

Please read this compendium before the lab session.

**Practical Lab Session in Computational Physics:**

**TFYA90**

# **Molecular dynamics**

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## 1. Introduction

In the next two lab sessions, you will get hands on experience in using the Molecular Dynamics (MD) simulations technique. As you know from the lectures, MD is a tool that is widely used in materials science, as well as in other physics fields and/or chemistry and biology. The main aim of these lab sessions is to learn how to correctly setup and run a MD simulation, to understand the advantages and limitations of the method, but above all, to understand the meaning, or the actual physics, behind the actual numbers you will obtain at the end of each simulation.

As always, when using computer simulations, a trade-off has to be made between the accuracy of the model and the complexity of the simulation. In addition, don't forget that the size scale of the system to be simulated and time scale chosen will generally dictate the type of problem that can be studied using MD simulations. Consequently, during the lab session, and whenever you use computer simulations, **you should always think of the approximations made, the limitations of the model, the accuracy expected, and the reasonable conclusions that can be drawn based on all of the above arguments.**

We start out by introducing the tools needed to do the lab, which is the MD program used. We will use an MD code called **MDSinecura**. Many programs used for computer modeling are difficult to use and require quite some time to learn. **MDSinecura** is, however, designed to be easy to use and can be controlled completely via the GUI. It has been developed here at the university and the version you will run is a beta version, so please be patient as there might be a few bugs left...

## 2. Computer Tools

### Setting up the necessary files & directories

The simulations will be run in a UNIX environment on PCs using the Linux Operating system. You should login in one of the PCs using the student username and password you received upon starting your studies at the university (**bring this password to the lab if you do not remember it**). After the successful login, you need to do several operations necessary for the proper setup of your working environment, especially for those not used with the Unix/Linux operating system. Here they are:

1. Right click the mouse, and from the menu choose with the mouse pointer **OPEN TERMINAL**. A smaller window should now open on the monitor after this selection.

2. Point the mouse cursor in the newly open window and type: **mkdir mdlab** and press **Enter**. This will create a new directory in your so-called home directory. Notice that there should be a SPACE (highlighted in RED) between the command **mkdir** and the name of the new directory **mdlab**. Nevertheless you can use whatever directory name you want, but in this compendium, the newly created directory will be referred to as **mdlab**.

3. Now type **cd mdlab** and press **Enter**. This command will take you in the newly created **mdlab** directory.

4. You need to start a web browser. Type "firefox" and press enter directly in the terminal. That should work. Otherwise, find the application tab in linux and run a web browser.

5. Use the browser to go to the following site:  
[http://www.ifm.liu.se/theomod/theophys/scientific\\_software/mdsinecura/](http://www.ifm.liu.se/theomod/theophys/scientific_software/mdsinecura/)

6. Once there, download **MDSinecura Linux** (double click) into the newly created directory in your home directory (**mdlab**). When this operation is completed, **CLOSE** the browser window

7. Now move the mouse pointer on top of the Linux terminal window and left click. This should take you back in the **mdlab** directory (you can check this by typing in the command **pwd**, followed by **Enter**; you should see something like edu/student\_name/mdlab). Just make sure you are in the **mdlab** directory.

8. Now type in the following command: **tar zxvf MDSinecura.tar.gz** and press **Enter**. Notice the SPACE after **tar** and the SPACE after **zxvf**. This command will unzip the MDSinecura code you just downloaded and create a new directory, named **MDSinecura**, containing all the program files required for the lab session.

9. As you still are/should be in the MDLAB directory, at the command prompt type the following command: **mkdir lab1** then press **Enter**. The command creates a new directory in which all the results from this lab session will be stored.

**OBS: PLEASE DO NOT STORE THE LAB RESULTS IN THE MDSinecura directory!!!**

10. We now need to change directory in order to start the MDSinecura program. To do that, at the command prompt type **cd MDSinecura** then press **Enter**.

11. Now, you can start the MD program. At the command prompt type the following command: `./MDSinecura`, then press `Enter`. Notice that this time there is NO SPACE between the `.`, the `/` and `MDSinecura`.

12. The MDSinecura window should pop up now and welcome you to the wonderful world of MD simulations. You can of course enlarge it to suit your needs.

At this point, the following instructions should also be completed:

13. Minimize the previously used terminal window as it should not be needed anymore. **ATTENTION: DO NOT CLOSE the window, just MINIMIZE it, this is important!!!**

14. Open up a new terminal window (right click on the Linux desktop and choose Terminal Window), it might be useful to locate certain files created by MDSinecura.

**OBS: All students attending the lab should arrive at this point at approximately the same time, since this is also an interactive lab session, in which one might have to compare many sets of results, to make the most of the lab session. The students with Linux expertise are kindly requested to assist those who may get lost in the sequence of the above operations. I will of course do it myself, but if you help me, the lab session will progress in a smooth manner with no delays. Thank you!**

### 3. The MD Program

MDSinecura uses the following classes in the approach. When you first run the program, you will be asked to **Choose a Workspace**. This is the place where all files created by MDSinecura will be stored. You have already created this Workspace, it is the **lab1** directory in your **mdlab** directory. At this time, you should then select this directory following the prompts on the MDSinecura window.

Every time you start a new session with MDSinecura, you will be asked to create a *New Project* and/or a *New Simulation* within the project. Both these classes can be created from within MDSinecura. You create *New Projects* and *New Simulations* using the two tabs on the upper left of the MDSinecura window, or using the **File** menu. Typically, the project will contain all the work related to a certain chemical element, material or specific surface, for example *Argon*, *Platinum*, or *Silver\_Surface*. In each project you can then create new simulations related to the particular material. The name given to each simulation is of course entirely up to you, but the suggestion here is that the name reflects to some extent the purpose of the simulation. For Argon, you can use for example *Ar\_1*, *Ar\_2*, *Ar\_3*, or, *Ar\_relax*, *Ar\_Bulk*, *Ar\_3D*, *Ar\_2D*, *Ar\_MSD*, *Ar\_Debye* etc. The choice is yours as long as you remember what simulation does what.

All settings and output data in MDSinecura can be selected, accessed, controlled and/or visualized by (*left*) **double-clicking** on the different **Tabs** displayed in the left-hand part of the project and/or simulation window. Each time you select and double-click on one of the tabs, a new window will open giving you further options in terms of selecting/modifying the different parameters available under the particular tab. To close any of the newly open windows, you must **left-click on the cross** on the upper right part of the screen. Here's a quick summary of the choices available:

#### BEFORE THE MD RUN

**CONFIG** - Here you set up your simulation. To the right you will see three more tabs:

**SIMULATION:** - typically, under this tab you can select the *size* of the MD time step, *number* of time steps to be executed, the *temperature* of the simulation, the *thermostat* type (including none), settings for periodic boundary conditions (PBC), and a number of other MD runs parameters such as plot frequency, back-up and sampling intervals, etc. Under this tab, note the **VISUALIZATION** settings, which you can use to set the storage/frequency parameters required for the production of MD movies, which can be viewed at the end of the MD run.

**POTENTIAL:** - useful to modify the interaction potential parameters for each chemical element, potential cut-off, and potential tabulation settings.

**CALCULATION:** - use the options available under this tab to select to quantities you want to be calculated in a particular MD run. You can choose to calculate the specific heat, mean square displacement (MSD), the radial distribution function, pressure, energies and a number of other properties. Make sure you GIVE CONSIDERABLE THOUGHT to **what, when and how** you calculate. Simply by TICKING the boxes for **ALL** properties to be calculated will not be very useful or instructive....

**GEOMETRY** - Here you set up the geometry of the system to be simulated.

The default settings will take you to a so-called **Groups** tab (on the right of the window). A number of crystallographic lattice types can be used (primarily fcc and diamond-like). You can choose to create bulk unit cells (3-D simulations), surfaces (2-D simulations), and more complex arrangements such as adatoms

on surfaces. In each case, you must click on the respective tab (**Bulk**, **Surface**, etc) and you just specify the number of unit cells to be created in X, Y and Z. When you are finished with your settings, press the **Edit** button. You can also **Export** and/or **Import** an existing atomic configuration by using the respective tabs.

**IMPORTANT:** you must use the list of available chemical elements for the respective interaction potential (displayed above the Bulk, Surface, tabs) to **CORRECTLY SELECT THE CHEMICAL ELEMENT** you want to simulate.

**SIMULATION** - Double-click on this tab when you are finished with a particular setup. Start the simulation by pressing the **Simulate** button.

### AFTER THE MD RUN

**PLOTS** - When the MD run has finished, the results for a number of properties (total, potential, cohesive energies, temperature, pressure etc), can be viewed under this tab.

**RESULTS** - Final average values for a number of properties are tabulated here.

**VISUALIZATION** - Movies of the entire MD run can be accessed and viewed under this tab. Animations can be controlled using the controls displayed in the movie window.

## Project 1: fcc Argon

### LAB EXERCISES

First select project "argon" with one left-click

#### Exercise 1.

Start a *New Project* named *argon*. In the New Project start a New Simulation which should be called *bulk\_40K*. Click on the **CONFIG** tab, then under **SIMULATION** make sure the following settings are set correctly (you can simply tick below on your notes to make sure of this):

Time step = 1 fs (default)  
Timesteps = 20000 (default 1000)  
Temperature = 40 K (default 300 K)  
Scaling Time = 3 fs (default 300 fs)  
Thermostat = None (default)

Note that the default empirical potential is a variant of the Lennard Jones (LJ), named **Lennard Jones numerical gradient**.

On the right side, under Visualization, set **Store Frequency at 100** (default value is 25). You can now inspect the values under the **POTENTIAL** tab. Move on to the **CALCULATION** tab to the right and make sure YOU **DON'T CALCULATE** the following properties (un-tick the respective boxes): Specific Heat ( $C_V$ ), Mean Square Displacement (MSD), Radial Distribution Function (RDF), nor pressure (which has been incorrectly implemented in MDSinecura).

Now click on the **GEOMETRY** tab to set-up your simulation atomic slab. The *Groups* tab will show up to the right, make sure you click on the *Bulk* tab to the right. Here you MUST select the chemical element to be simulated from the available list:

- select **Argon**
- change the number of unit cells to **6** (default is 8) in each Cartesian direction.
- click on **Save** to actually generate your starting atomic configuration.

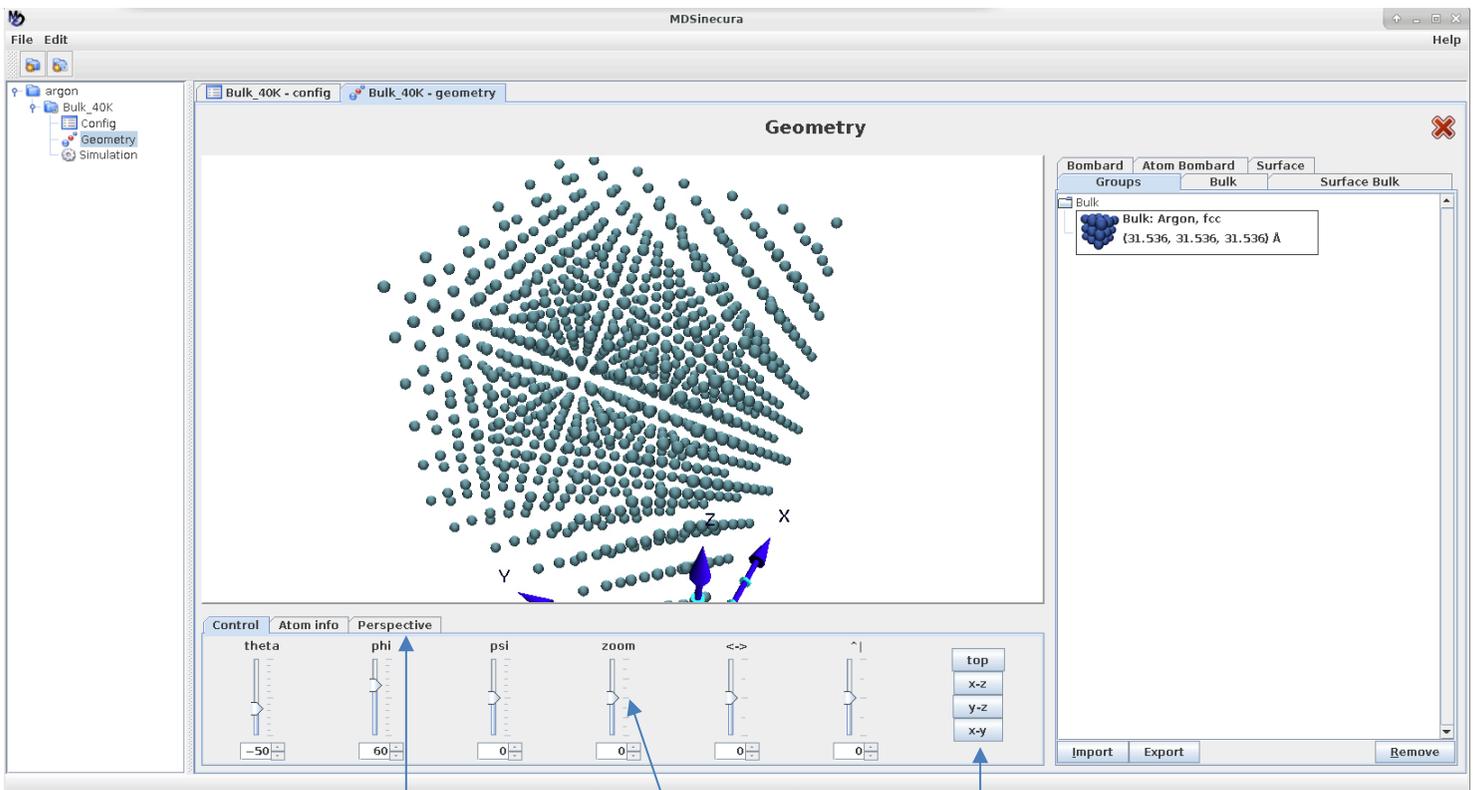
(fcc Argon is the default, which is fine)

To start the simulation, double-click on the **SIMULATION** tab, then press the *Simulate* button. Closely follow the information displayed. Upon the completion of the simulation, you can use the *Results* and/or *Plots* tabs to inspect the final results. Use **Visualization** the tab to view a movie of the MD run. **OBS:** There is **BUG** in the program which is very difficult to find & fix. To view the MD movie under double-click on **Visualization**, then open (double-click) one of graphs available under *Plots*, then close the graph displayed. The same sequence should be followed to view the atomic slab under **GEOMETRY**.

Comment the results (WRITE DOWN on your notes), what you observe. Is the system in equilibrium? What happens to the temperature? Write down all values for  $E_{kin}$ ,  $E_{pot}$ ,  $E_{tot}$ ,  $E_{coh}$ , as well as other important values. How does the cohesive energy of your system compare with the tabulated/text book value of 0.08 eV/atom? What is the reason for what you observe?

This parameter controls the number of initial time steps during which the velocities of the atoms are rescaled to achieve the target temperature (40 K in the present case).

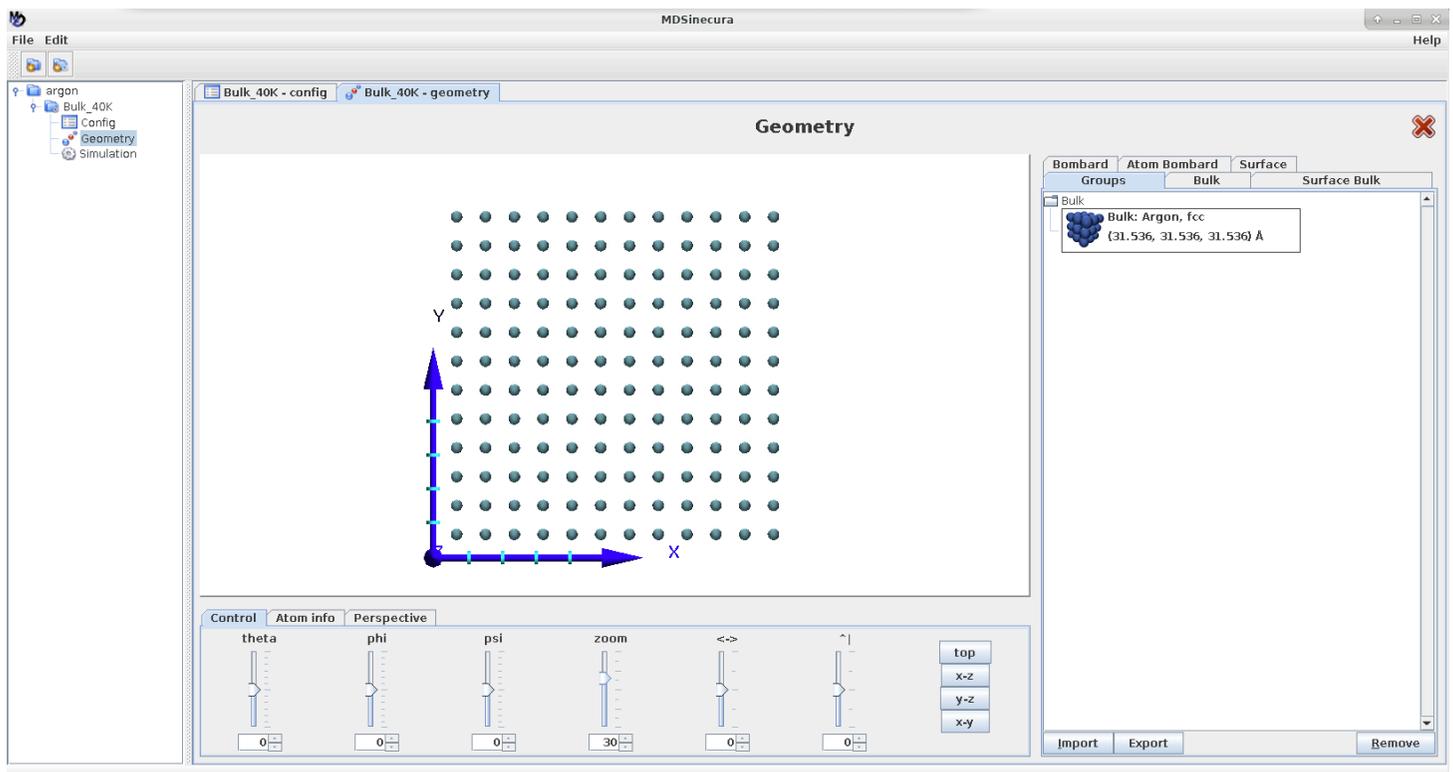
Look at the next page of this pdf to see how it should look like



Can be good to switch to "parallel projection"

Zoom-in and out

Here you can change the plane of view



## Exercise 2.

Within the same project (*argon*), point the mouse cursor to the *bulk\_40K* simulation and right-click on it. You see the option the *Copy to a New Simulation*. Do that, and at the prompt use the name *cutoff* for this new simulation (it will immediately be displayed under *bulk\_40K*). In the new simulation, *cutoff*, make the following changes:

- under **SIMULATION** **TURN OFF Visualization** (un-tick the respective box).
- under **POTENTIAL** examine carefully the lattice constant value for Argon (5.31) and compare it with the cutoff value displayed above. These are the parameters used in Exercise 1, so write down how many neighbor shells have been included in the previous Exercise.

Nr. of neighbor shells in Exercise 1: \_\_\_\_\_

Change cutoff to 10 Å. How many neighbor shells are now included?: \_\_\_\_\_. Enter value 10.0 in the respective field and press **Enter**. Make sure the new value is properly entered, otherwise you just repeat the previous MD run.

- under **GEOMETRY**, MAKE SURE you double-click on the atomic slab displayed under Groups, then press Bulk -- > Save, to make sure the new parameters in POTENTIAL have been updated.
- double-click on **SIMULATION**, then press *Simulate* to start the new MD run.

At the conclusion of the MD run, write down all values of interest and everything else you observe. How long it took to complete this MD run? How does that compare with the previous run (you can still access this information under SIMULATION window under the *bulk\_40K* run. What should happen to energy, accuracy etc.

### Exercise 3.

As in Exercise 2, copy the *bulk\_40K* run to a new simulation named **scaling**. We'll keep using this initial MD run for a while, as it has all settings in it, so please DO NOT DELETE IT! In the new

simulation, *scaling*, make these changes:

- Under **Simulation**, switch on the thermostat to "scaling".

- use the same procedure under **GEOMETRY** as in the previous exercise to make sure the new parameters are loaded in the new run.

- double-click on **SIMULATION**, then press *Simulate* to start the new MD run.

Write down again all relevant values and describe what you observe.

### Exercise 4.

Copy the *bulk\_40K* run to a new simulation named **epsilon\_1**. In the new simulation, *epsilon\_1*, insert the following changes/settings:

- under **SIMULATION** **TURN OFF** *Visualization* (as before, un-tick the respective box).

- under **POTENTIAL** change the value of **EPSILON for Argon** to **0.1**.

- use the same procedure under **GEOMETRY** as in the previous exercise to make sure the new parameters are loaded in the new run.

- double-click on **SIMULATION**, then press *Simulate* to start the new MD run.

Upon completion, write down the relevant values and describe what you observe. Explain why the values of total and potential energy are so different ( $\approx 10$  times larger) in comparison to exercise 1.

Also check the video under visualization. Although the average temperature is nearly the same, note that the atomic vibrations in this simulation look very different in comparison to exercise 1 (re-look at the video of exercise 1). Why?

Consider the LJ mathematical formalism (see below) for the potential energy "V". What do you expect would happen to the results of another simulation which employs an epsilon  $\epsilon$  value **0.2**?

$$V_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

### Exercise 5.

- Copy the *bulk\_40K* run to a new simulation named *sigma\_1*. In the new simulation, *sigma\_1*, insert the following changes/settings:
- under **SIMULATION** **TURN OFF Visualization** (as before, un-tick the respective box).
  - under **POTENTIAL** change the value of **SIGMA for Argon** to **3.2**.
  - use the same procedure under **GEOMETRY** as in the previous exercise to make sure the new parameters are loaded in the new run.
  - double-click on **SIMULATION**, then press *Simulate* to start the new MD run.

Upon completion, write down the relevant values and describe what you observe. Explain why the values of total and potential energy slightly differ from those of exercise 1.

Also check the video under visualization. Note that the atomic vibrations in this simulation are very different in comparison to exercise 1 and differ even more (much wider vibrations) in comparison to exercise 4. Why?

### Exercise 6.

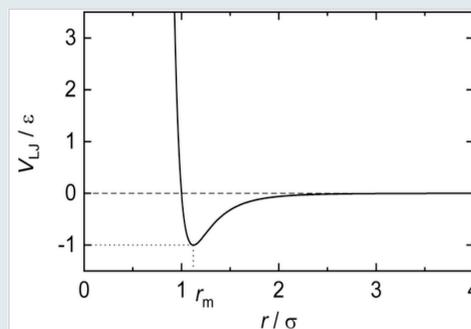
Copy again the *bulk\_40K* folder into 6 new simulations which you can name *lat\_par1*, ..., *lat\_par6*. In each simulation, go to the **GEOMETRY** tab, create bulk structures (always 6x6x6 atoms) with lattice parameters = 5.3, 5.4, 5.8, 5.1, 5.0, 4.6 Å. You should be able to run all simulations in parallel: Just go in each simulation tab and press “simulate”.

Collect the total energies from each run. Create a plot of energy vs. lattice parameter. What do you observe? Can you estimate a more accurate lattice constant (which, of course, depends on the LJ parameters sigma and epsilon you are using) than the value (5.256 Å) tabulated in the potential table?

### Exercise 7.

The model of Argon bulk that you are using has a fcc lattice. Use the equilibrium lattice constant that you computed in exercise 6 to calculate the nearest-neighbor distance  $d_{\text{NN}}$  in the fcc lattice.

Consider that the LJ equilibrium distance ( $r_m$  in the figure) between two atoms of a diatomic molecule is equal to  $2^{1/6} \cdot \sigma$ . Compare  $2^{1/6} \cdot \sigma$  with  $d_{\text{NN}}$ . You should see that those values differ slightly. Why are they different?



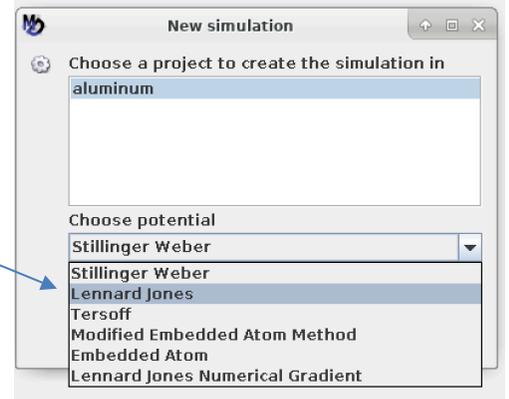
**Figure 1.** Graph of the Lennard-Jones potential function: Intermolecular potential energy  $V_{\text{LJ}}$  as a function of the distance of a pair of particles. The potential minimum is at  $r = r_m = 2^{1/6} \sigma$ .

# Project 2: fcc Aluminum

## Exercise 1

Create a new project named aluminum. Within the project, create a new simulation named **bulk\_energy**.

Make sure that you select the potential “**Lennard Jones**”.

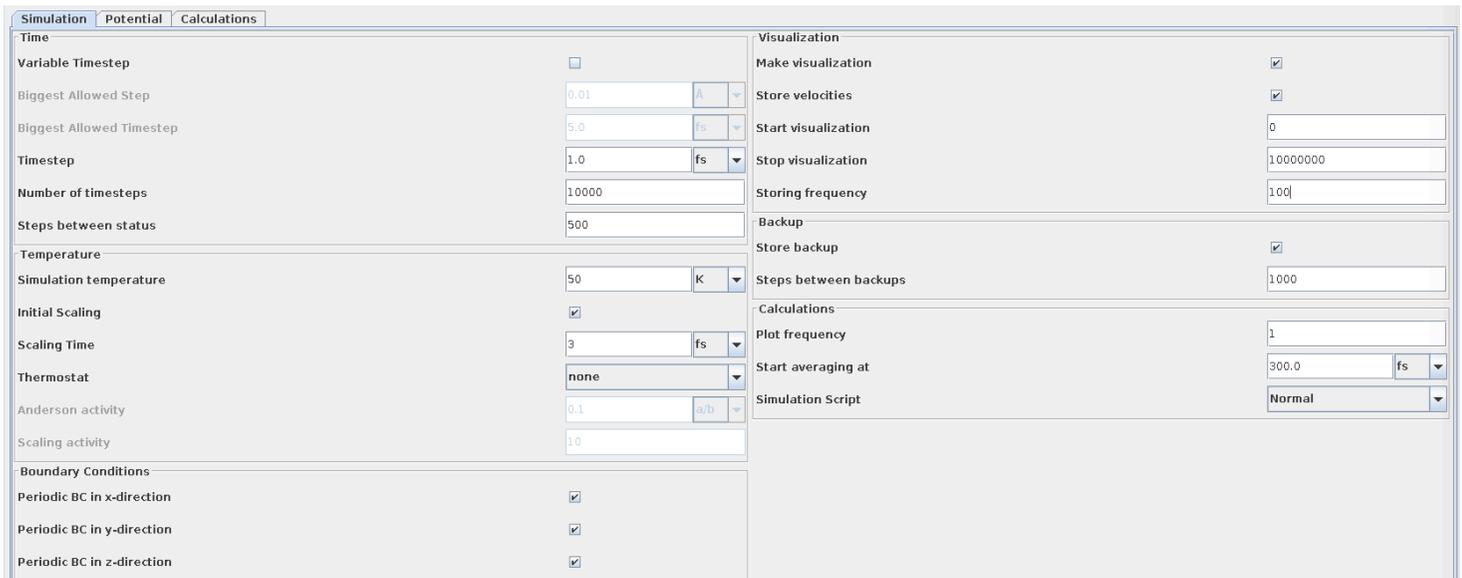


Inspect the LJ parameter of Aluminum under **Config/potential**. They are obviously very different from those of Argon.

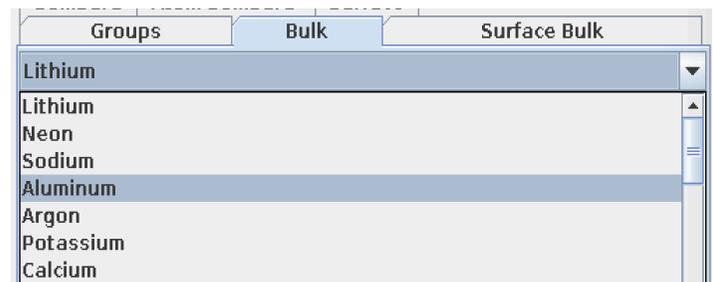
Lithium	6.941	3.51	0.205362	2.839
Neon	20.1791	4.429	3.121E-3	2.74
Sodium	22.98977	4.2906	0.137885	3.475
Aluminum	26.98154	4.0495	0.392196	2.62
Argon	39.948	5.256	0.010323	3.4
Potassium	39.0983	5.328	0.114444	4.285
Calcium	40.078	5.5884	0.215186	3.6

Under Config/simulation, we start with a very low temperature in order to calculate the total energy per atom (cohesive energy) of silver and later (exercises 2 and 3) calculate surface energies. Keeping temperature low is good because one reduces vibrational entropy effects on the crystal free energy.

Insert 10 000 timesteps, a simulation temperature of 40 K, a scaling time of 3 fs (but no thermostat). Storing frequency 100 steps.



Under “Geometry”, choose the bulk tab and make sure you select **aluminum** in the scroll bar (see figure below). Change also the number of cells to  $6 \times 6 \times 6$ . Save it! Then go the “Simulation” tab and press “simulate”.



You should get a cohesive energy of approximately **-3.0826 eV/atom**. This value is much larger (in absolute sense) than that obtained for bulk argon. Briefly explain why this is expected.

## Exercise 2

The surface energy is the energy per unit area required to cleave a crystal lattice on a specific crystallographic plane. Materials are generally (thermodynamic equilibrium) terminated with the surface which has lowest formation energy.

Copy the first simulation to a new one that you name **111\_surface**. In order to create a surface, one needs to remove the lattice periodicity along one direction. Go to “Config/simulation”. Switch off “Periodic BC in z-direction”. Add an extra z-size of 20 Å.

Boundary Conditions	
Periodic BC in x-direction	<input checked="" type="checkbox"/>
Periodic BC in y-direction	<input checked="" type="checkbox"/>
Periodic BC in z-direction	<input type="checkbox"/>
Extra z-size for neighbourlists	20 Å

Now go to “Geometry”. Select the surface bulk tab, select **aluminum**, and change the hkl Miller indexes to **1 1 1** (the intention is to simulate a 111 surface).

Bombard	Atom Bombard	Surface
Groups	Bulk	Surface Bulk
hkl		
1	1	1
Aluminum		
fcc		
Lattice constant (Å)		
4.0495		

You can add or remove atomic layers with the green + and – button at the bottom. Add six layers (from 0 to 5). For the moment, you have only 2 atoms in each layer. Manually change the number of periods in x and y to 6. **Save it!** If you select the view on the xz plane, your surface slab should look like the one below.

The screenshot displays the software interface for configuring a surface slab. The 'Surface Bulk' tab is active, showing the following configuration:

- hkl: 1 1 1
- Material: Aluminum
- Structure: fcc
- Lattice constant (Å): 4.0495

Layer index	Nr of layers	Type
0	1	Common
1	1	Common
2	1	Common
3	1	Common
4	1	Common
5	1	Common

The 'Geometry' panel shows a 3D visualization of the surface slab with axes x, y, and z. The 'X period' and 'Y period' are set to 6. The estimated number of atoms is 432.

NOTE: If you visualize the video (view on xz or yz plane), you will see that the surface slab layers oscillate upward and downward. This is due to the fact that the distance between surface layers is different than in the bulk (surface relaxation).

Check how many atoms  $N$  you have in this simulation. Compute the energy of formation (also named surface energy) of the 111 surface using formula:

$$E_{111} = \frac{U_{111} - N * E_{\text{coh}}}{2 * A},$$

where  $E_{\text{coh}}$  (from exercise 1) is the cohesive energy (=potential energy per atom in the bulk),  $U_{111}$  is the total potential energy of the slab and  $A$  is the surface area. Removal of periodicity along  $z$  creates 2 surfaces, which is why there is a factor of 2 at the denominator.

You can calculate the area  $A$  by looking at the bottom of the **surface bulk** tab under **geometry**.

Express the value  $E_{111}$  in  $\text{eV}/\text{\AA}^2$ .

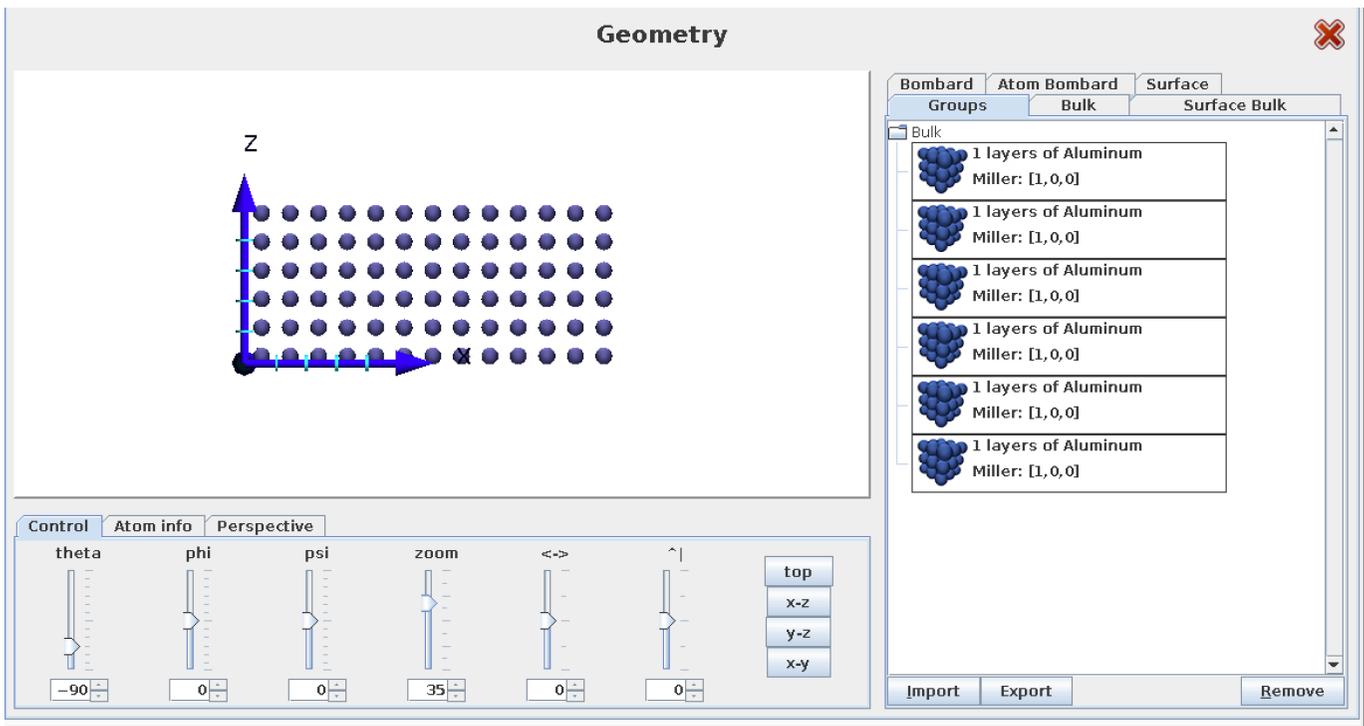
The close-up shows the 'Surface Bulk' configuration panel with the following values:

- X period: 4.0495000000000003E-10
- nr of periods: 6
- Y period: 4.0495000000000003E-10
- nr of periods: 6
- Estimated number of atom: 432

### Exercise 3

Copy the previous simulation to a new one that you name **100\_surface**.

In “Geometry”. Go to the **surface bulk** tab, select **aluminum**, but leave the hkl Miller indexes to the default values **1 0 0**. Create a surface with 6 layers and 6x6 periods in x and y. In parallel projection (view on xz plane), your simulation slab should look as illustrated below



Go to the simulation tab and run the simulation. Calculate the surface energy:

$$E_{100} = \frac{U_{100} - N * E_{\text{coh}}}{2 * A}$$

Which surface is more stable, 001 or 111? How do these values compare with experimental and ab initio values, which are typically around  $70 \text{ meV}/\text{\AA}^2$ . Do you think that the deviation of Lennard-Jones predictions from ab initio and experimental values are reasonable? Why?