SCM
Software for Chemistry & Materials

force-bias Monte-Carlo/MD

NSCCS ADF/ReaxFF Workshop

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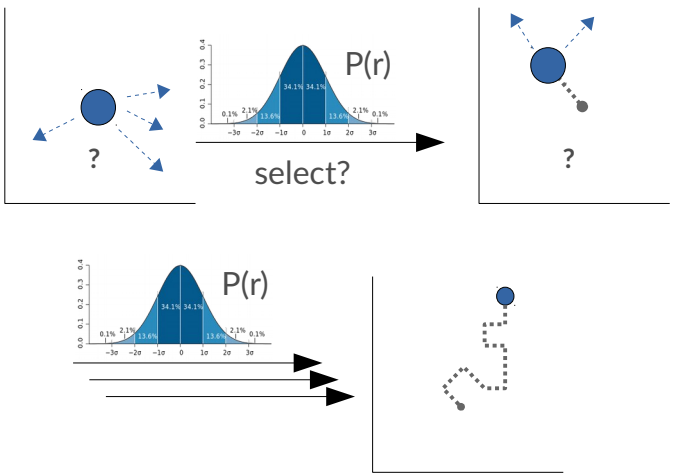
Intro: uniform acceptance force-bias Monte-Carlo (fbMC)

The idea…

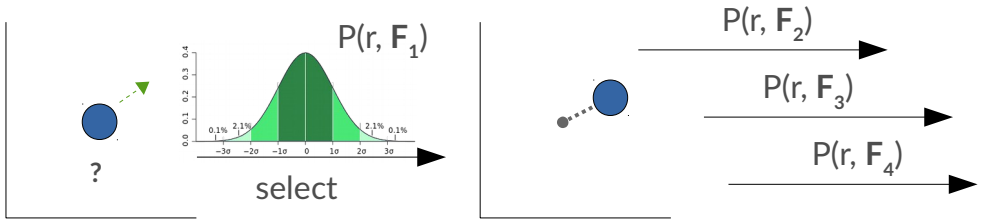
Metropolis MC



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 >> F → completely random movement
  T << F → 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:

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

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

$F_{i,j}$: 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* Δ → 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 $m^{-1/2}$

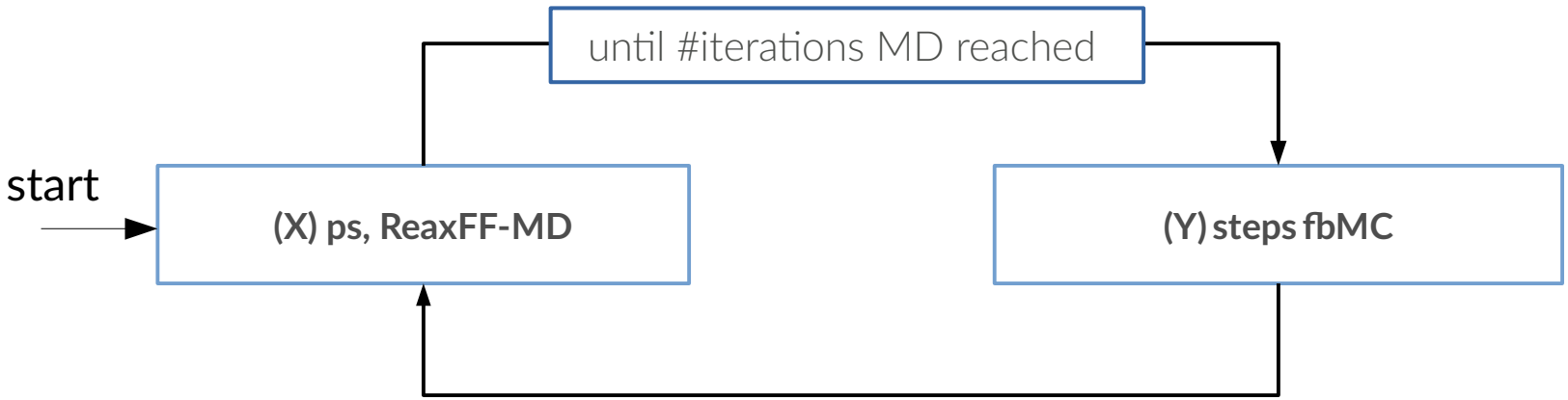
$$\Delta_i = \Delta\left(\frac{m_{\min}}{m_i}\right)^{1/4}$$

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

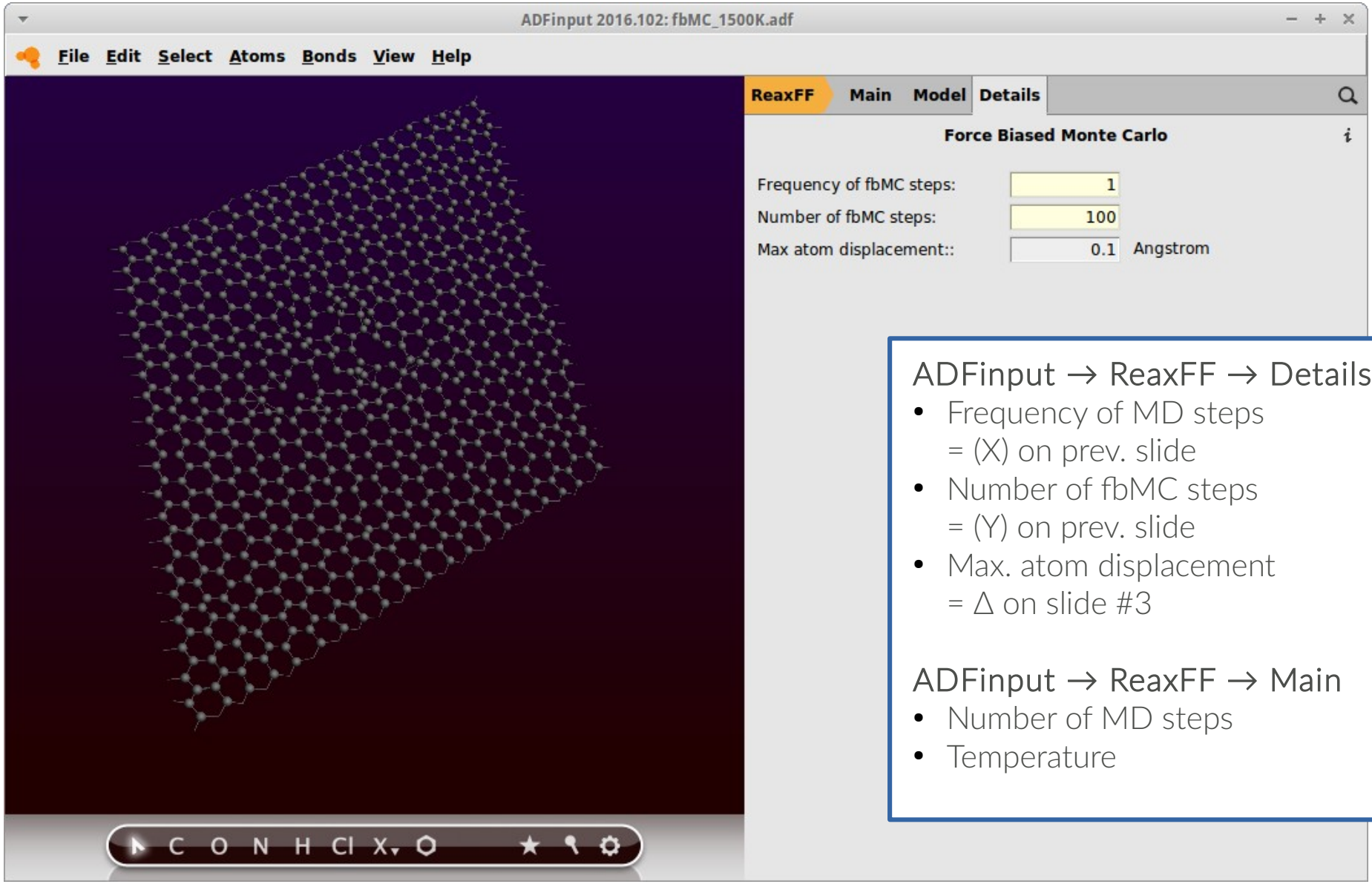
Σ_{MD} = 10 000 steps

Σ_{fbMC} = 5000 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



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)

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Science & Environment

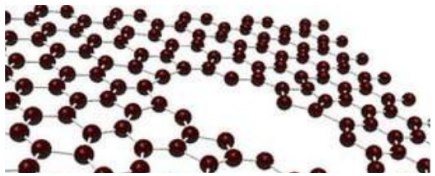
Graphene holes 'heal themselves'

By Jason Palmer
Science and technology reporter, BBC News

11 July 2012 | Science & Environment

Share

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.

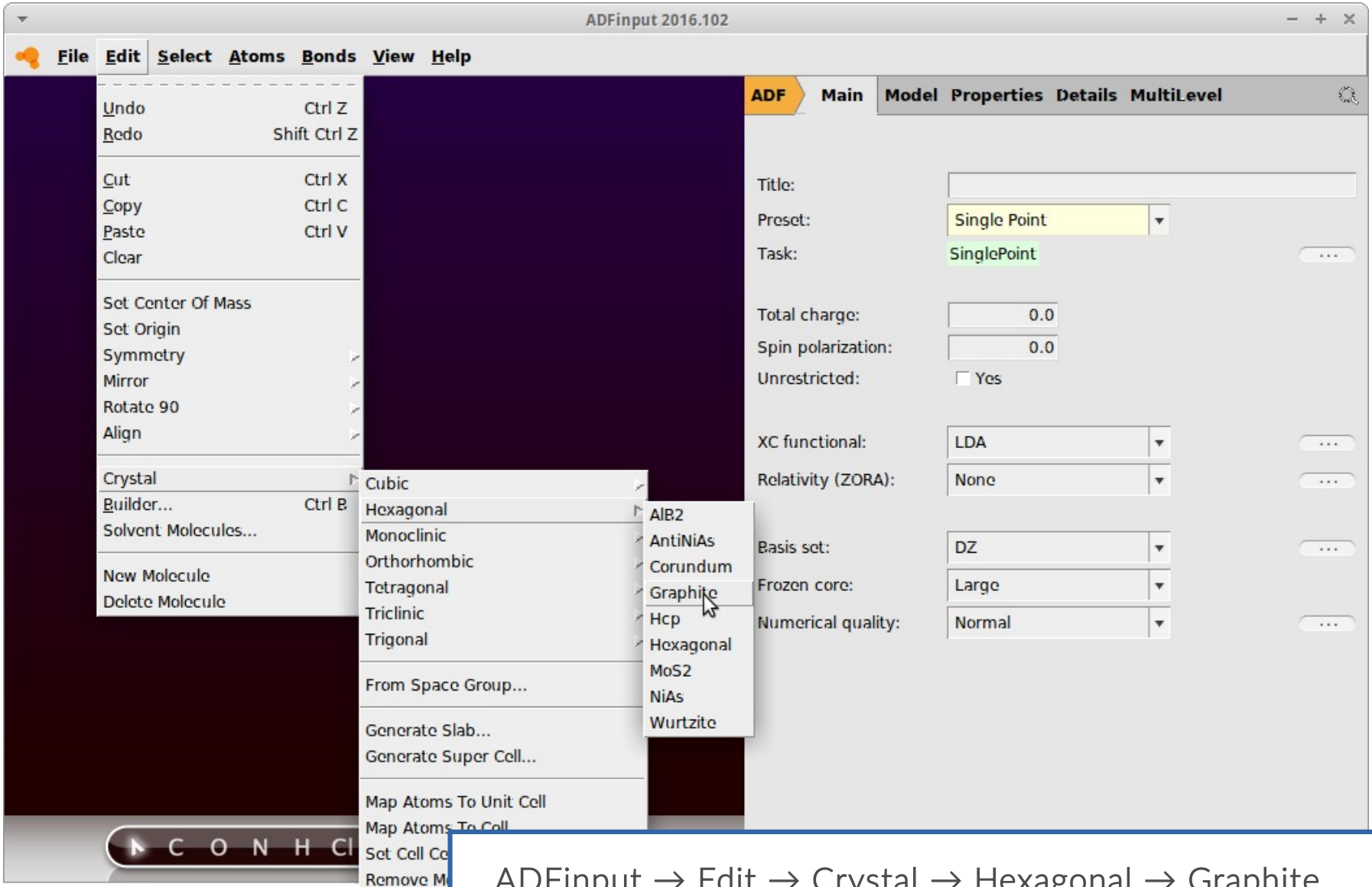
Researchers hope that the 'reknitting' process can be used to help control nanometre-scale etching of graphene.

Nano. Lett. 12, **3936–3940 (2012)**

Exercise 1:
Create a Graphene sheet

Hands-on: Create graphene

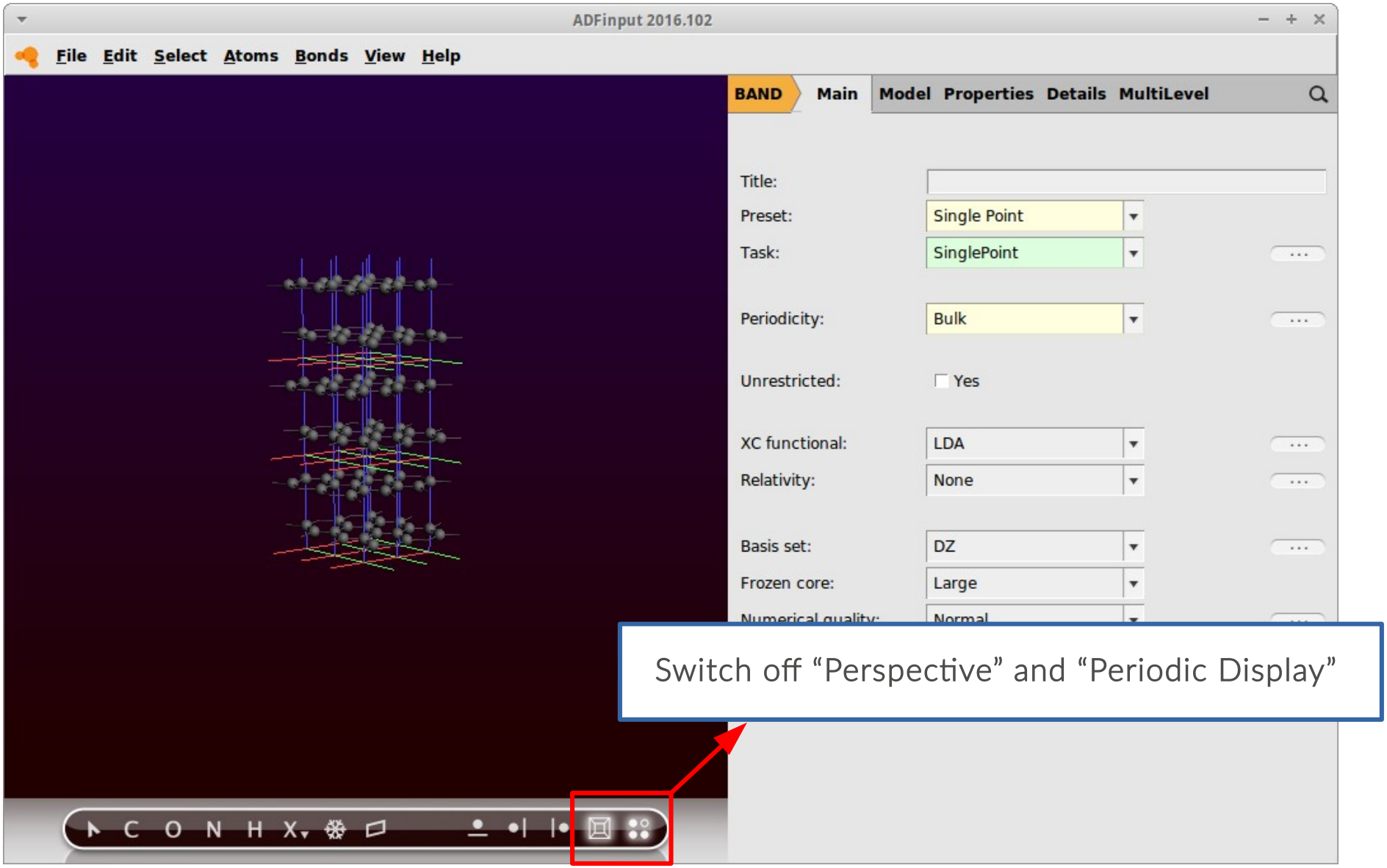
create a graphene sheet



ADFinput → Edit → Crystal → Hexagonal → Graphite

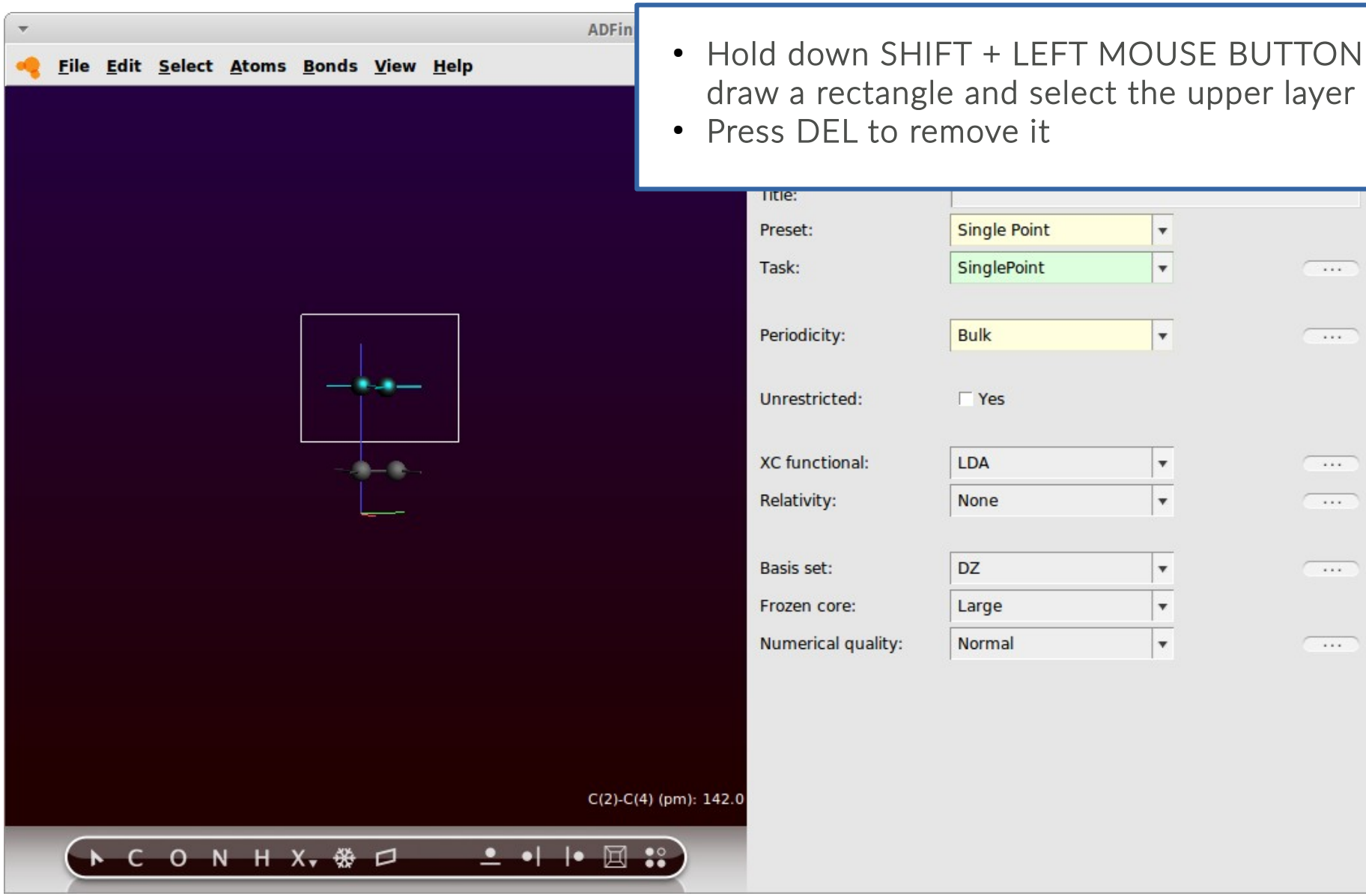
Hands-on: Create graphene

create a graphene sheet



Hands-on: Create graphene

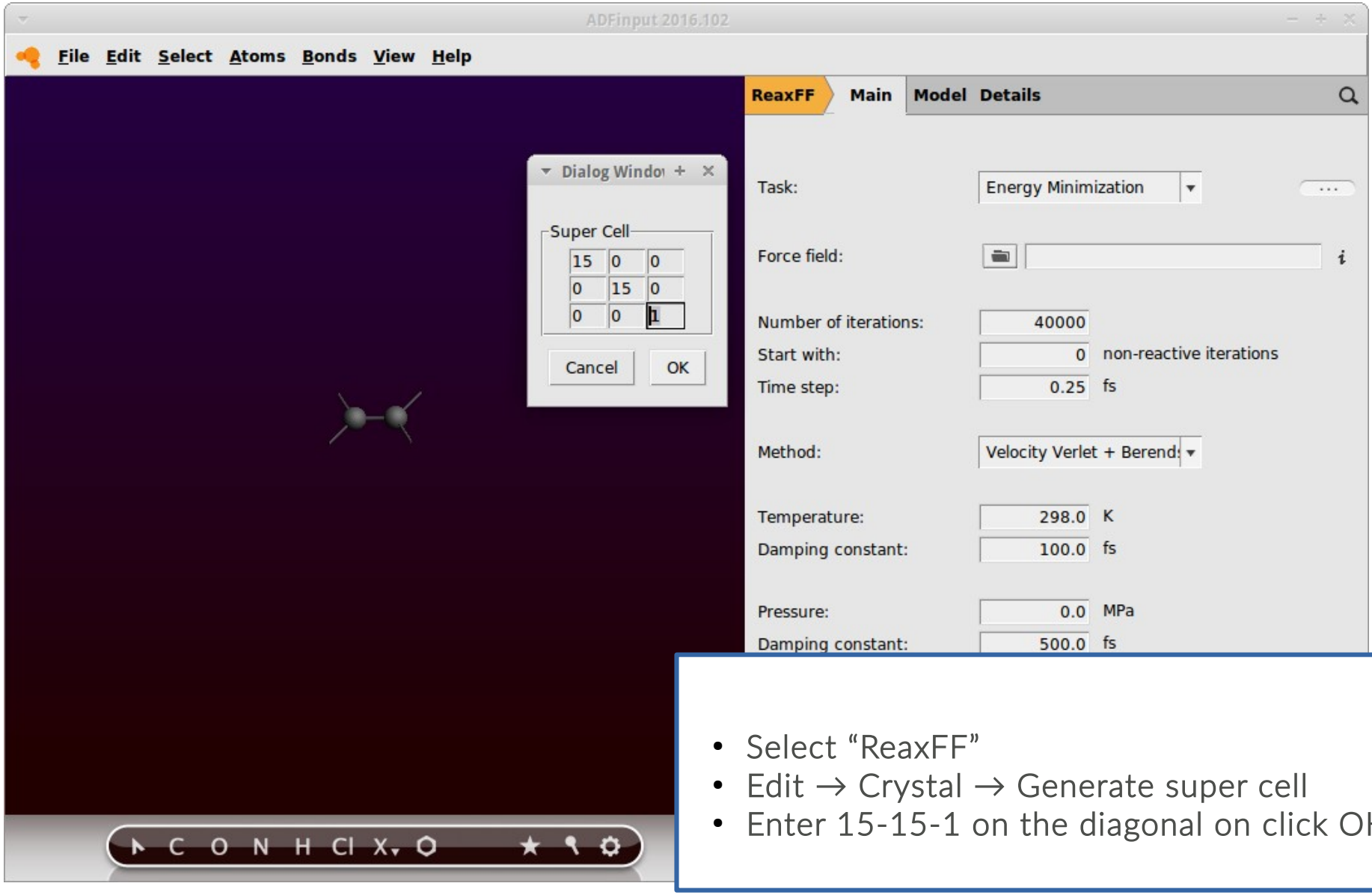
create a graphene sheet



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

Hands-on: Create graphene

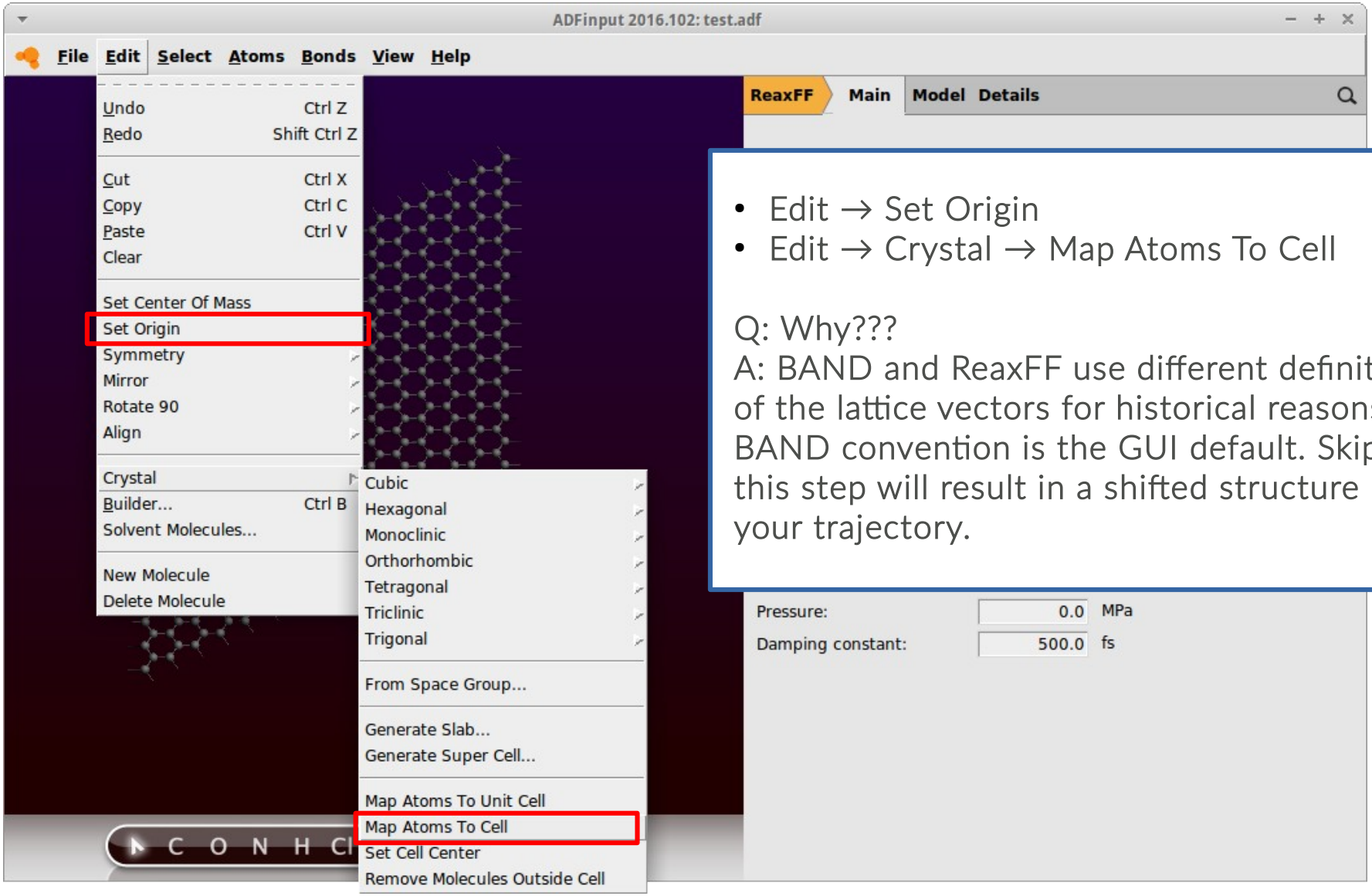
create a graphene sheet



- 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

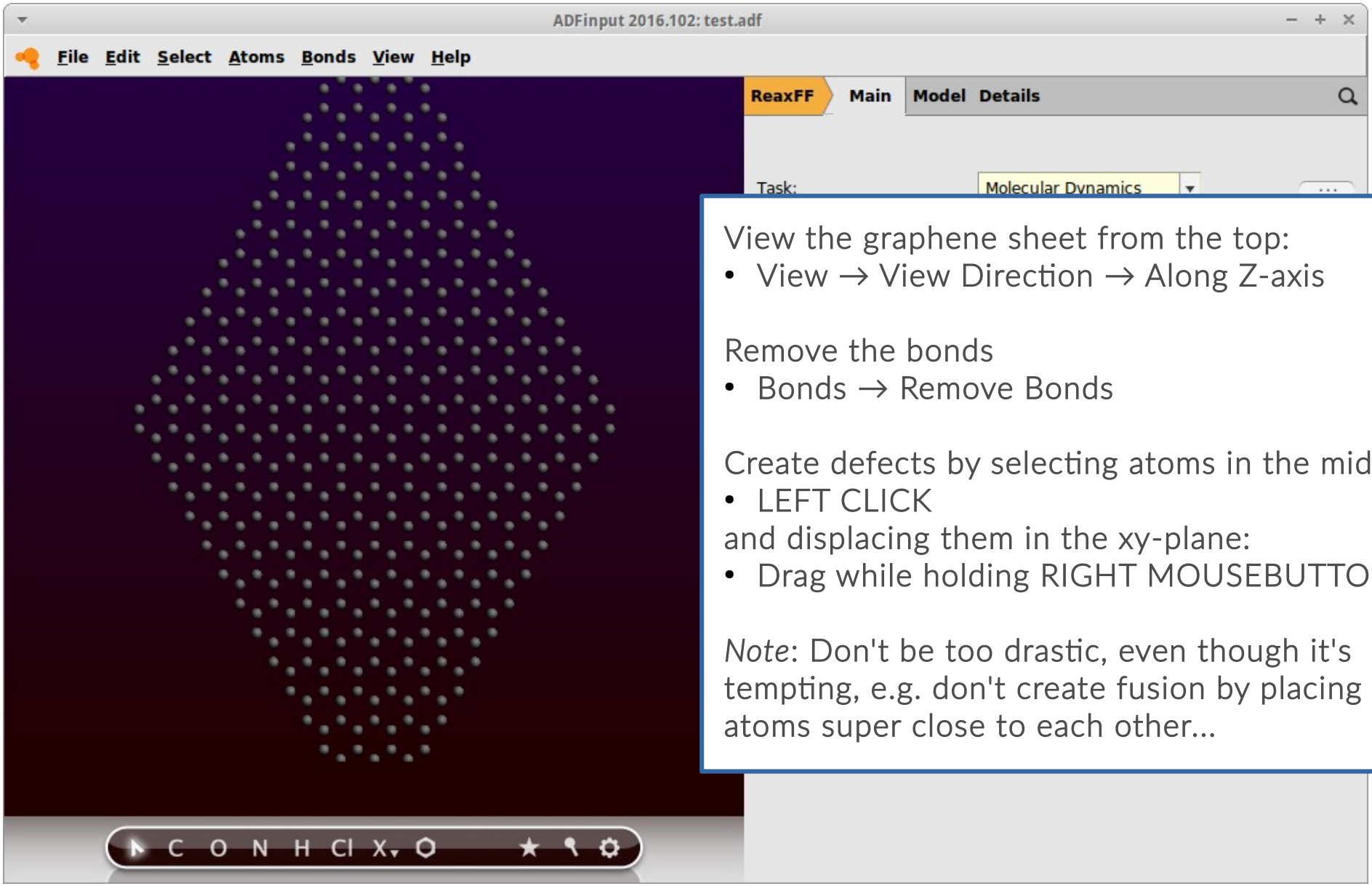


- Edit → Set Origin
- Edit → Crystal → Map Atoms To Cell

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.

Hands-on: Create graphene

creating the defects



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

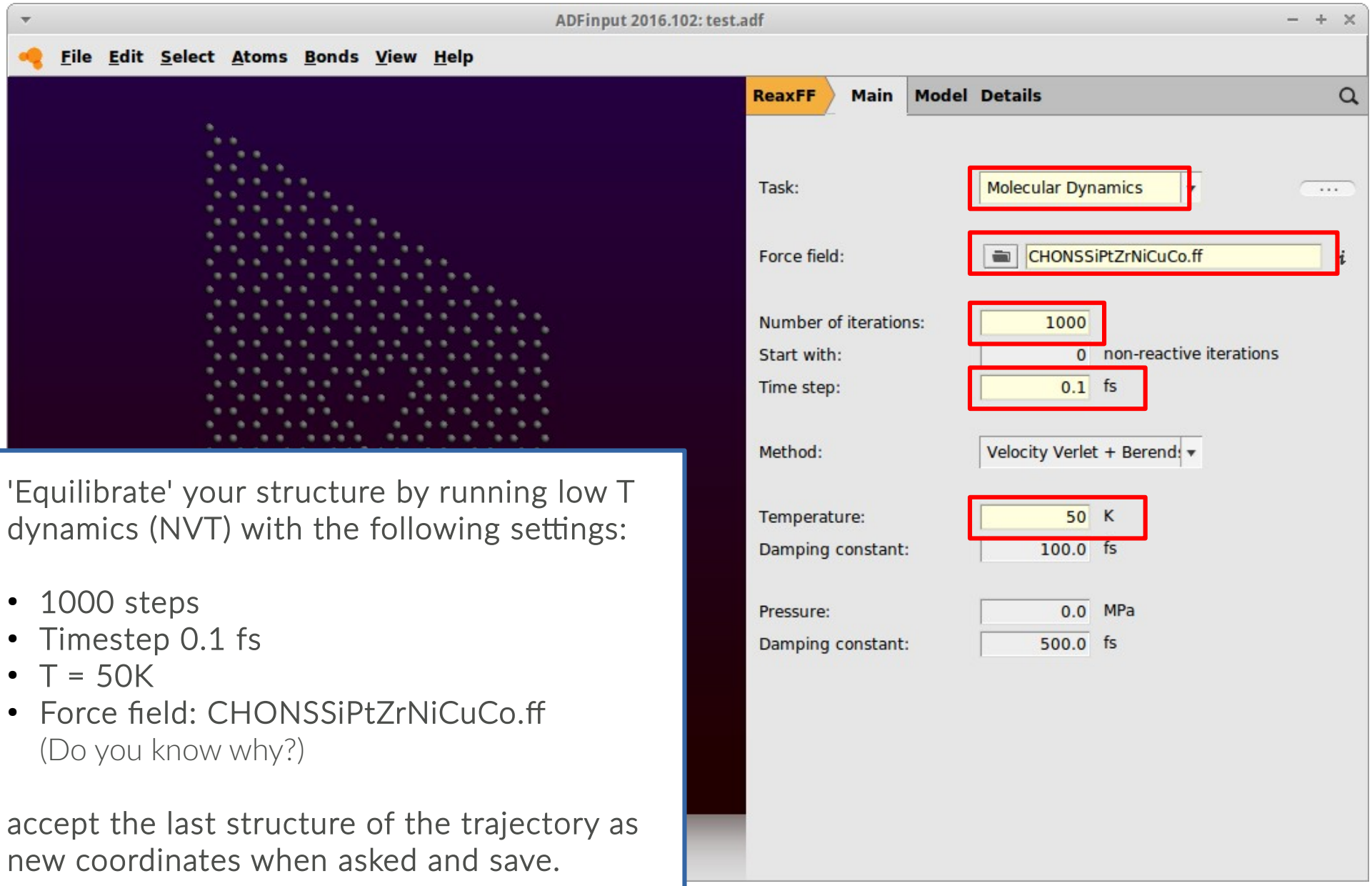
and displacing them in the xy-plane:

- 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



'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

ReaxFF | Main | Model | Details

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

ReaxFF | Main | Model | Details

Force Biased Monte Carlo

Frequency of fbMC steps: 1

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: 1

Energies, temperatures and more: 50

Coordinates: 1000000

Remove Rot/Trans every: 25 iterations

→ 10 000 fBMC steps @ 800K, Δ = 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 + Berend	
Temperature:	800	K
Damping constant:	100.0	fs
Pressure:	0.0	MPa
Damping constant:	500.0	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

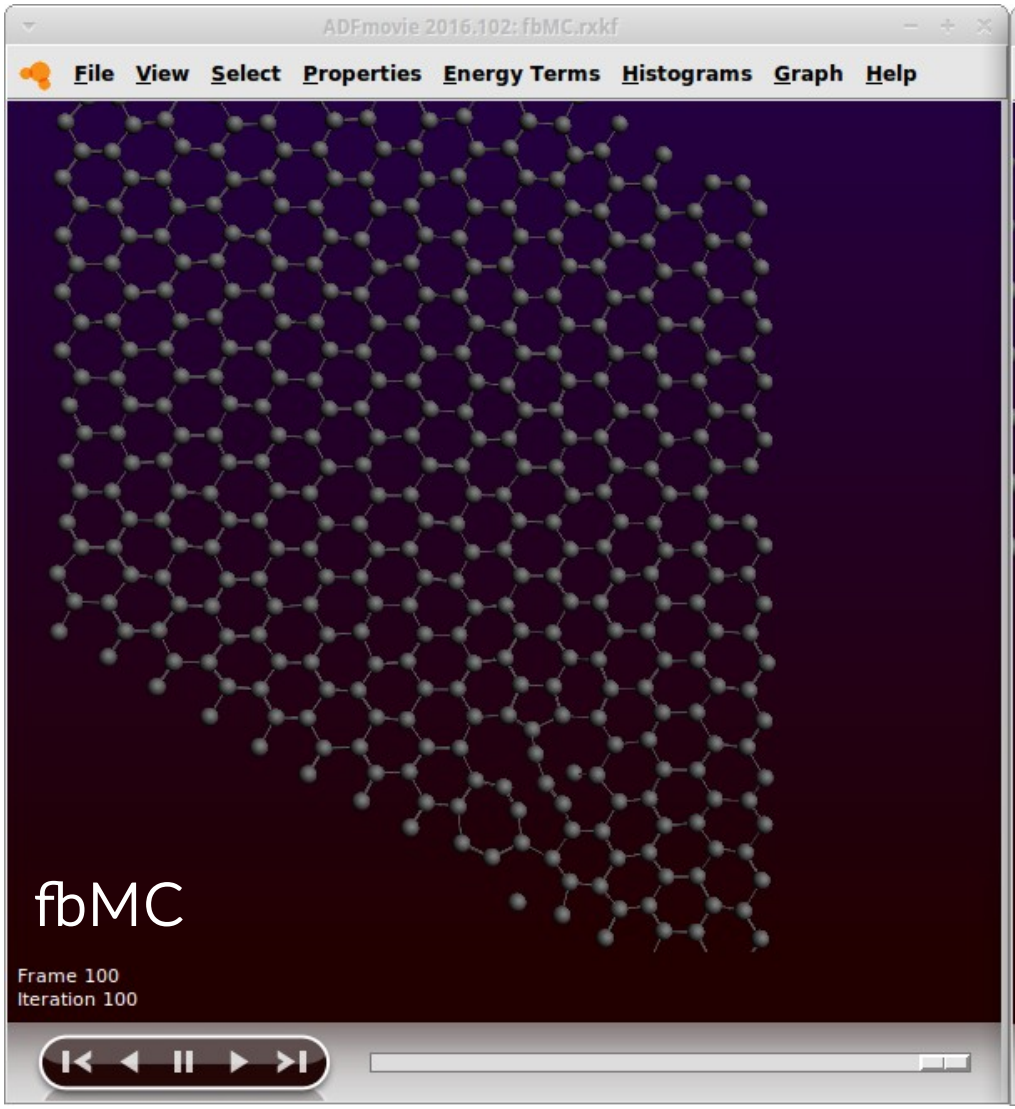
Molecular Dynamics

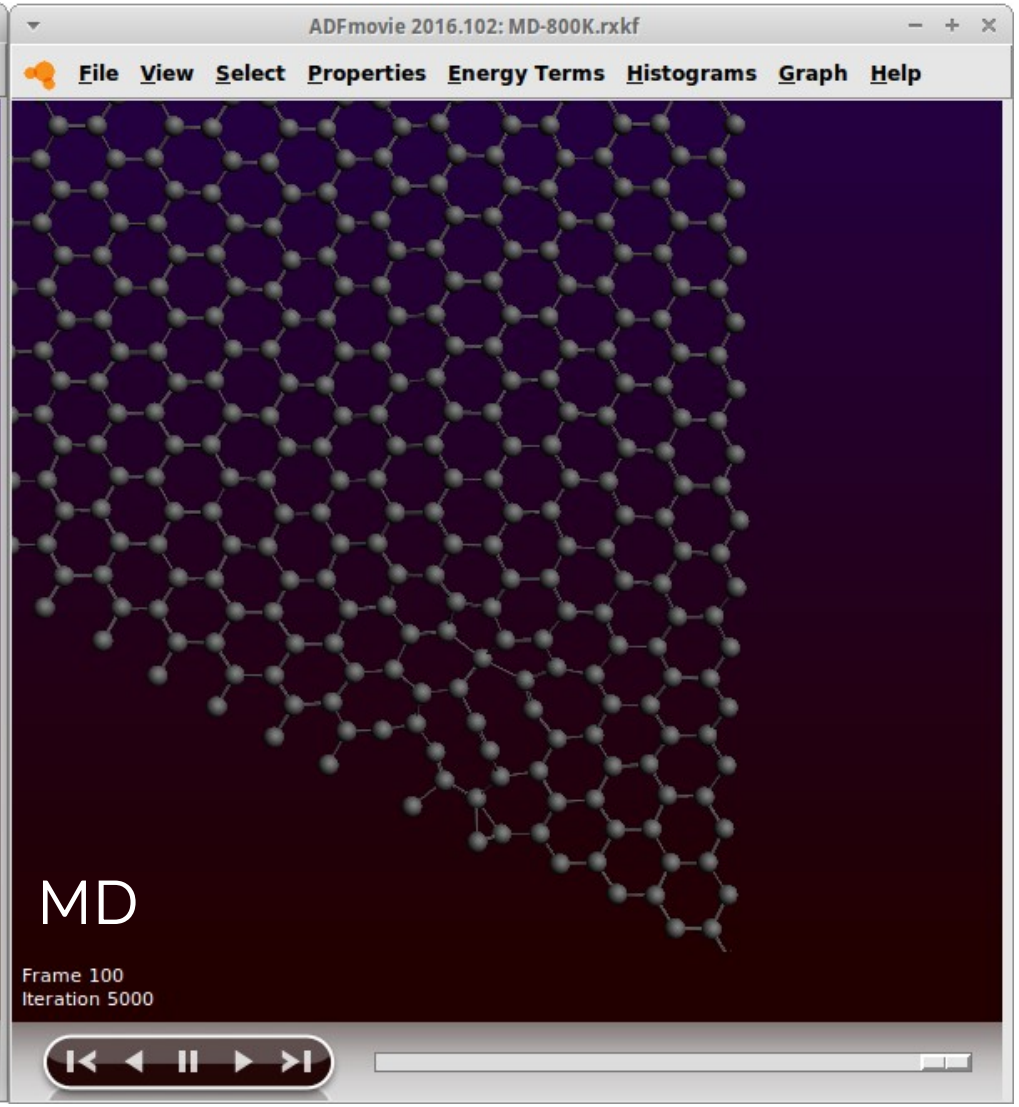
Fix cell parameters (NPT only):	None	in NPT
Output frequencies		
KF result file:	50	
Energies, temperatures and more:	50	
Coordinates:	1000000	
Remove Rot/Trans every:	25	iterations

→ 10 000 MD steps @ 800K, Δt = 0.2 fs

Hands-on: Simulate Graphene Healing

Look at both trajectories with ADFmovie





Can you already spot a difference?

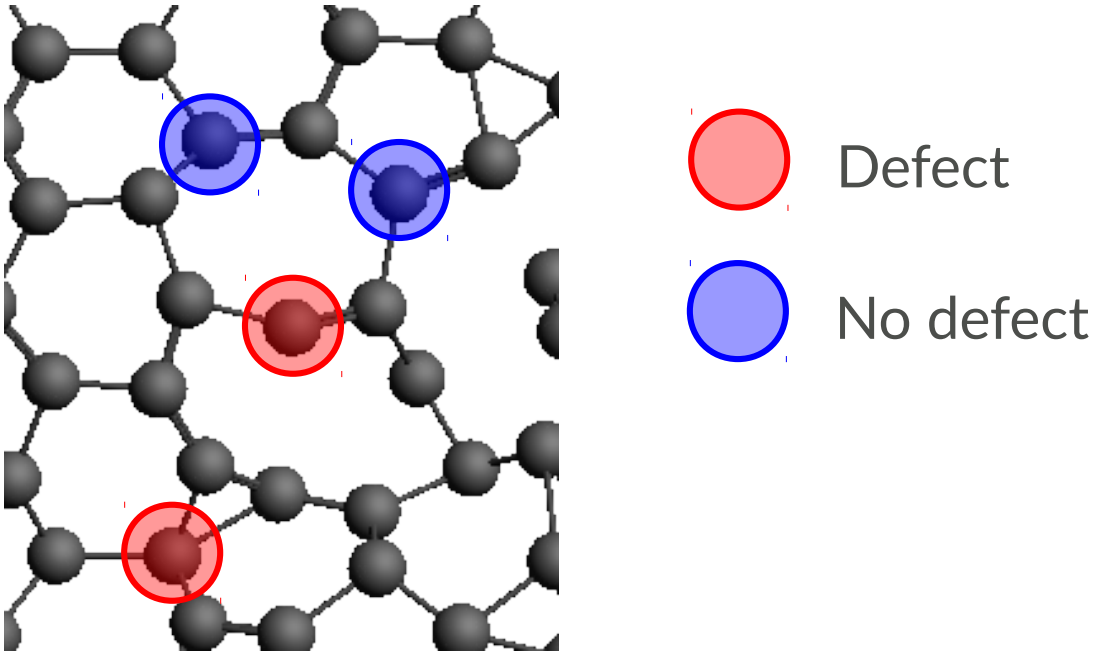
Exercise 3:
Take a closer look with Python

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

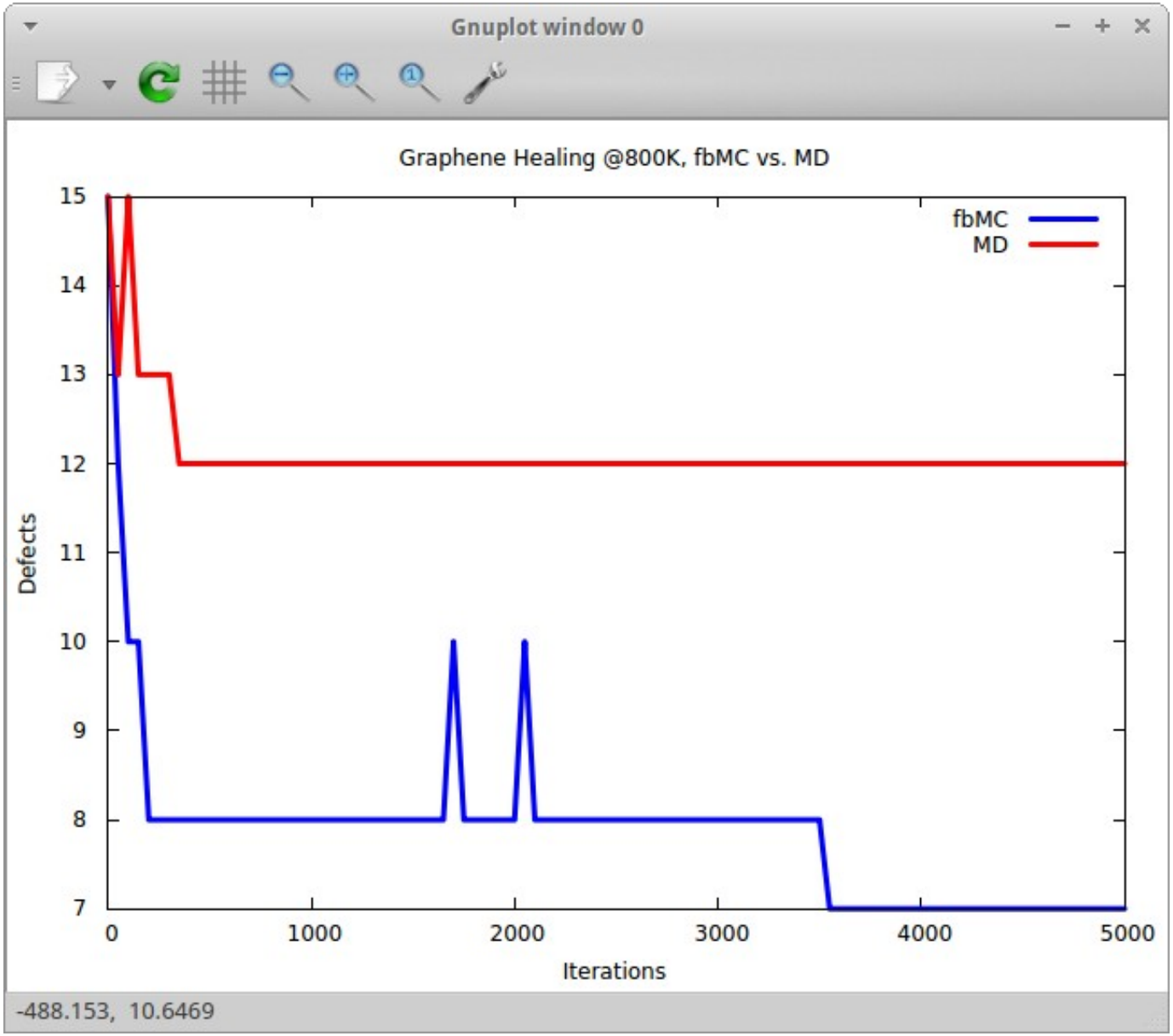
Use the PLAMS template in the scripts folder and turn the following pseudo code into a PYTHON script:

```
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
- Δ = 0.01 (small) and Δ = 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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