Controlled healing of graphene nanopore

Konstantin Zakharchenko
Alexander Balatsky
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Zakharchenko K.V., Balatsky A.V. Controlled healing of graphene nanopore. Carbon (80), December 2014, pp. 12–18.
http://dx.doi.org/10.1016/j.carbon.2014.07.085

Outline

- Introduction – how can we study graphene
  - Empirical potential and Monte Carlo simulations
- Graphene nanopores
  - Applications and limitations
- Re-growth/healing of nanopores
  - Mechanisms
  - Quality

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Motivation

- Graphene is a material with many exceptional properties:
  - Electronic, optical, structural, mechanical, …
  - Simplest 2D membrane (and also 2D crystal)
  - Natural benchmark of physics in 2D
  - etc…

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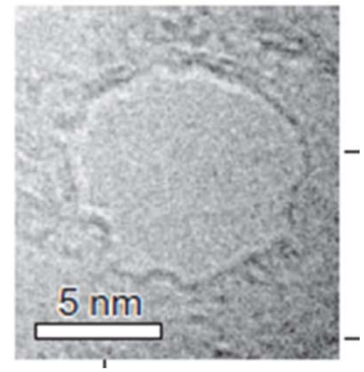
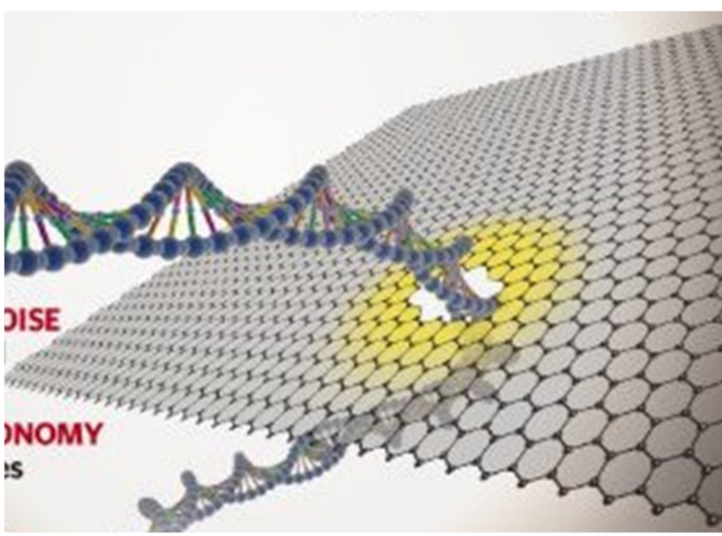
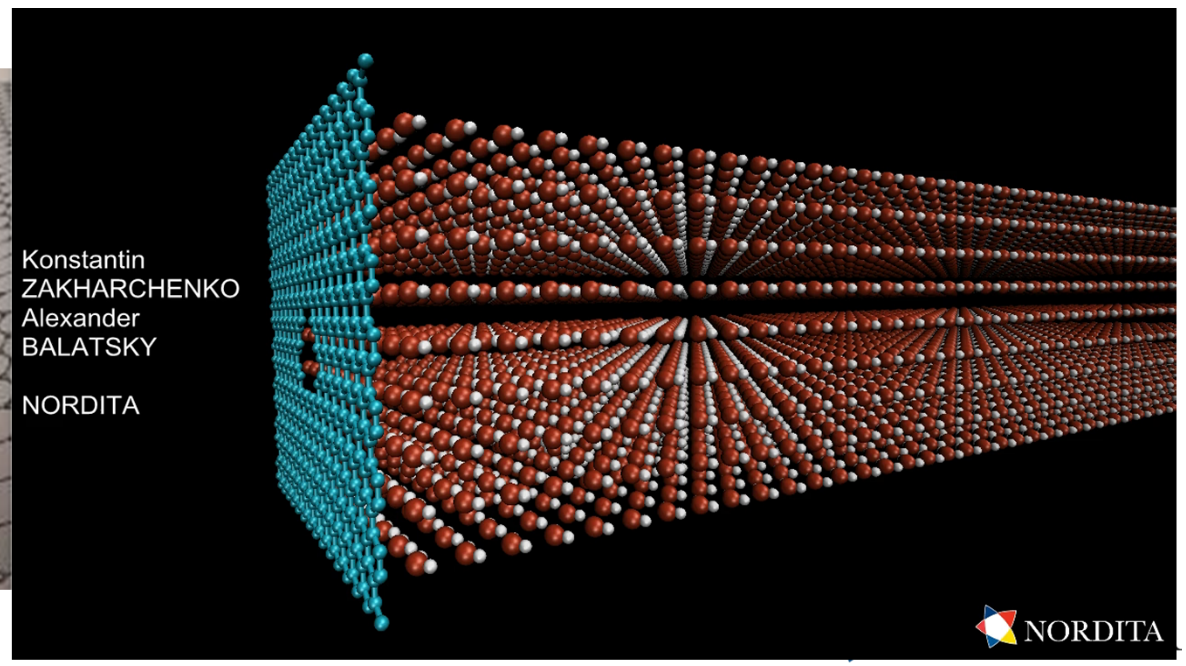
Motivation

- Graphene nanopores – practical interest:
  - DNA sequencing
  - Molecule detection
  - Sensing and biosensing
  - Water filtration & desalination
  - etc…

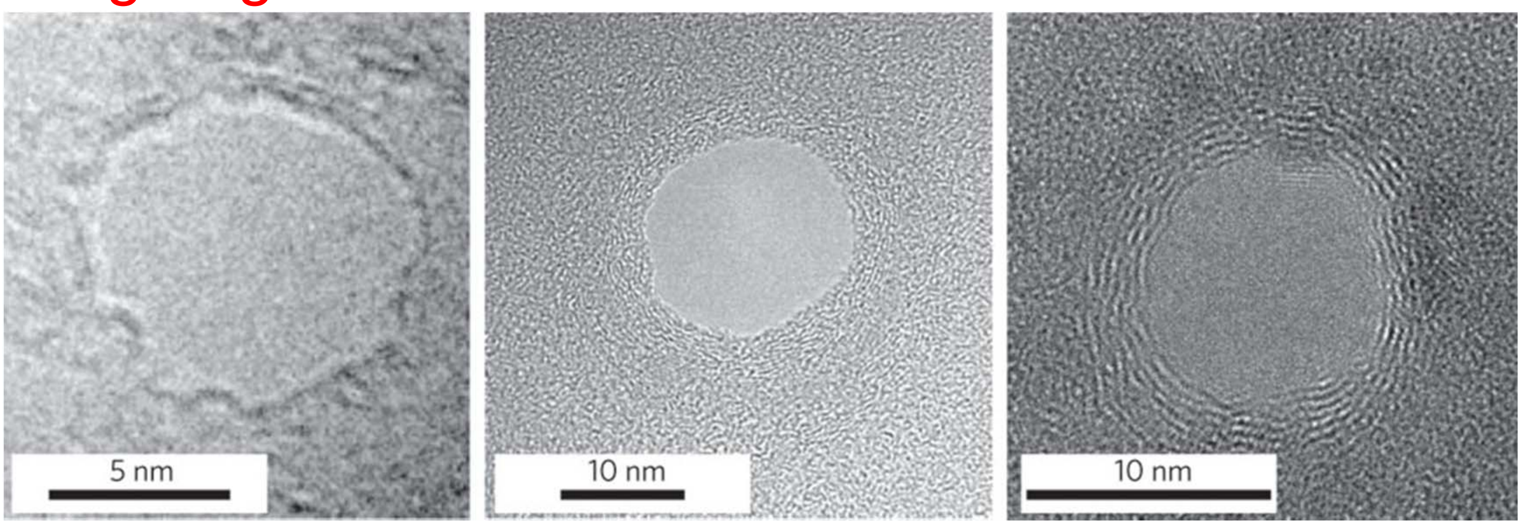






Motivation

- Fabrication technologies (electron beam drilling, etc…) limit minimal nanopore size: 2-5 nm
- Different applications require different pore sizes: 0.5-3 nm
- Size of nanopore affects performance of nanodevices
- If fabricated nanopore is too big → healing/re-growth is needed



Garaj et all, *Nature* 467, 190-194 (2010).

Modelling problems

Numerical simulations

- Many properties can be studied with numerical simulations (Molecular Dynamics, Monte Carlo):
  - Structure, transitions, mechanical properties, etc…
- Quantum calculations →
  - *Hundreds of atoms*
  - *Low temperature*
- Empirical potentials to describe interactions between atoms + MC/MD →
  - **tens of thousand atoms + any finite temperature!**

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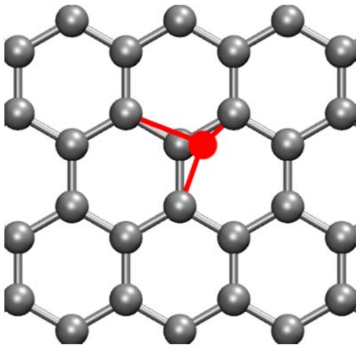
Monte Carlo simulations

- **Monte Carlo** computer simulations to find equilibrium structure of 'many' carbon atoms:
  1. Take initial configuration
  2. Two types of moves
     1. move randomly one atom
     2. vary the box size (in NPT simulations)
  3. Recalculate the energy, accept or reject the move according to Boltzmann distribution (Metropolis algorithm)
  4. Repeat steps 2-3 for a millions of times for averages



- Potential which describes interactions between carbon atoms is needed →

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Empirical potentials

- Aim of an empirical potential:
  - enabling fast and sufficiently accurate large scale simulations (MC or MD) of real systems
- Specific for carbon:
  - different equilibrium structures (diamond, graphite, …)
  - low coordination (3 graphite and graphene, 4 diamond)
  - allow changes of coordination
  - treat covalent bonding and weak interactions between graphitic planes (van der Waals, dispersive interaction)

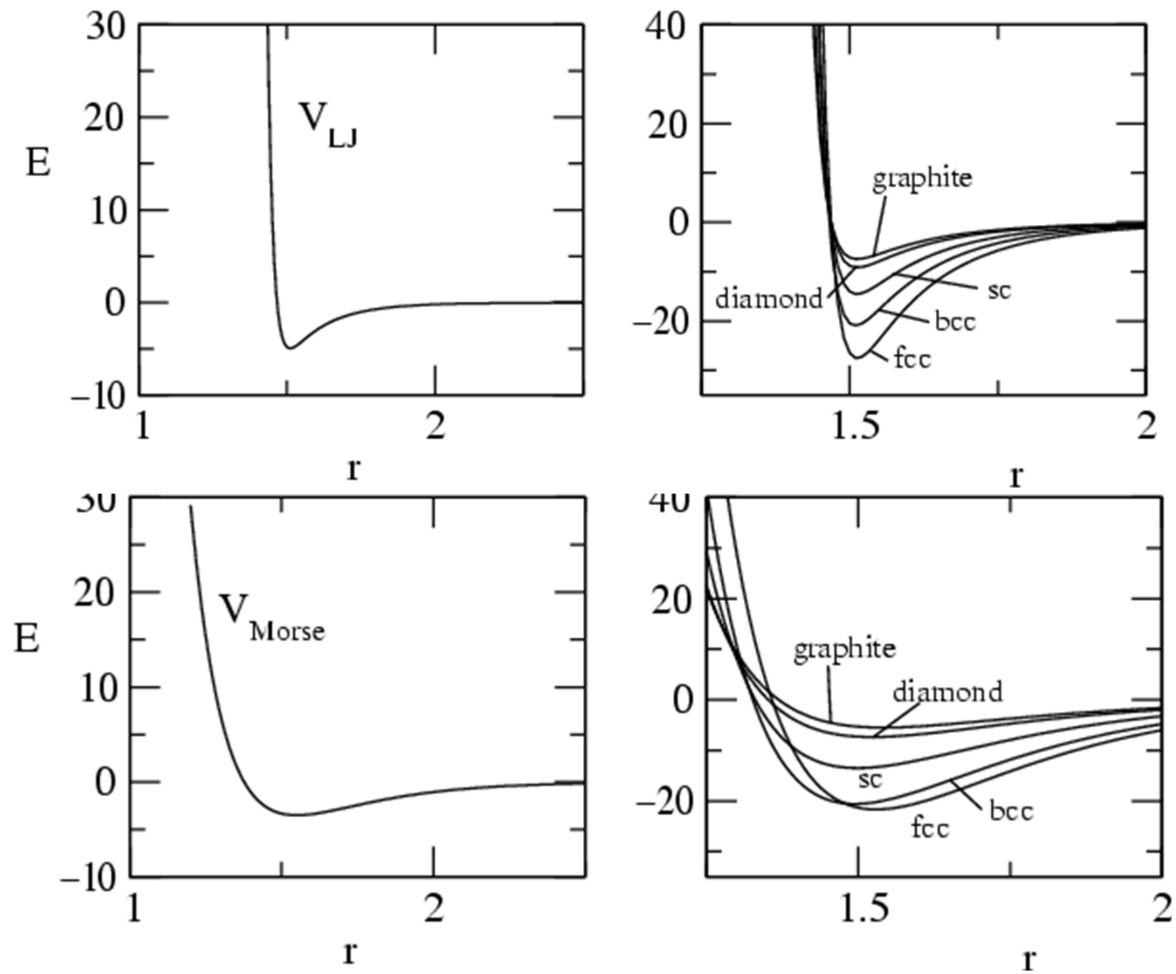
Pair potentials favour high coordination

Lennard Jones

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Morse

$$V(r) = D_e\left(1 - e^{-\alpha(r - r_e)}\right)^2$$



Other concept is needed →

Bond Order Potentials

J. Tersoff, Phys. Rev. B **37**, 6991 (1988).

- The strength of a bond between two atoms is not constant, it depends on local environment

$$E_b = \frac{1}{2}\sum_{i,j}^{N} V_{ij} = \frac{1}{2}\sum_{i,j}^{N}\left(V_R\left(r_{ij}\right) - B_{ij}V_A\left(r_{ij}\right)\right)$$

- B_{ij} – depends on the environment, and decreases with the number of neighbors

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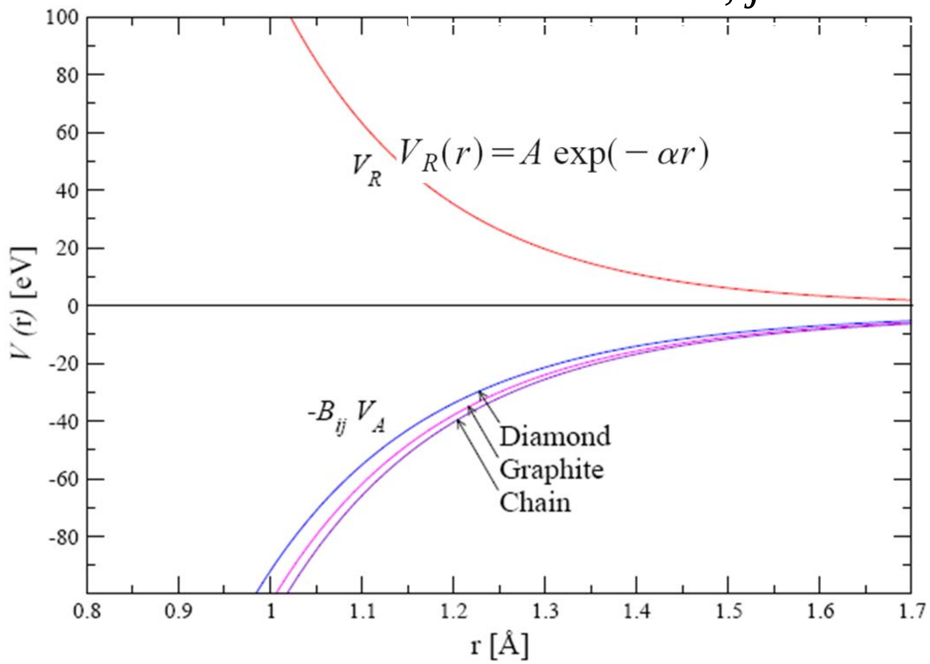
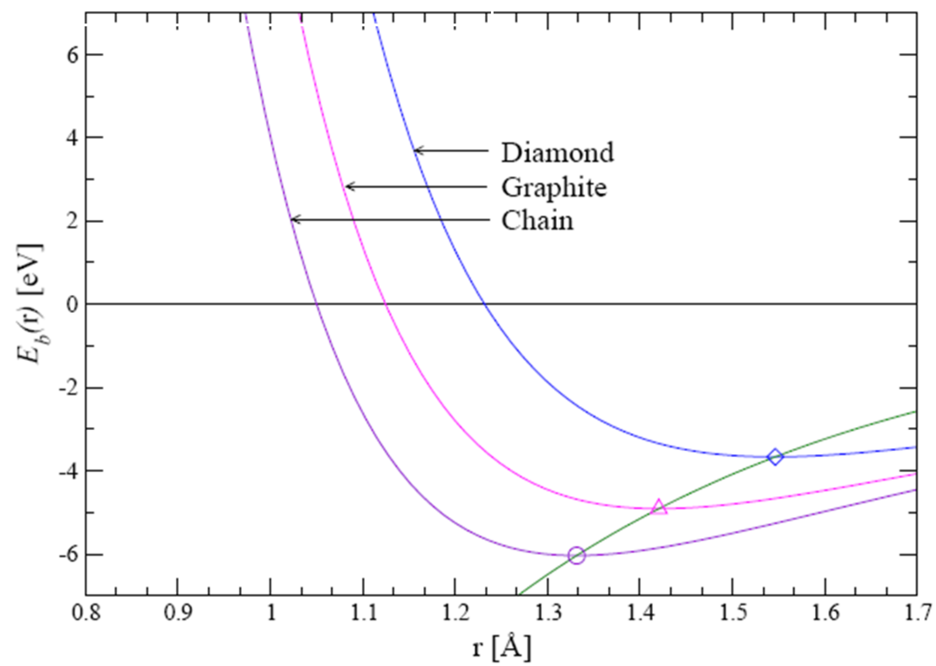
Bond Order Potentials

$$E_b = \frac{1}{2}\sum_{i,j}^{N}\left(V_R\left(r_{ij}\right) - B_{ij}V_A\left(r_{ij}\right)\right)$$





- Long range Carbon Bond Order Potential

J.H. Los, A. Fasolino, Phys. Rev. B 68, 024107 (2003)

J.H. Los et al. Phys. Rev. B 72, 214102 (2005)

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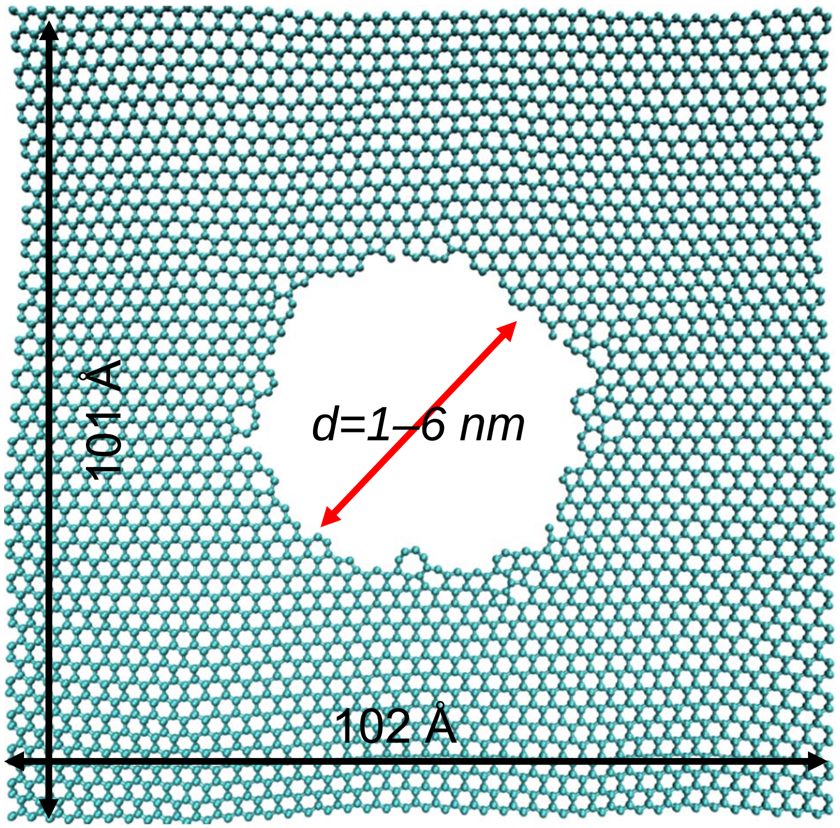
Healing and Control

Modelling



- Monte-Carlo simulations with empirical potential (LCBOPII)
- Graphene sample:
  - ~4k atoms
  - Sample size is about 10x10 nm
  - Periodic boundary conditions
  - Temperature: 500–2500K
  - Nanopores diameter: 1–6 nm
- Free carbon atoms were supplied to simulate healing

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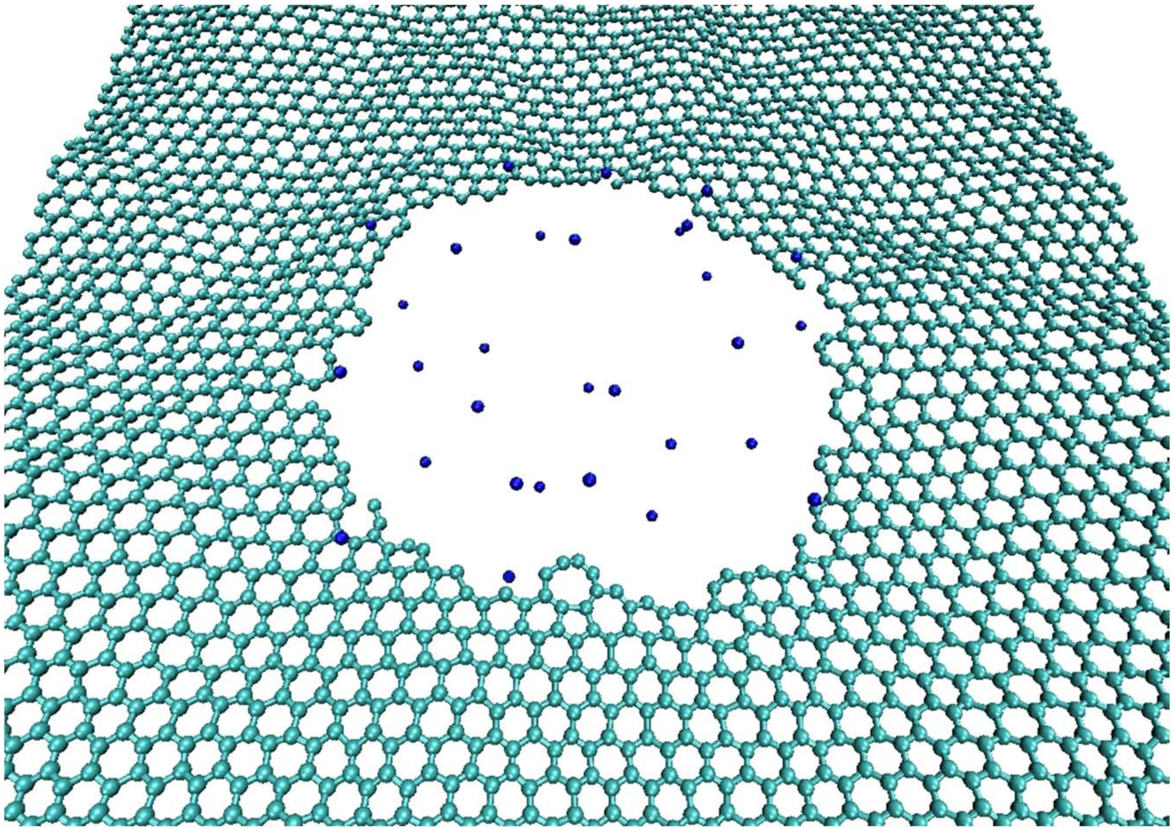
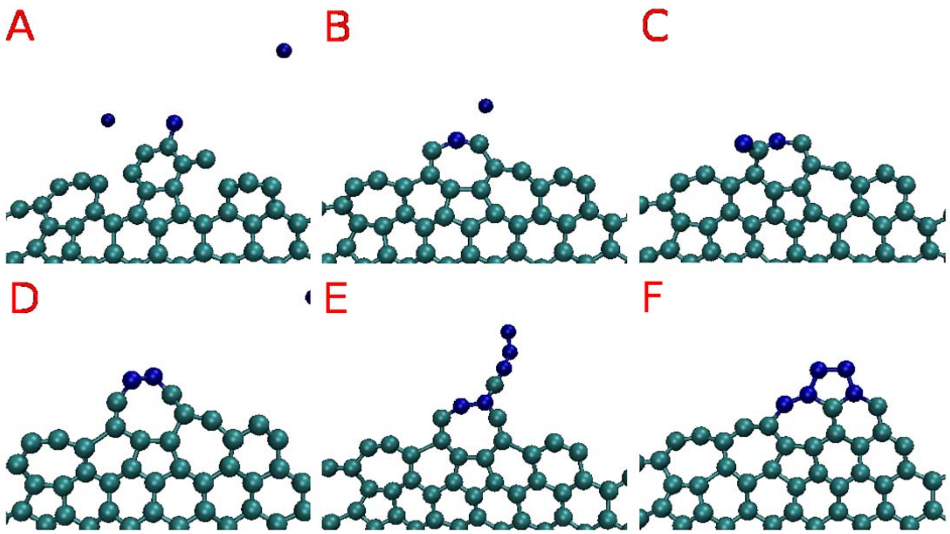
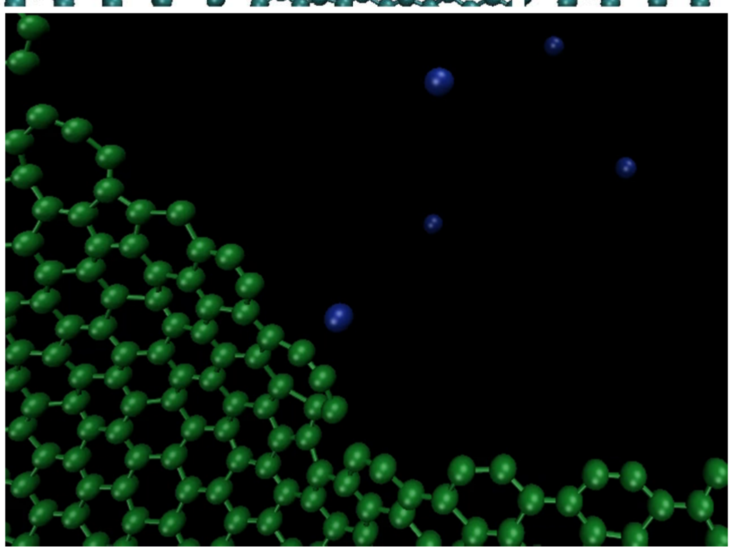
How does it work?



1. Prepare and relax nanopore
2. Add free carbon atoms
   1. Let them find their places
   2. Wait…
3. Repeat

First healing mechanism:
Edge healing





- Expected, has analogy in 3D
- Starts at the open edge
- Reconstruction of graphene sample atom-by-atom
- Formation of chains
- Slow speed
- Work as long as open edge exists
- Not affected by temperature

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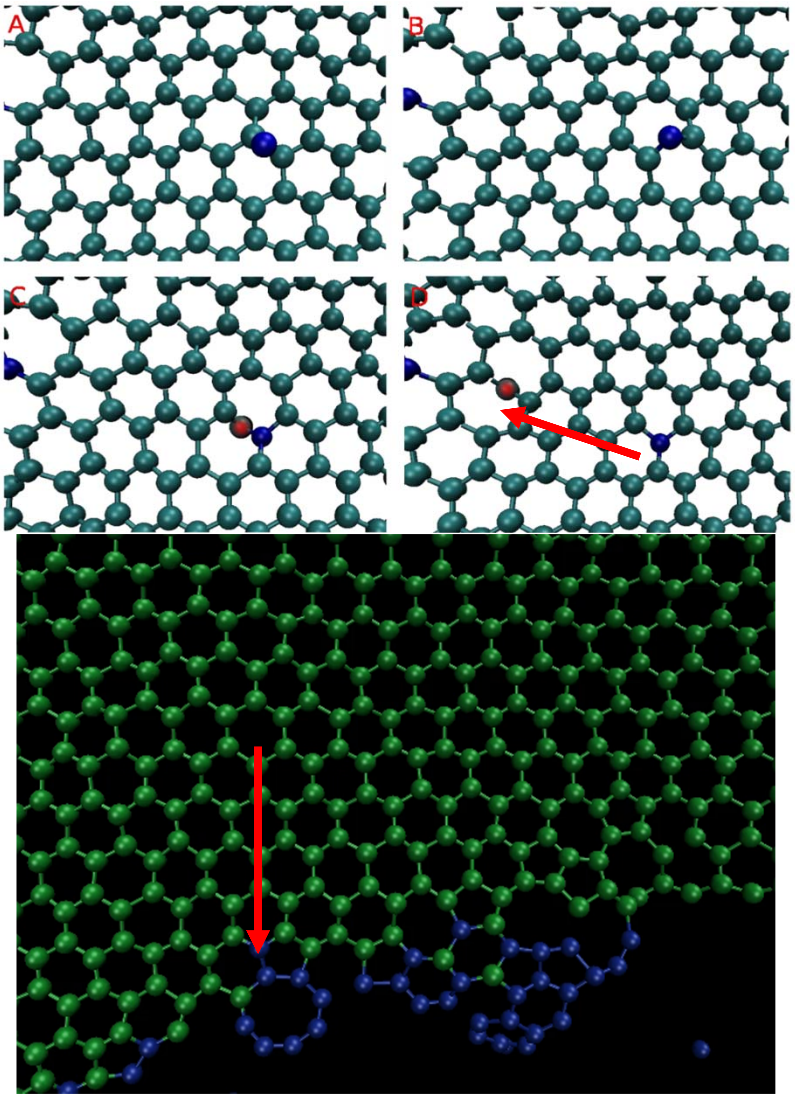
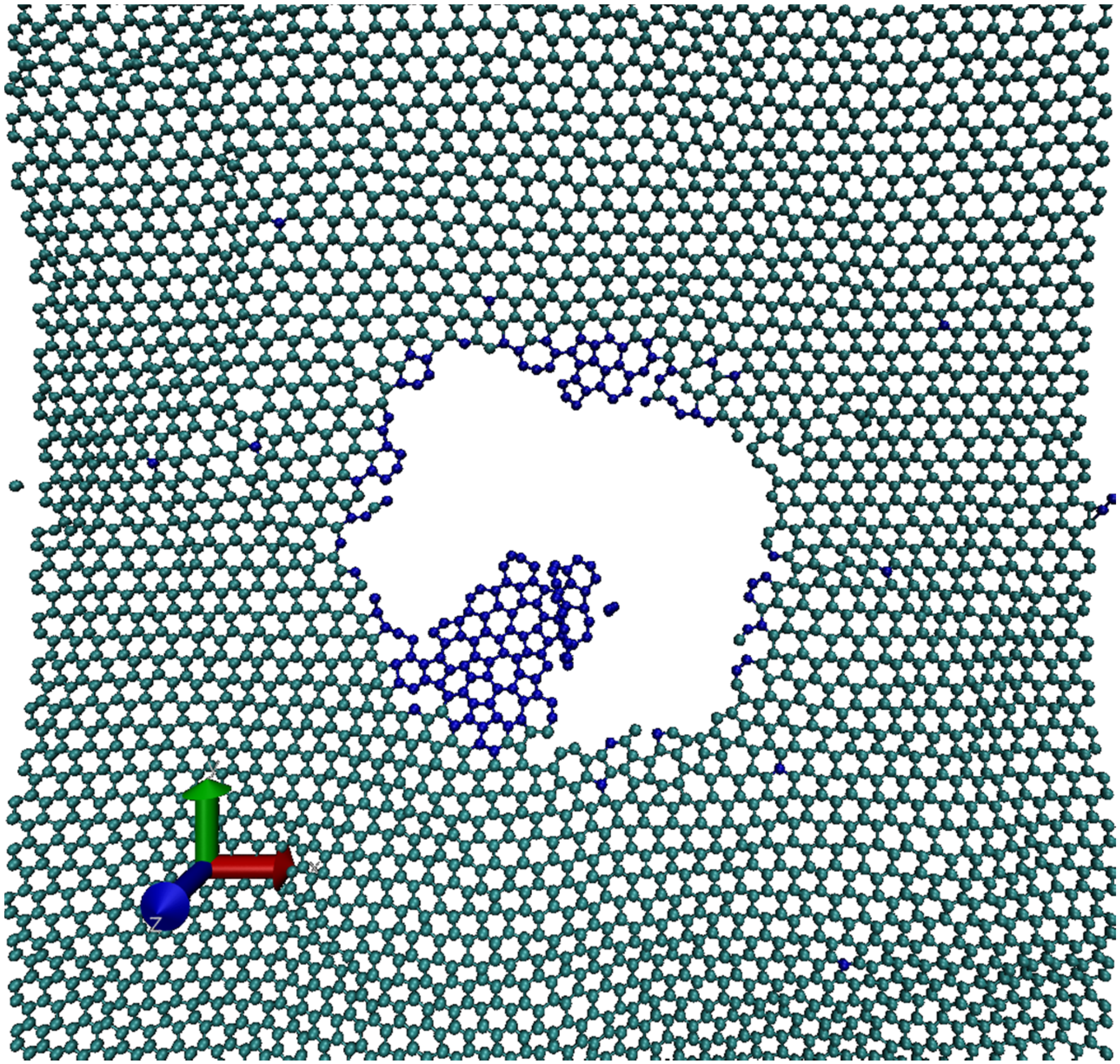
Second healing mechanism:
Atoms insertion



- Has no analogy in 3D
- Atom attaches to the plane:
  - Formation of two heptagons (R7) instead of hexagons (R6) – topological defect
  - Slow (Brownian-like) drift of defect towards nanopore
- Temperature affected
  - T > 900 K
- Goes everywhere over the sample area

Healing mechanism: Accidents



- Asymmetric healing
- Fingering:
  - Biology, wound healing
- Result of:
  - Statistical event
  - Chain formation at the edge
  - Attachment of floating chain, ring, or small flake
- Is it good or bad?
  - Looks nice
- 5-15% chance of "asymmetry"

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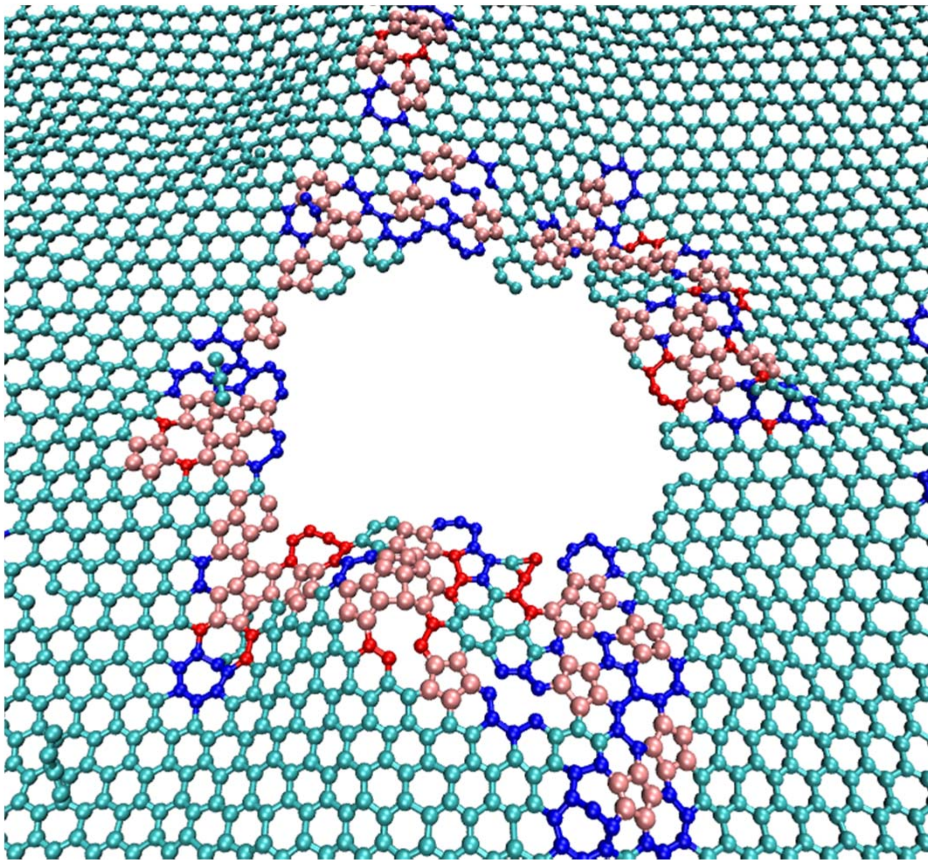
Structure of healed area



- T<1500 K
  - Hexagons (R6) ~ 40%
  - Pentagons (R5) ~ 40%
  - Heptagons (R7) + Octagons (R8) ~ 20 %
- T>1500 K
  - Hexagons (R6) ~ 60%
  - Pentagons (R5) ~ 20%
  - Heptagons (R7) + Octagons (R8) ~ 20 %
- Number of pentagons and heptagons are not equal, non zero sample curvature!
- Irregularity is more influential for smaller pores

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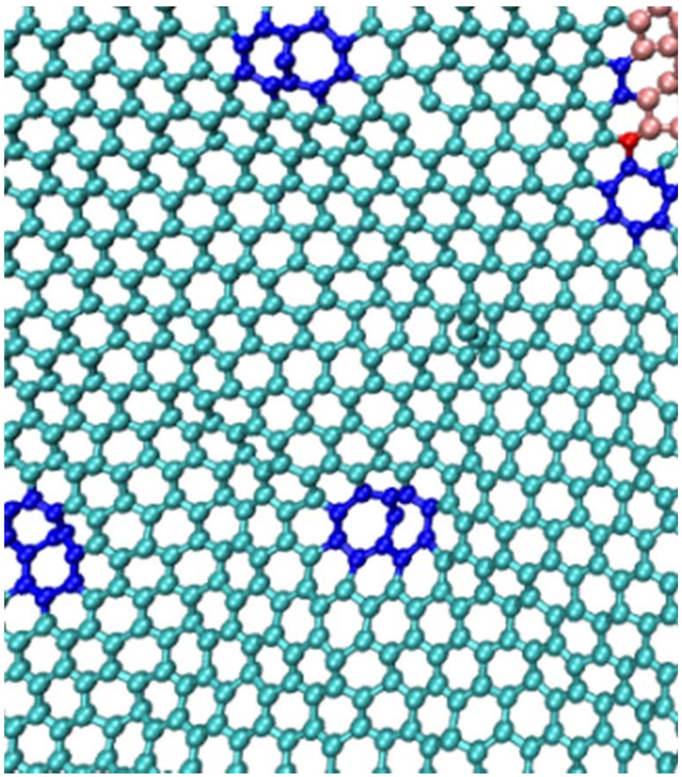
And distortions outside of the healed area…



- Atom insertion healing in action:
  - Slow drift of defects
  - Significant number heptagons (R7) outside of the healed area
- Higher temperature results in faster migration of defects towards open edge (nanopore or boundary)
- Number of pentagons and heptagons are not equal!

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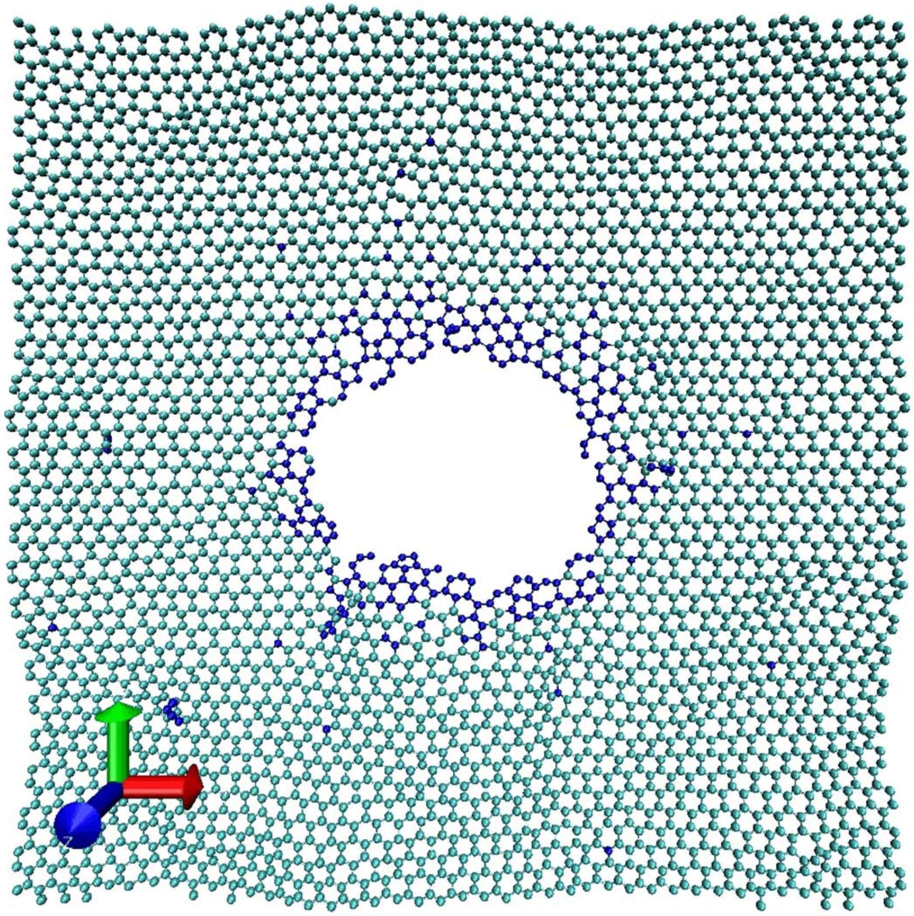
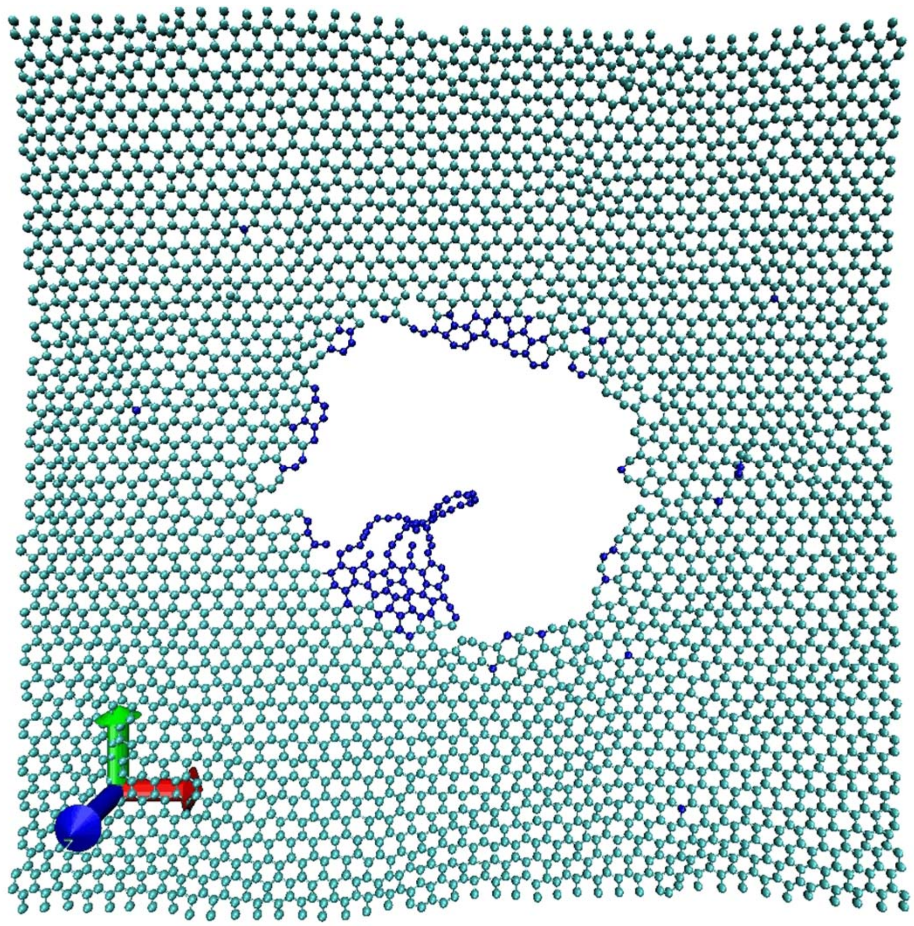
Healing in progress, T=2100 K

- $d_0 = 4$ nm





- $d_F = 3$ nm
- *Accident, 5-15% chance*

Conclusions

- At least two different healing mechanisms
  - Edge healing: works always (any T)
  - Insertion healing: works at T>900 K
- Possibility to control the final size of healed pore
- Asymmetries in re-grown pores
- Imperfections in the structure
  - Healed area
  - Whole sample is affected
- Future
  - influence of quality of healed area on properties of nanodevices
  - water filtration and desalination

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Thank you!