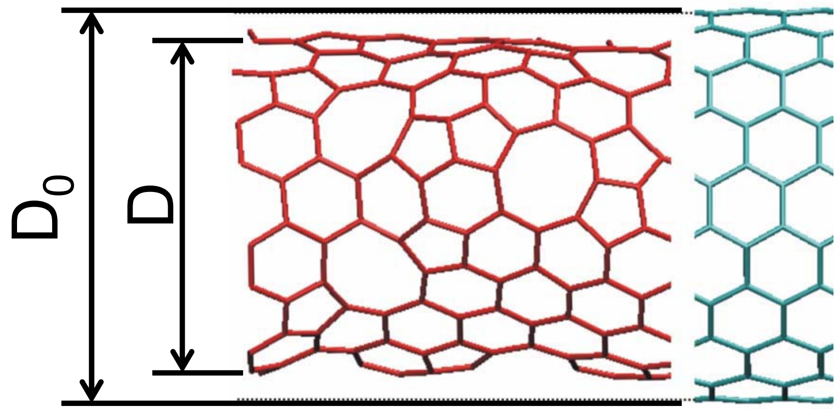
Local decrease in the diameter

Top view

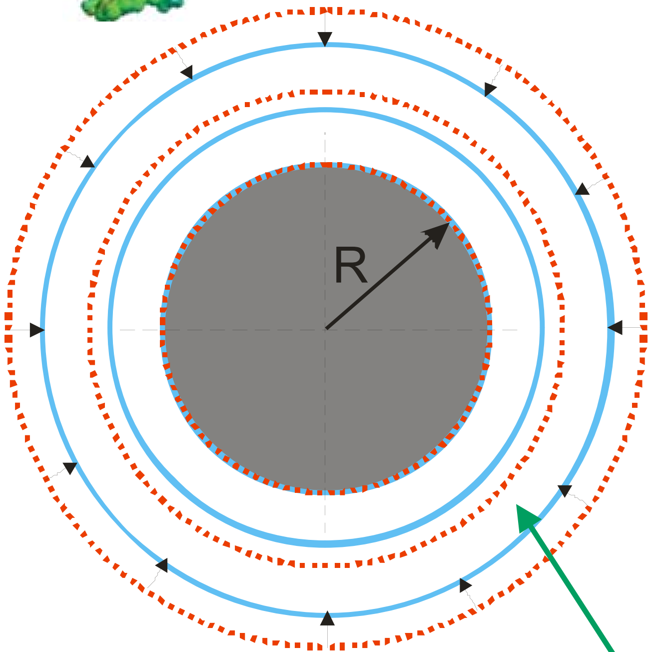


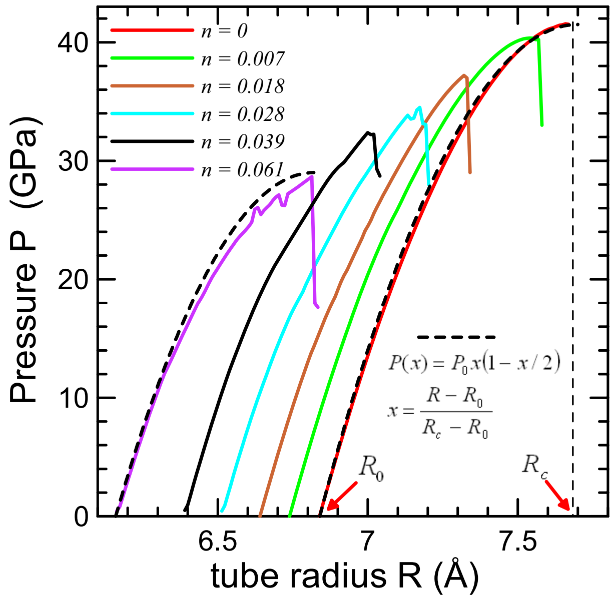
<u>Many divacancies</u>

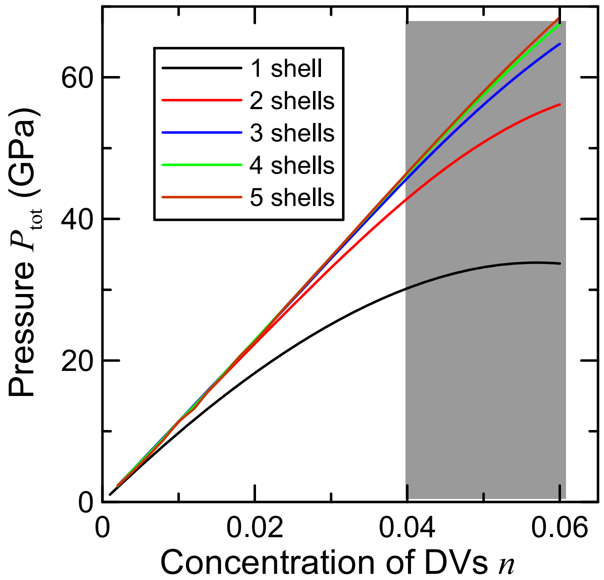
Diameter decreases!



The origin of the pressure and the maximum pressure







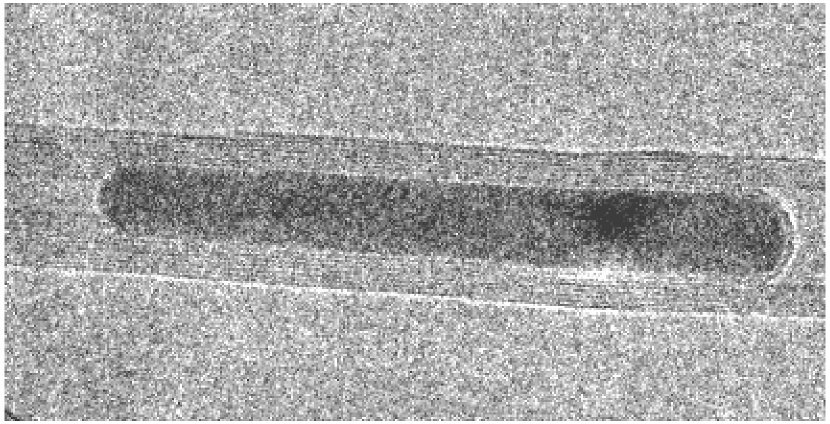
Van der Waals interaction between shells

Elasticity theory with the parameters derived from atomistic (DFTB) simulations

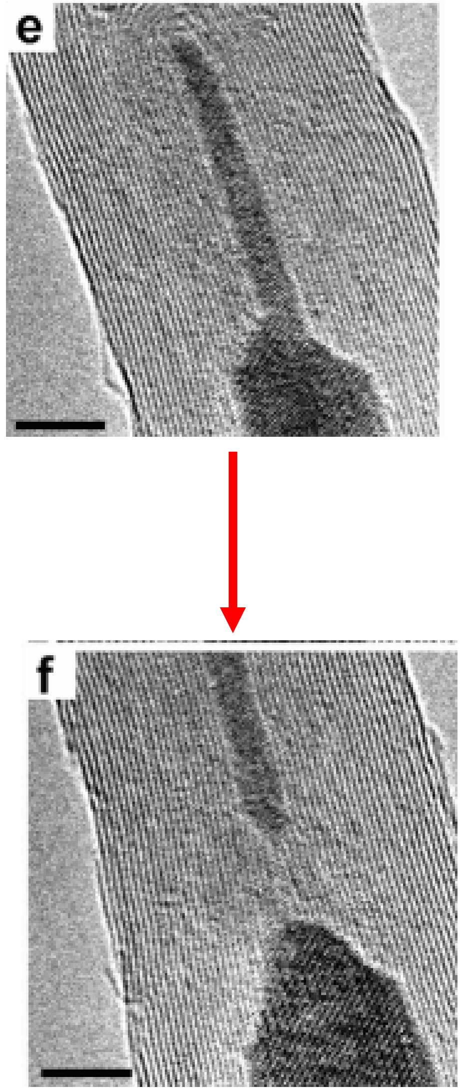
Contracting shells exert high pressure (~40 GPa) on the tube interior!

Transformations of the metal rod inside contracting nanotubes

Experiment:

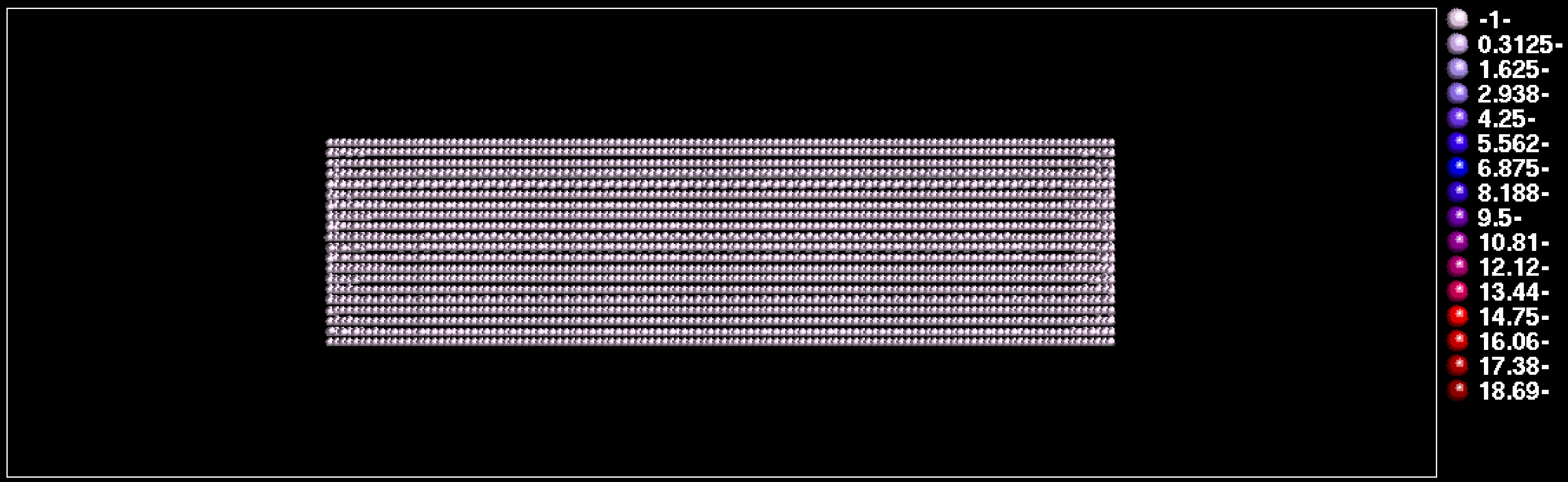


Courtesy of F. Banhart and M. Terrones



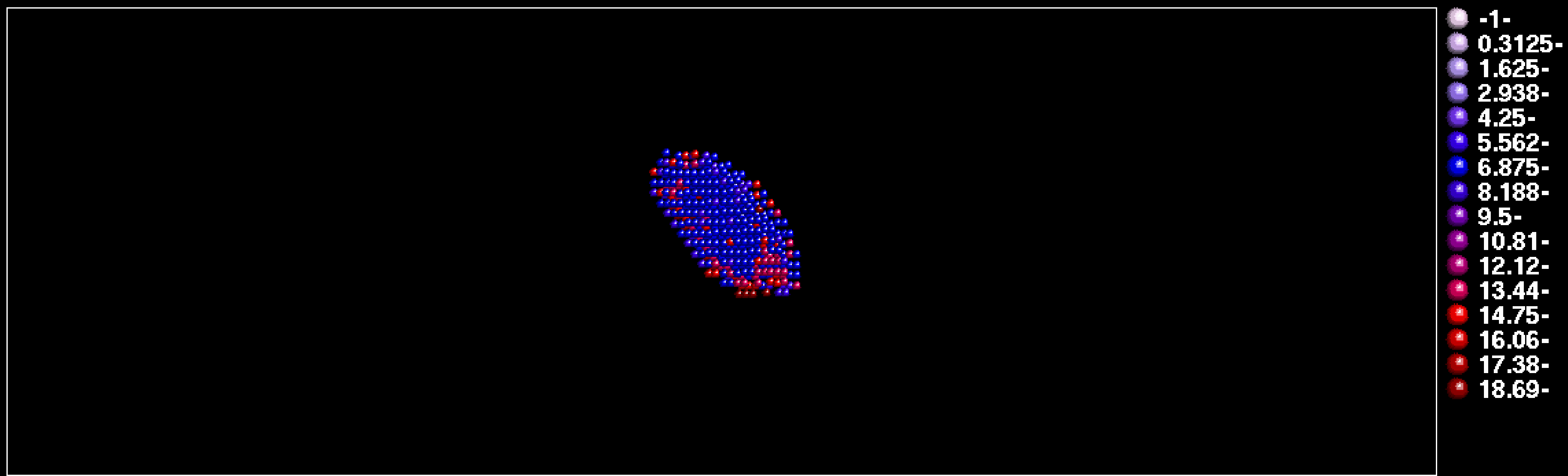
Our simulations show this is explained by dislocations

time 4.27



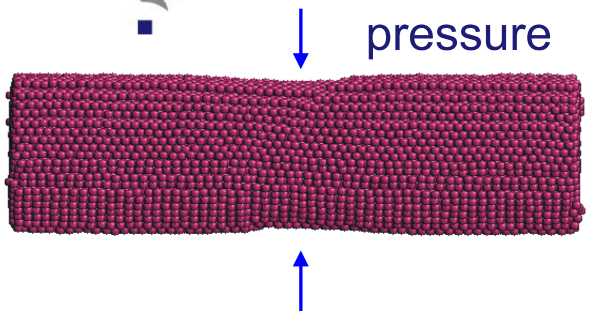
x (-150 - 150) y (-50 - 50) z (-22.75 - 22.756)

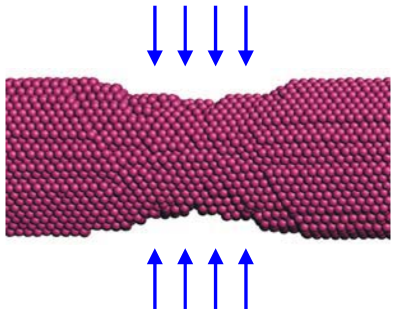
time 9e+04



x (-150 - 150) y (-50 - 50) z (-16.024 - 19.387)

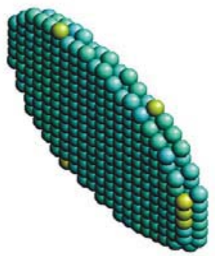
Detailed analysis of the dislocation activity





T = 0 K

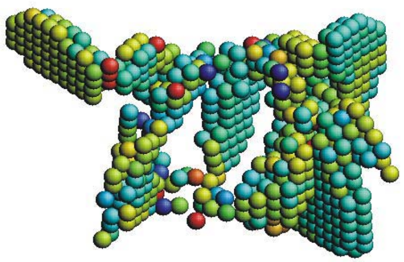
T = 873 K



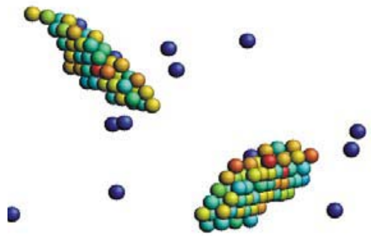
t=0.25ns

t=0.25ns

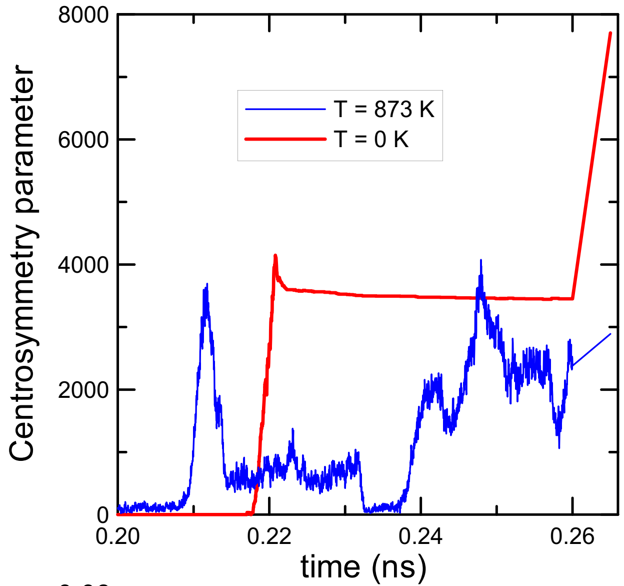
<1-21>

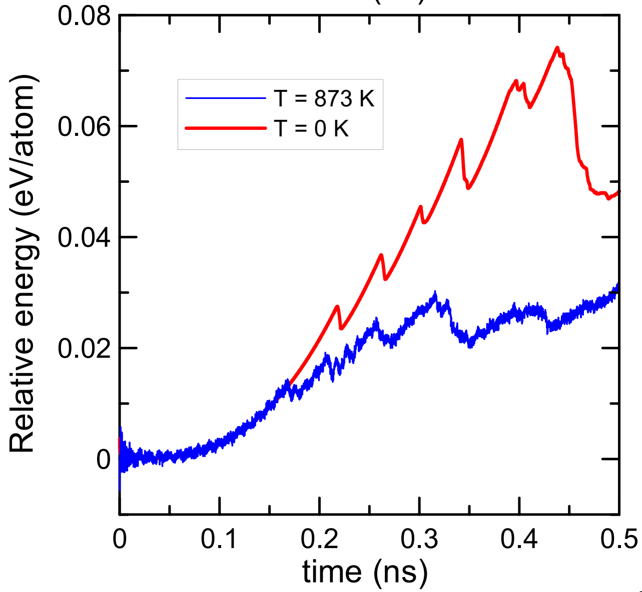


t=0.5ns



t=0.5ns

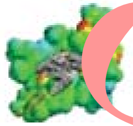




Conclusions

- Ion irradiation can be used to modify nanotube-surroundings interactions in interesting and potentially useful ways

The guilty parties



University of Helsinki

Arkady Krasheninnikov

Emppu Salonen

Jani Kotakoski

Jens Pomoell

Antti Kuronen

Juhani Keinonen

Kai Nordlund

Helsinki Univ. Techn.

Risto Nieminen

Adam Foster

Petri Lehtinen

Yuchen Ma

Kimmo Kaski

Maria Sammalkorpi

CSC, Finland

Jan Åström

Mainz

Florian Banhart

Litao Sun

Great thanks to them all!