



force-bias Monte-Carlo/MD
NSCCS ADF/ReaxFF Workshop

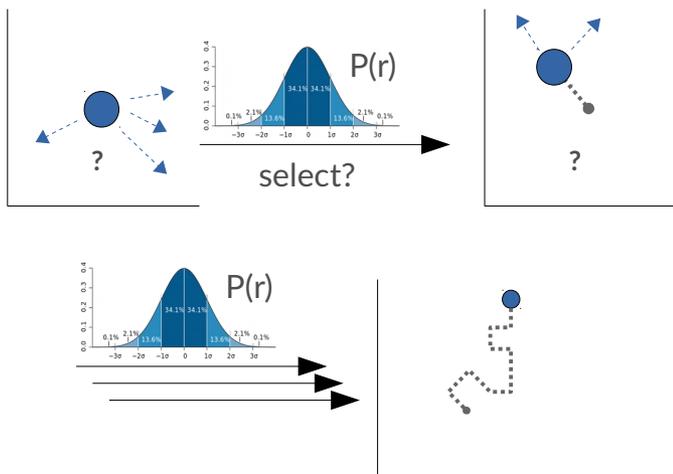
Ole Carstensen
Fedor Goumans
Anna Shchygol

Imperial College London
27-28 September 2016

Intro: uniform acceptance force-bias Monte-Carlo (fbMC)

The idea...

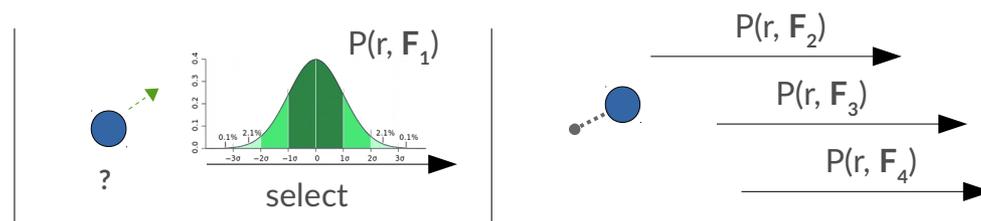
Metropolis MC



Sampling structural *Phase Space*

according to *one* well known ensemble distribution function (e.g. NVT)

fbMC



Sampling the *Dynamics*

- each change driven by “instantaneous” and “local” Probability Distributions
- irrespective from distance to equilibrium
- Limits of $P(r, F)$
 - $T \gg F \rightarrow$ completely random movement
 - $T \ll F \rightarrow$ Particle moves exactly in direction of force

Derivation.....Timonova *et al.*, Phys. Rev. B **81**, 144107 (2010); <http://dx.doi.org/10.1103/PhysRevB.81.144107>

Applicability...Bal and Neyts, J. Chem. Phys. **141**, 204104 (2014); <http://dx.doi.org/10.1063/1.4902136>

Application.....Mees *et al.*, Phys. Rev. B **85**, 134301; <http://dx.doi.org/10.1103/PhysRevB.85.134301>

Intro: fbMC

under the hood...

During a *single* fbMC step *each* atom is displaced by $\xi_{i,j} \cdot \Delta_i$ in every cartesian direction, with $\xi_{i,j}$ stochastically distributed as follows:

$$p(\xi_{i,j}) = \begin{cases} \frac{e^{\gamma_{i,j}(2\xi_{i,j}+1)} - e^{-\gamma_{i,j}}}{e^{\gamma_{i,j}} - e^{-\gamma_{i,j}}} & \text{if } \xi_{i,j} \in [-1, 0[\\ \frac{e^{\gamma_{i,j}} - e^{\gamma_{i,j}(2\xi_{i,j}-1)}}{e^{\gamma_{i,j}} - e^{-\gamma_{i,j}}} & \text{if } \xi_{i,j} \in]0, 1] \end{cases}$$

$$\gamma_{i,j} = \frac{F_{i,j} \Delta_i}{2k_B T}, \quad \Delta_i = \Delta \sqrt{\frac{m_{\min}}{m_i}},$$

$F_{i,j}$: Force along component j
acting on atom i
 m_i : mass of atom i
 m_{\min} : smallest mass in the system
 Δ : system wide parameter

*** required input: T, Δ ***

The choice of Δ is crucial:

- large $\Delta \rightarrow$ faster system evolution & larger violation of detailed balance
- formally correct only for *infinitesimal small* Δ
- recent finding: diffusion coefficients and reaction rate coefficients scale as $m^{-1/2}$

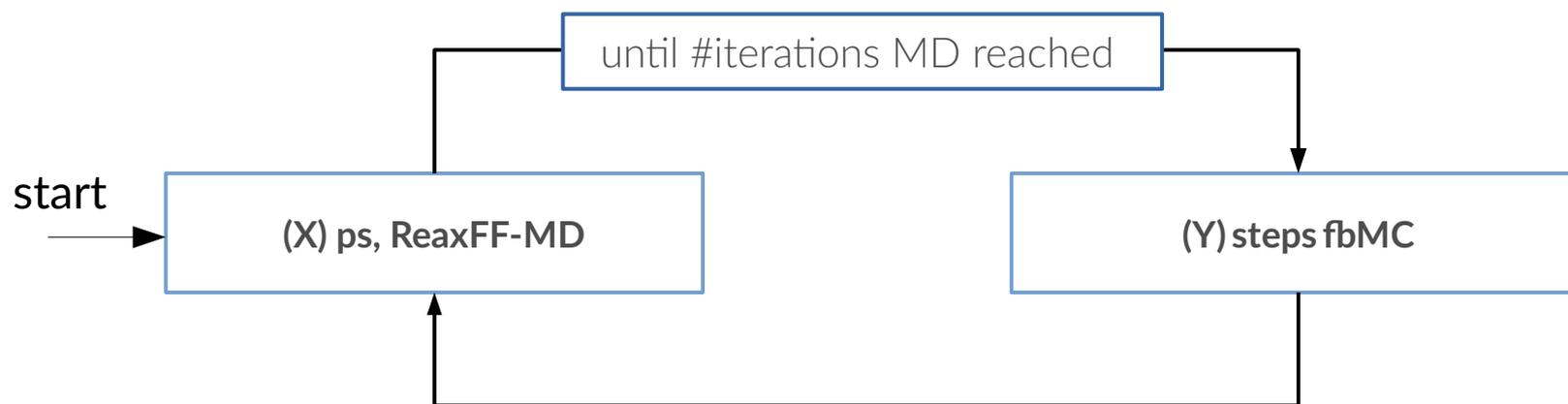
$$\Delta_i = \Delta \left(\frac{m_{\min}}{m_i} \right)^{1/4}$$

flexible mass scaling is supported by ADF/ReaxFF
but needs to be explicitly specified in the control file:
`imcroe=4`

Bal and Neyts, J. Chem. Phys. **141**, 204104 (2014); <http://dx.doi.org/10.1063/1.4902136>

Intro: fbMC + MD

Within ADF/ReaxFF fbMC and MD will alternate at a specified rate following the strategy described in the study of carbon nanotube growth on Ni-catalysts^[1]



(X) : “Frequency of fbMC steps” = start fbMC from last MD structure after (X) steps

(Y) : “Number of fbMC steps” = make (Y) fbMC steps before restarting the MD

Example:

(X) = 1000

(Y) = 500

Number of Iterations = 10 000



1. 1000 steps MD
2. 500 steps fbMC
3. 1000 steps MD
4. 500 steps fbMC
5.

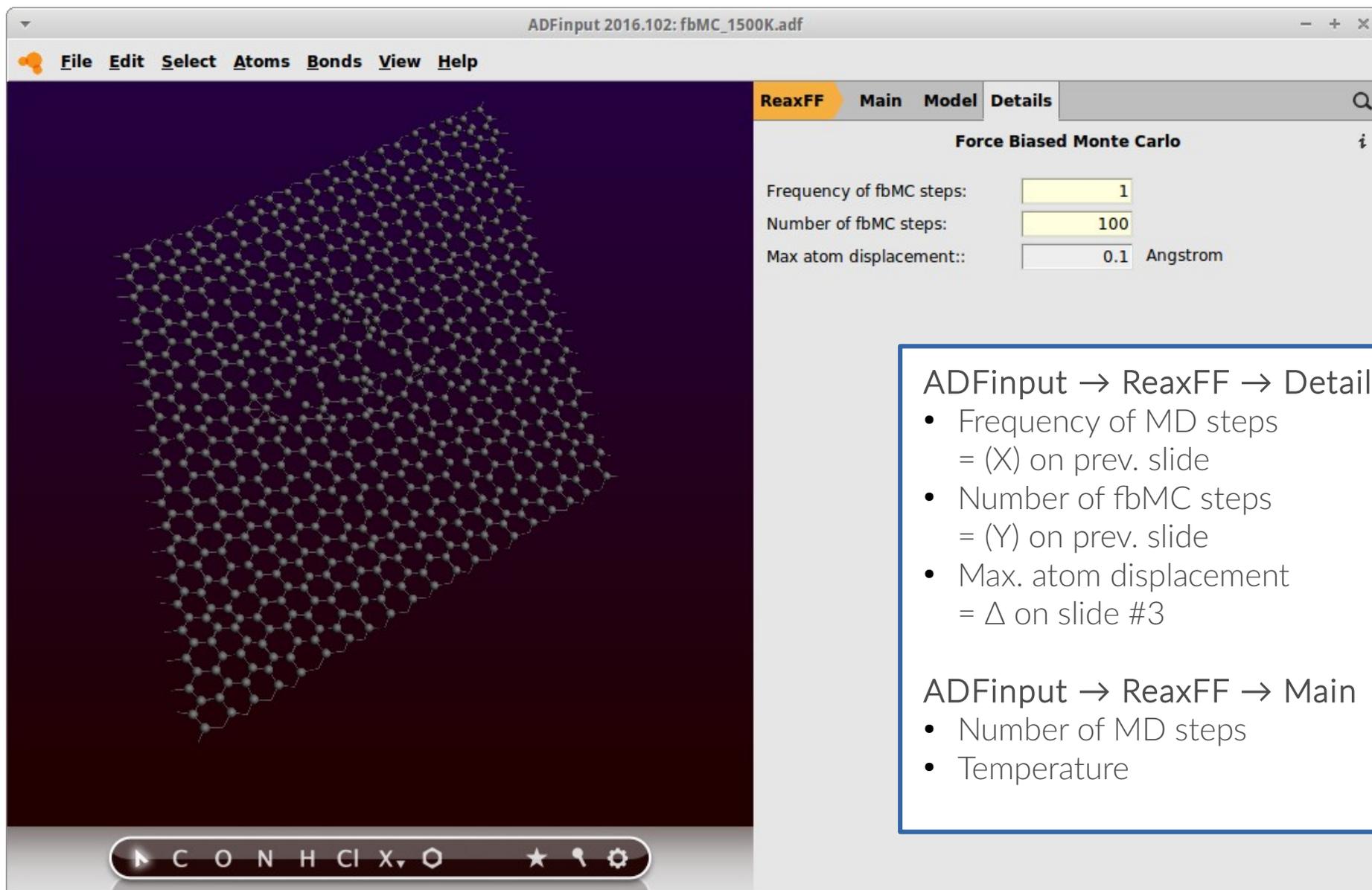
$$\Sigma_{\text{MD}} = 10\,000 \text{ steps}$$

$$\Sigma_{\text{fbMC}} = 5000 \text{ steps}$$

[1] Neyts *et al.*, J. Am. Chem. Soc. **133**, 17225 (2011); <http://dx.doi.org/10.1021/ja204023c>

Intro: fbMC + MD

using the GUI



The screenshot shows the ADFinput 2016.102: fbMC_1500K.adf window. The main view displays a 3D ball-and-stick model of a molecular structure. The right-hand panel is titled 'Force Biased Monte Carlo' and contains the following settings:

- Frequency of fbMC steps: 1
- Number of fbMC steps: 100
- Max atom displacement: 0.1 Angstrom

Navigation instructions are provided in a blue-bordered box:

ADFinput → ReaxFF → Details

- Frequency of MD steps = (X) on prev. slide
- Number of fbMC steps = (Y) on prev. slide
- Max. atom displacement = Δ on slide #3

ADFinput → ReaxFF → Main

- Number of MD steps
- Temperature

Hands-on: Simulate Graphene Healing

Learn how to:

- use the GUI to create a graphene sheet
- use the structure with ReaxFF
- run fBMC + MD
- use Python for custom analysis of trajectories
- choose the Δ (look at the influence of various Δ)



[Science & Environment](#)

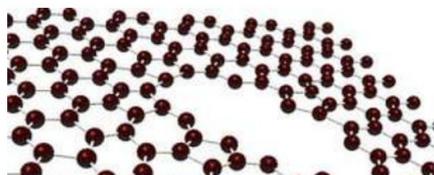
Graphene holes 'heal themselves'

By Jason Palmer
Science and technology reporter, BBC News

© 11 July 2012 | [Science & Environment](#)



Graphene - the "wonder material" made of sheets of carbon just one atom thick - undergoes a self-repairing process to correct holes, researchers report.



RESEARCH HIGHLIGHTS THIS WEEK

COMMUNITY CHOICE

The most viewed papers in science

MATERIALS

Graphene, heal thyself

 **HIGHLY READ**
on [pubs.acs.org](#)
in July

Graphene, atom-thick sheets of carbon, has a multitude of unusual properties, and self-healing can now be added to the list.

Quentin Ramasse of the SuperSTEM Laboratory in Daresbury, UK, and his colleagues deposited metals on sheets of graphene and then scanned the sheets using an electron microscope. The metals catalysed the breaking of carbon bonds, making holes in the carbon's honeycomb structure. When the supply of catalysts had been exhausted, the graphene healed itself. In the presence of other hydrocarbons, the graphene sheet filled its gaps with variably sized rings of additional carbon atoms. However, if no hydrocarbons were present, the carbon atoms rearranged themselves into their original two-dimensional hexagonal structure.

Researchers hope that the 'reknitting' process can be used to help control nanometre-scale etching of graphene.

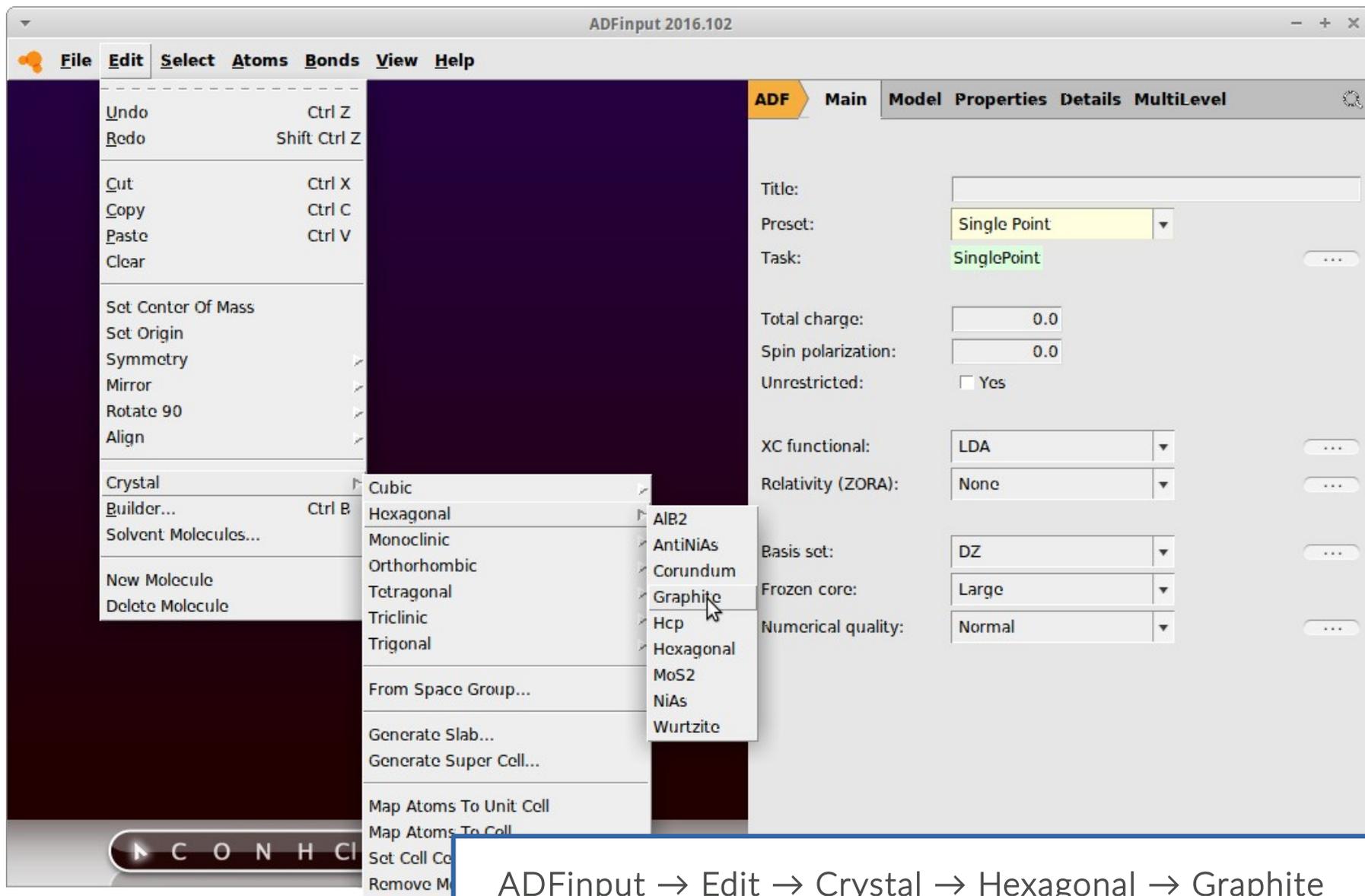
Nano. Lett. 12, 3936–3940 (2012)

Exercise 1:

Create a Graphene sheet

Hands-on: Create graphene

create a graphene sheet



The screenshot shows the ADFinput 2016.102 software interface. The menu bar includes File, Edit, Select, Atoms, Bonds, View, and Help. The 'Edit' menu is open, showing options like Undo, Redo, Cut, Copy, Paste, Clear, and Crystal. The 'Crystal' menu is further open, showing options like Cubic, Hexagonal, Monoclinic, Orthorhombic, Tetragonal, Triclinic, Trigonal, From Space Group..., Generate Slab..., Generate Super Cell..., Map Atoms To Unit Cell, Map Atoms To Cell, Set Cell Co, and Remove M. The 'Hexagonal' menu is open, showing options like AlB2, AntiNiAs, Corundum, Graphite, Hcp, Hexagonal, MoS2, NiAs, and Wurtzite. The 'Graphite' option is highlighted. The right panel shows the 'Main' tab with various settings for a 'Single Point' calculation, including Title, Preset, Task, Total charge, Spin polarization, Unrestricted, XC functional, Relativity (ZORA), Basis set, Frozen core, and Numerical quality.

ADFinput → Edit → Crystal → Hexagonal → Graphite

Hands-on: Create graphene

create a graphene sheet

The screenshot shows the ADFinput 2016.102 software interface. The main window displays a 3D model of a graphene sheet, which is a two-dimensional lattice of carbon atoms. The interface includes a menu bar (File, Edit, Select, Atoms, Bonds, View, Help) and a toolbar at the bottom. A configuration panel on the right side is visible, with the following settings:

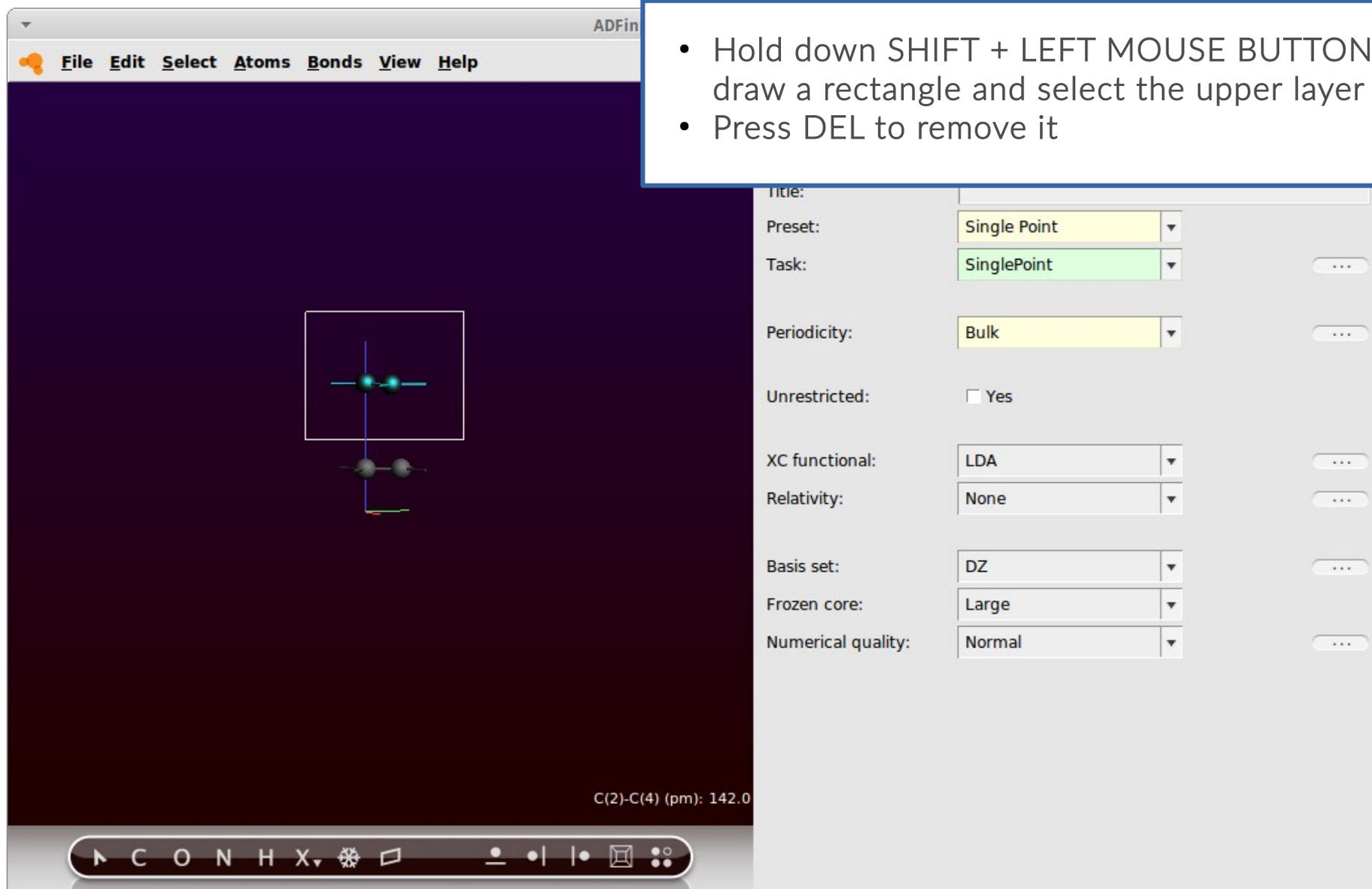
- Title: [Empty text box]
- Preset: Single Point
- Task: SinglePoint
- Periodicity: Bulk
- Unrestricted: Yes
- XC functional: LDA
- Relativity: None
- Basis set: DZ
- Frozen core: Large
- Numerical quality: Normal

A callout box with a blue border and white background contains the text "Switch off 'Perspective' and 'Periodic Display'". A red arrow points from this box to a toolbar icon at the bottom of the window, which is highlighted with a red square. The toolbar icon consists of a cube and a grid of dots.

Hands-on: Create graphene

create a graphene sheet

- Hold down SHIFT + LEFT MOUSE BUTTON draw a rectangle and select the upper layer
- Press DEL to remove it



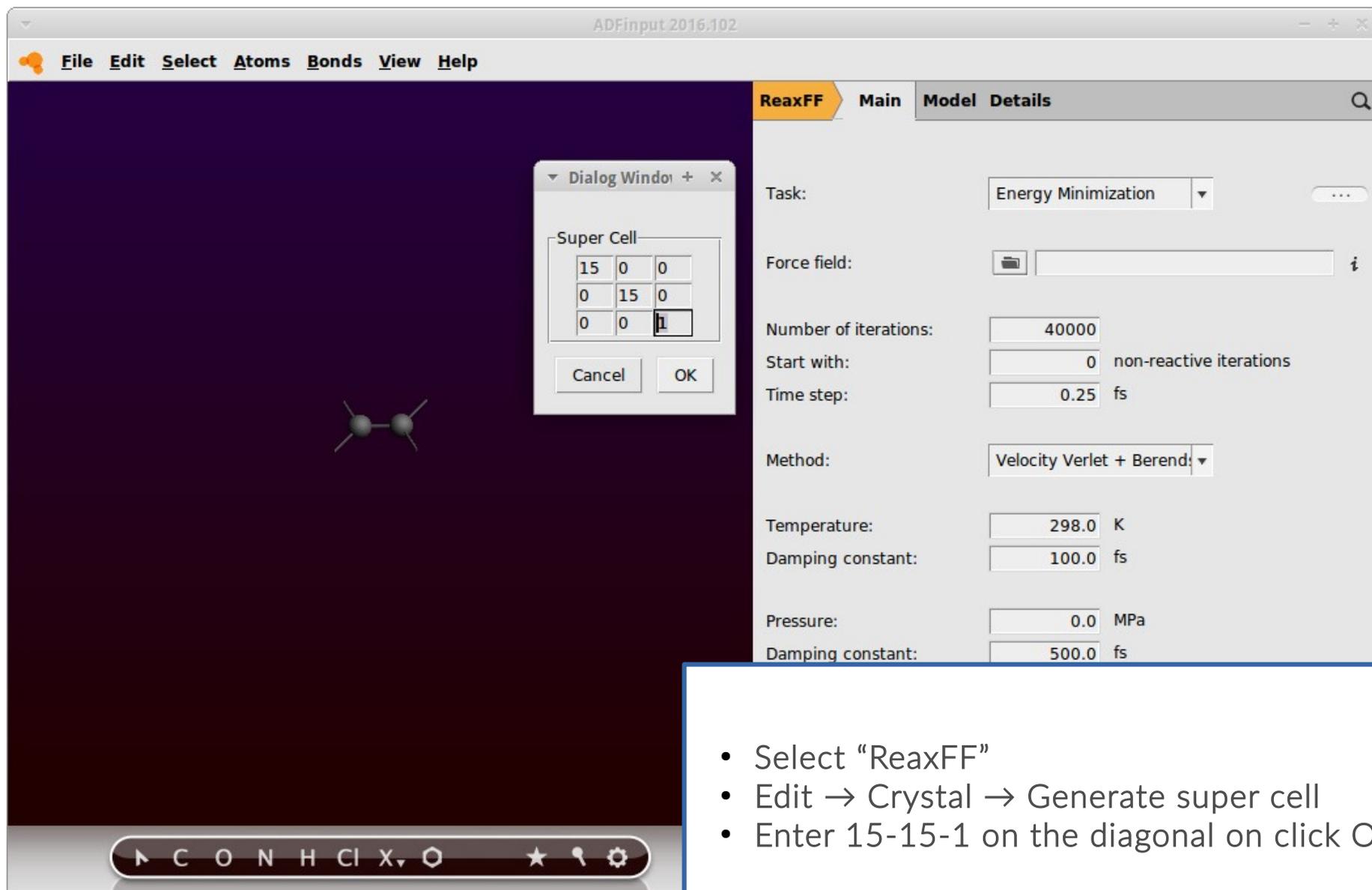
The screenshot shows the ADF software interface. The main window displays a molecular model with a white rectangular selection box around the upper layer of atoms. The settings panel on the right is open, showing the following configuration:

Title:	
Preset:	Single Point
Task:	SinglePoint
Periodicity:	Bulk
Unrestricted:	<input type="checkbox"/> Yes
XC functional:	LDA
Relativity:	None
Basis set:	DZ
Frozen core:	Large
Numerical quality:	Normal

At the bottom of the main window, the text "C(2)-C(4) (pm): 142.0" is visible. The bottom toolbar contains icons for navigation and editing.

Hands-on: Create graphene

create a graphene sheet

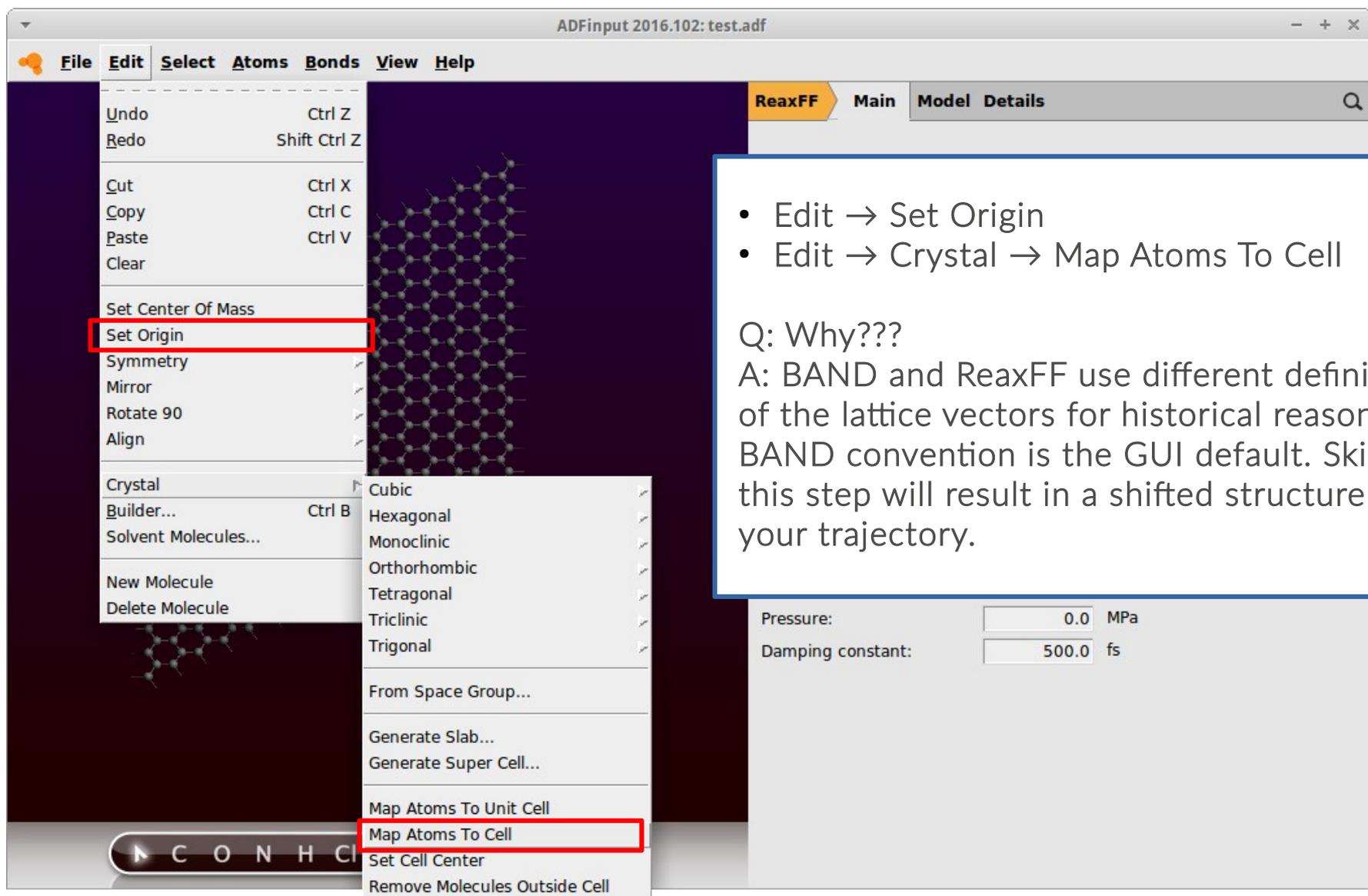


The screenshot shows the ADFinput 2016.102 software interface. The main window has a menu bar with File, Edit, Select, Atoms, Bonds, View, and Help. The ReaxFF panel is open, showing settings for Energy Minimization, Force field, Number of iterations (40000), Start with (0 non-reactive iterations), Time step (0.25 fs), Method (Velocity Verlet + Berend), Temperature (298.0 K), Damping constant (100.0 fs), Pressure (0.0 MPa), and Damping constant (500.0 fs). A Dialog Window titled 'Super Cell' is open, showing a 3x3 grid of input fields with values 15, 0, 0; 0, 15, 0; and 0, 0, 1. The 'OK' button is highlighted. A molecular model of a diatomic molecule is visible in the background.

- Select “ReaxFF”
- Edit → Crystal → Generate super cell
- Enter 15-15-1 on the diagonal on click OK

Hands-on: Create graphene

adjust the lattice vectors for your graphene sheet



The screenshot shows the ADF software interface with a graphene sheet model. The 'Edit' menu is open, and 'Set Origin' is highlighted with a red box. The 'Crystal' sub-menu is also open, and 'Map Atoms To Cell' is highlighted with a red box. The 'ReaxFF' tab is active in the top right. The 'Pressure' and 'Damping constant' fields are visible in the bottom right.

- Edit → Set Origin
- Edit → Crystal → Map Atoms To Cell

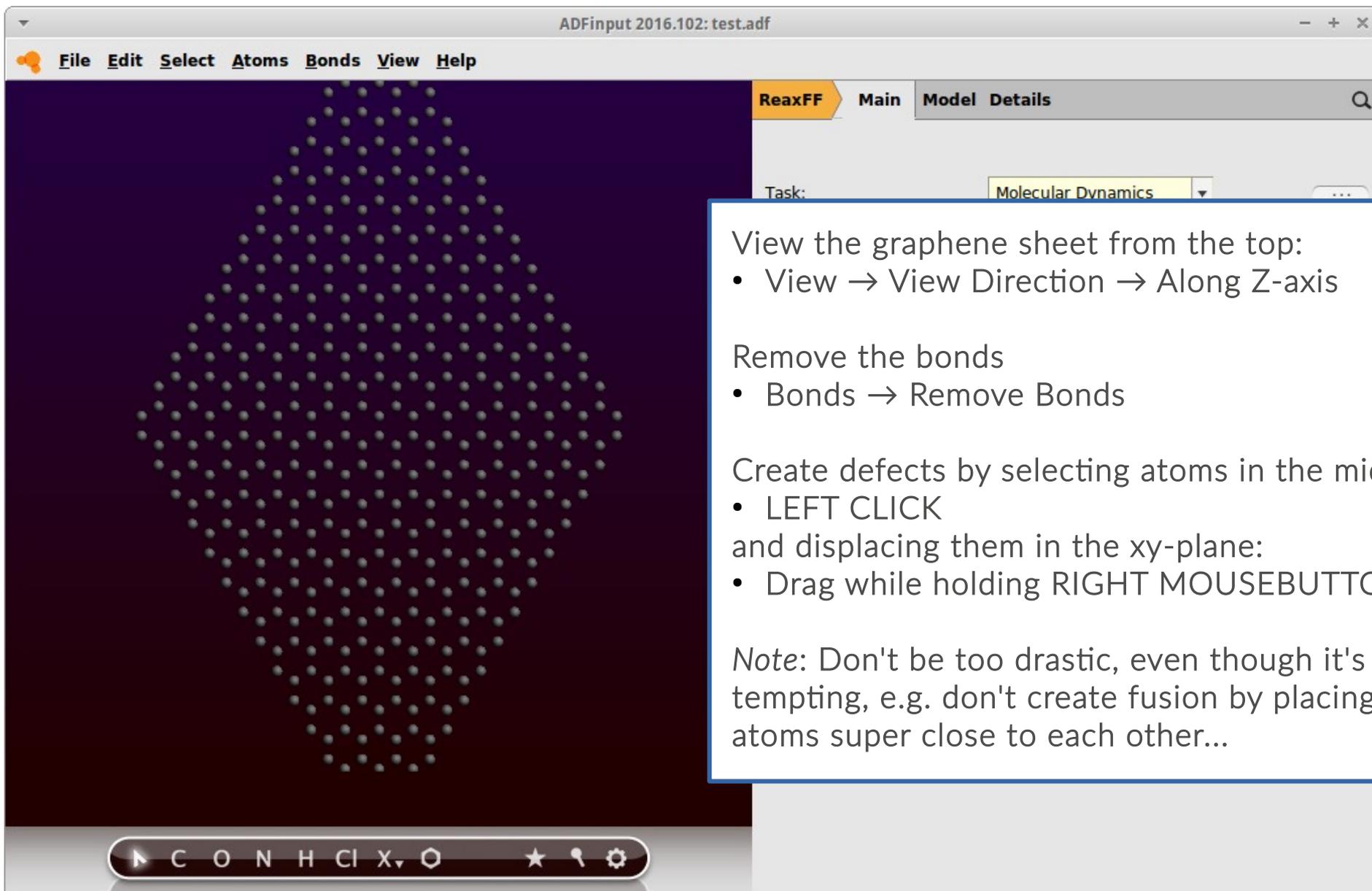
Q: Why???

A: BAND and ReaxFF use different definitions of the lattice vectors for historical reasons. The BAND convention is the GUI default. Skipping this step will result in a shifted structure in your trajectory.

Pressure: 0.0 MPa
Damping constant: 500.0 fs

Hands-on: Create graphene

creating the defects



ADFFinput 2016.102: test.adf

File Edit Select Atoms Bonds View Help

ReaxFF Main Model Details

Task: Molecular Dynamics

View the graphene sheet from the top:

- View → View Direction → Along Z-axis

Remove the bonds

- Bonds → Remove Bonds

Create defects by selecting atoms in the middle

- LEFT CLICK

and displacing them in the xy-plane:

- Drag while holding RIGHT MOUSEBUTTON

Note: Don't be too drastic, even though it's tempting, e.g. don't create fusion by placing atoms super close to each other...

Hands-on: Create graphene

relaxing the structure

ADFinput 2016.102: test.adf

File Edit Select Atoms Bonds View Help

ReaxFF Main Model Details

Task: Molecular Dynamics

Force field: CHONSSiPtZrNiCuCo.ff

Number of iterations: 1000

Start with: 0 non-reactive iterations

Time step: 0.1 fs

Method: Velocity Verlet + Berendsen

Temperature: 50 K

Damping constant: 100.0 fs

Pressure: 0.0 MPa

Damping constant: 500.0 fs

'Equilibrate' your structure by running low T dynamics (NVT) with the following settings:

- 1000 steps
- Timestep 0.1 fs
- T = 50K
- Force field: CHONSSiPtZrNiCuCo.ff (Do you know why?)

accept the last structure of the trajectory as new coordinates when asked and save.

Exercise 2:

Running MD and fbMC/MD

Hands-on: Simulate Graphene Healing

Set up the following *fbMC* calculation, save and run it

The image shows two screenshots of the ReaxFF software interface. The left screenshot displays the 'Model Details' panel for a Molecular Dynamics simulation. The right screenshot displays the 'Details' panel for a Force Biased Monte Carlo simulation.

Left Screenshot (Molecular Dynamics):

- Task: Molecular Dynamics
- Force field: CHONSSiPtZrNiCuCo.ff
- Number of iterations: 200
- Start with: 0 non-reactive iterations
- Time step: 0.1 fs
- Method: Velocity Verlet + Berend
- Temperature: 800 K
- Damping constant: 100.0 fs
- Pressure: 0.0 MPa
- Damping constant: 500.0 fs

Right Screenshot (Force Biased Monte Carlo):

- Frequency of fbMC steps: 1
- Number of fbMC steps: 50
- Max atom displacement: 0.11 Angstrom

Bottom Screenshot (Molecular Dynamics):

- Fix cell parameters (NPT only): None in NPT
- Output frequencies
- KF result file: 1
- Energies, temperatures and more: 50
- Coordinates: 1000000
- Remove Rot/Trans every: 25 iterations

→ 10 000 fbMC steps @ 800K, $\Delta = 0.11$

Hands-on: Simulate Graphene Healing

Set up the following MD calculation, save and run it

ReaxFF Main Model Details

Task: Molecular Dynamics

Force field: CHONSSiPtZrNiCuCo.ff

Number of iterations: 10000

Start with: 0 non-reactive iterations

Time step: 0.2 fs

Method: Velocity Verlet + Berends

Temperature: 800 K

Damping constant: 100.0 fs

Pressure: 0.0 MPa

Damping constant: 500.0 fs

→ 10 000 MD steps @ 800K, $\Delta t = 0.2$ fs

ReaxFF Main Model Details

Force Biased Monte Carlo

Frequency of fbMC steps: 0

Number of fbMC steps: 50

Max atom displacement:: 0.11 Angstrom

ReaxFF Main Model Details

Molecular Dynamics

Fix cell parameters (NPT only): None in NPT

Output frequencies

KF result file: 50

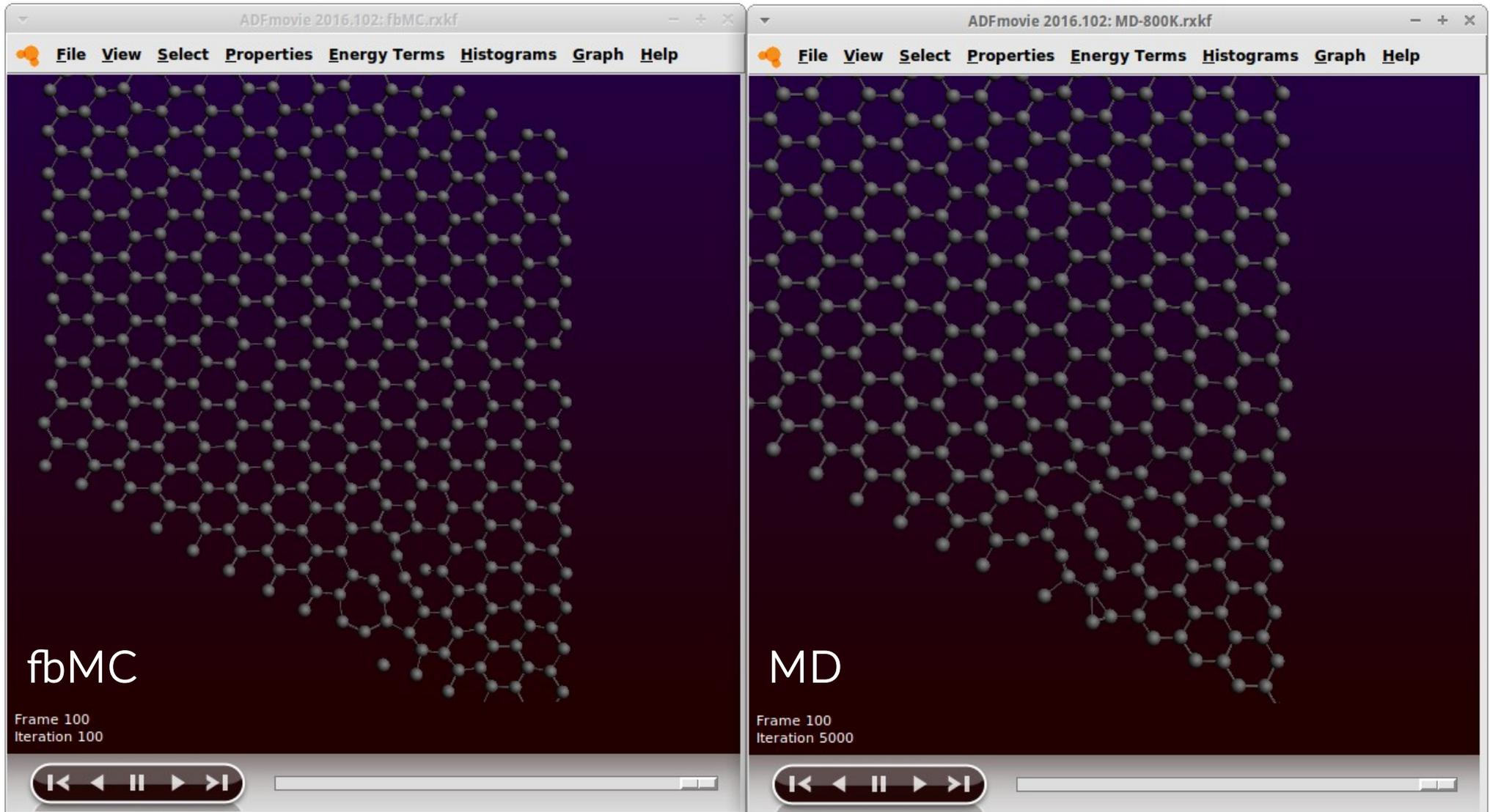
Energies, temperatures and more: 50

Coordinates: 1000000

Remove Rot/Trans every: 25 iterations

Hands-on: Simulate Graphene Healing

Look at both trajectories with ADFmovie



Can you already spot a difference?

Exercise 3:

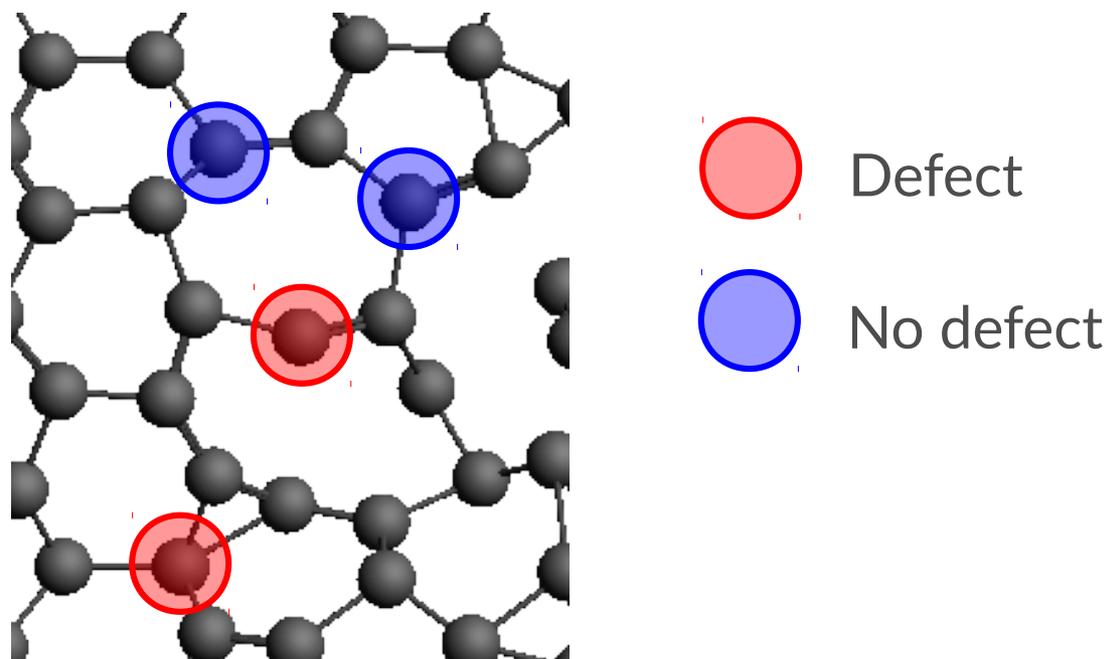
Take a closer look with Python

Hands-on: Analyze Graphene Healing

Analyzing the defects

Task: Get the number of defects per frame

Ansatz: Count every carbon atom not bonded to three other carbons as 'defect'



Note:

A (way) more detailed analysis would be possible, i.e. looking at the distribution of ring sizes, but this takes longer to setup. Consider it a quick way to get at least some insight :-)

Hands-on: Analyze Graphene Healing

Write a PYTHON script



Use the PLAMS template in the scripts folder and turn the following pseudo code into a PYTHON script:

```
Steps = "Read steps from RXKF"
```

```
for step in Steps:
```

```
    NumNeighbors = Read Num Neighbors of current step from RXKF
    Defects = 0.0
```

```
    for neighb in NumNeighbors:
```

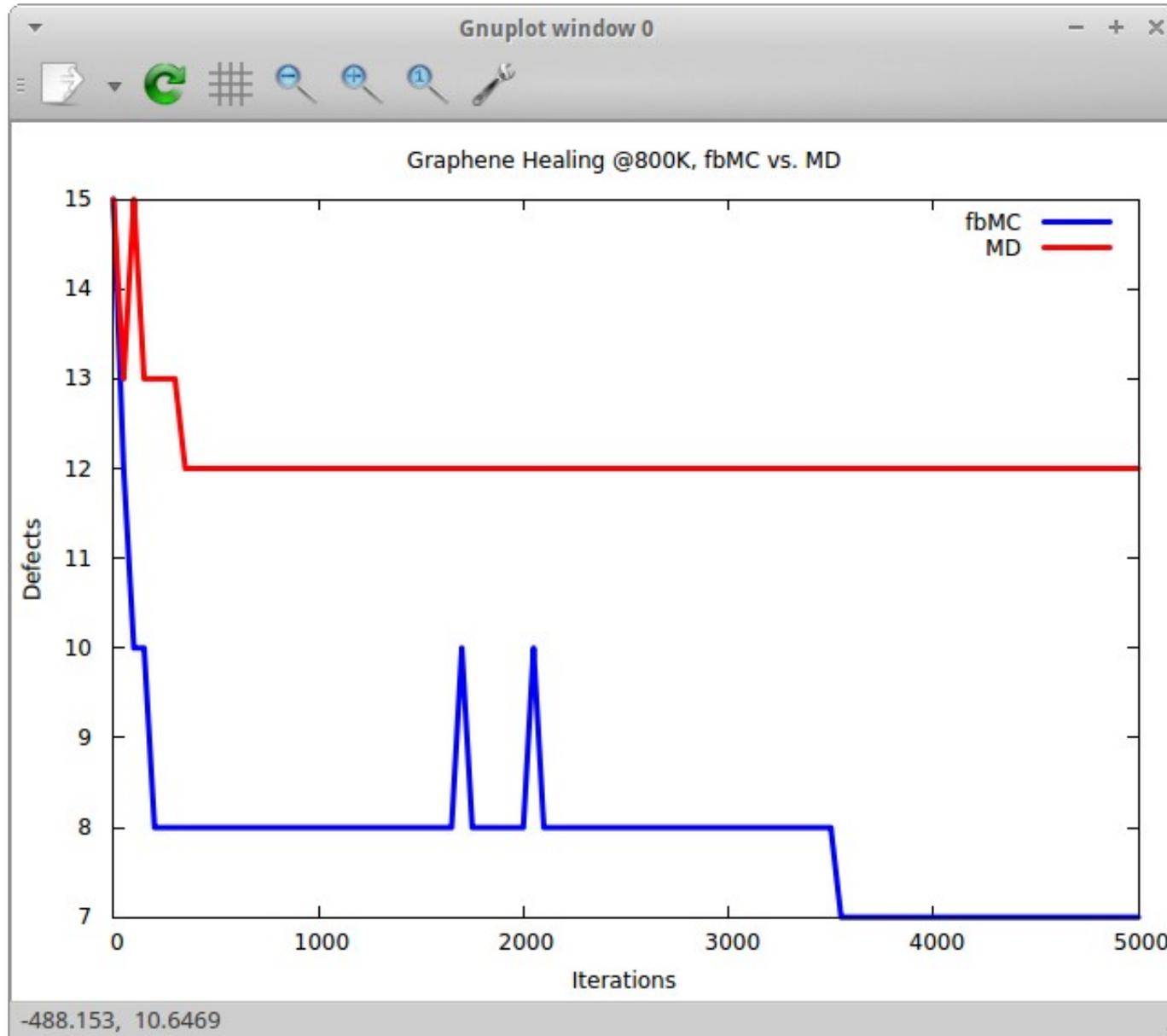
```
        if neighb != 3:
            Defects += 1
```

```
    print step and Defects
```

Note: If you don't feel comfortable writing PYTHON or time is short, you can just ask Ole for the finished script

Hands-on: Analyze Graphene Healing

Use Gnuplot (or other) for visualizing your results



Exercise 4:

Examine the limits of Δ

Hands-on: Analyze fbMC, Different settings of Δ

Bal & Neyts (2014) ^[1]:

[...] displacement lengths (Δ) between 0.1 and 0.15 Å (about 5%–10% of a typical nearest neighbor distance) lead to physically meaningful results, in agreement with either MD simulations or the experiment, and can be considered “conservative” choices.

Try it yourself:

- Run fbMC dynamics with above settings except:
- Number of Steps (in Main window): 100
- $\Delta = 0.01$ (small) and $\Delta = 0.25$ (large) or try your own

Use ADFMovie and your PYTHON script to investigate the resulting dynamics

[1] Bal and Neyts, J. Chem. Phys. **141**, 204104 (2014); <http://dx.doi.org/10.1103/PhysRevB.81.144107>



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