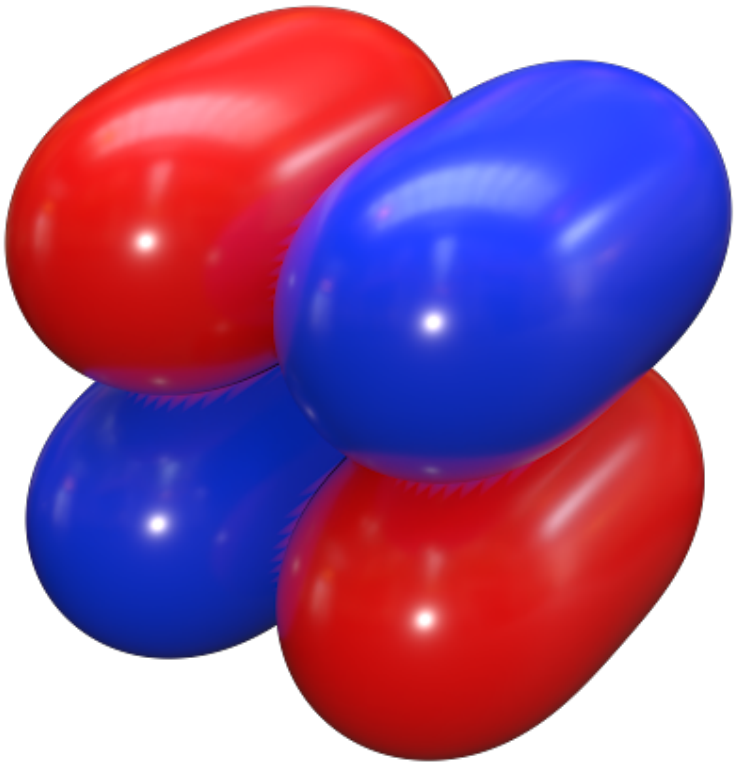
Sakura Science Computational Chemistry Workshop Series:

Molecular Simulation by Using Reactive Force-Fields (REAXFF)

March 4, 2025



1 Introduction

Reactive force fields (REAXFF)[1–4] are generally used to perform large-scale molecular dynamics (MD) simulations, which require a long time scale and a large system size (more than 2000 atoms). It enables us to observe reactive chemical systems with a relatively low computational cost compared to ab initio and semi-empirical methods. Moreover, MD simulation using REAXFF is generally faster than that of a machine-learning force field. Therefore, the REAXFF is still more favorable regarding computational cost than the machine-learning force field. The atomic charges during a REAXFF simulation can also change, which is great for investigating the charge transfer or charge-related chemical reactions, such as redox reactions or bond breaking of solid oxides.

In the present workshop, we will investigate the structure deformation of SiO_2 with the main objective of **calculating partial charges** of a system undergoing deformation, as well as the chemical bond formation and breaking. This feature is the most interesting part of the REAXFF simulation. In this tutorial, we will also learn how to visualize the LAMMPS output using the Matplotlib Python module.

2 Equilibration of Amorphous Silica Structure

1. Open Termius and enter the catalyst workstation by using the following information:

```
Address: catalyst.compscience.app
User: ssc
Password: sakura
```

2. Make a new directory under your name. For example:

```
mkdir yourname
```

   Replace `yourname` with your own name. If you did this in the previous workshop, you can skip this step.

3. Enter into your created directory:

```
cd yourname
```

   Again, in this case, you need to replace `yourname` with your own name.

4. Make a new directory, namely, `Equil` by typing:

```
mkdir Equil
```

Enter to the created directory:

```
cd Equil
```

5. In this case, the initial amorphous silica structure (SiO_2) was created and can be copied by using the following command:

```
cp /home/ssc/SSC_Workshop/Day5/Materials/Equil/silica.data .
```

6. Copy the force field file as well.

```
cp /home/ssc/SSC_Workshop/Day5/Materials/Equil/reaxCHOFe.ff .
```

7. Copy the running script by typing:

```
cp /home/ssc/SSC_Workshop/Day5/Materials/Equil/run.sh .
```

8. Copy the lammps input file by typing:

```
cp /home/ssc/SSC_Workshop/Day5/Materials/Equil/in.lammps .
```

9. Open the lammps input file by using vi editor:

```
vi in.lammps
```

In this case, the following are information about the LAMMPS input:

- `units real`: The simulation will be using the **real** type unit, which is the common unit that is used in the scientific world. For example, temperature should be in Kelvin units, energy in kcal/mol, mass in g/mol, distance in Å, velocity in Å/fs, and density in g/cm^3.
- `atom_style full`: The simulation will use the full atom style that usually includes bond information. However, in the REAXFF, the bond information is not used, thus in the current workshop, we ignore it.

- `read_data silica.data`: Reading the geometry and atom type from the provided `silica.data` file.
- `mass`: Defining the mass of each atom type. The LAMMPS program defines the atom type based on its mass. For example, in this case, atom types 1 and 2 have a mass of 28.0855 and 15.999 g/mol, respectively. Thus, they are Si and O, respectively.
- `pair_style`: Defining that we will use the REAXFF model with the `safezone` and `mincap` keywords were defined to prevent the memory allocation error that may appear during simulation due to bond breaking and formation events. You can refer to more details from the LAMMPS manual.
- `pair_coeff`: Reading the pair coefficients from the force field file. The atoms that are defined in this line should be in consistent order with the atom type that you define in the data file.
- `fix myqeq`: Equilibrate the atomic charges during the simulation. This becomes the power of REAXFF, where atomic charges will determine how the bonds are breaking and forming.
- `group grpSi type 1` and `group grpO type 2`: Defining the atom group for charge calculation.
- `variable qSi` and `variable qO`: Defining new variables, called `qSi` and `qO`. Each is used to record the charges of Si and O atoms.
- `termo 5`: Labeling the `thermo` function, which is used to define the thermodynamic quantities that are reported in the `log.lammps` file.
- `thermo_style custom step ...`: Defining what quantities to be listed in the LAMMPS output file. In this case, the MD step, temperature, total energy, pressure, volume, and the charges of Si and O atoms will be printed in the output file.
- `dump dmp all custom 100 npt.dump id type q x y z`: Specifying that the trajectory (dump) file will be printed every 100 MD steps under the file name of `npt.dump`. Inside this file, the atomic id, type, charge, and the Cartesian coordinate will be printed.
- `fix myspec all reaxff/species 5 1 5 species.log element Si O`: Creating `species.log` file that contains the molecular/atomic species that are involved in the simulation. It is necessary to monitor whether a certain chemical reaction occurs.
- `velocity all create 300.0 3482028`: Create initial velocities for the system at 300 K with a certain random seed.
- `fix mynpt all npt temp 300.0 300.0 100 aniso 1.0 1.0 1000`: Define the MD ensemble that is used. In this case, the *NPT* ensemble is used with the temperature and pressure of 300 K and 1 atm, respectively. The simulation box is relaxed anisotropically, where the a, b, and c cell dimensions are not uniformly changed.

- `timestep 0.5`: The time step of 0.5 fs will be used during the simulation. The REAXFF force field does not allow a higher timestep, thus typically a low timestep of 0.5 or 0.25 fs is used.
- `run 5000`: The MD simulation length. In this case, 5000 MD steps will be performed. It is equivalent to 2500 fs (2.5 ps). It is a short simulation compared to those published in many works.
- `write_data silica-npt.data`: Write the last frame of the trajectory into `silica-npt.data` file. This file will be necessary to continue the simulation.

10. Quit from the text editor by typing:

```
:q!
```

11. Submit the simulation by typing:

```
sbatch run.sh
```

Before typing this command, you can also check the submission file (`run.sh`) in case you wanna know more details about the number of nodes or the LAMMPS command that you use to run the simulation. Also, you will need to take note of your job ID. This will be required to monitor your job status.

12. Check your simulation status by typing:

```
squeue
```

Ensure that you have a running job status (**R** under the **ST** column). Normally, the equilibration will be finished in 5 to 6 minutes.

13. When you finished the equilibration, download `npt.dump` file into your computer. Visualize the file by using the Ovito visualization program. You can download Ovito here: `https://www.ovito.org/#download`. Note that you just need to download the basic version, not the pro one. The pro version needs a special license with a subscription. Play the trajectory and enjoy the movements of silica atoms during the *NPT* simulation. Fig. 1 represents the snapshot of the current MD trajectory.

14. Plot the temperature, charge of silicon, charge of oxygen, etc by using the Matplotlib module of the Python script. You can copy our premade python script by typing:

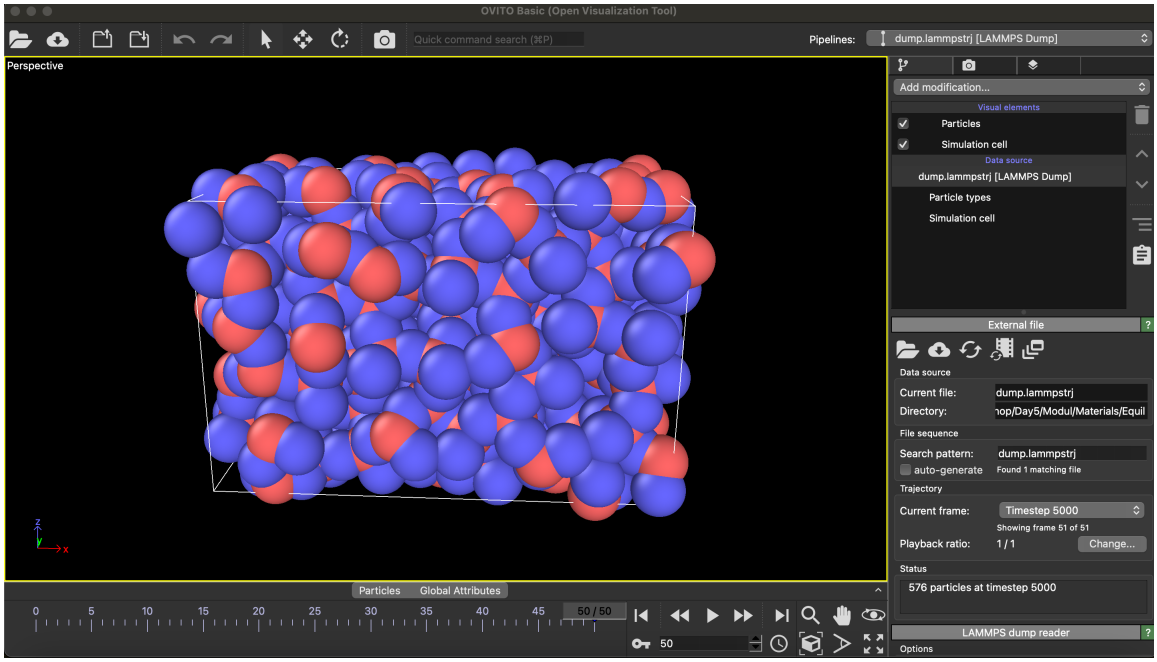


Figure 1: Snapshot of MD trajectory of SiO_2 bulk crystal under the NPT ensemble. The red and blue colors represent silicon and oxygen atoms, respectively.

```
cp /home/ssc/SSC_Workshop/Day5/Materials/plot_loglammps.py .
```

15. Plot the time-course changes of the printed quantities by typing:

```
./plot_loglammps.py -dt 0.5 log.lammps
```

where `-dt` is the time step that you used (in femtosecond) in the simulation. The example of time course changes in temperature, charges of oxygen, and charges of silicon are shown in Figs. 2, 3, and 4, respectively.

3 Identifying Chemical Reaction during Silica Deformation

1. Ensure that you have finished the previous equilibration step.

2. Edit the obtained `silica-npt.data` by typing:

```
vi silica-npt.data
```

Type the following:

```
/cluster
```

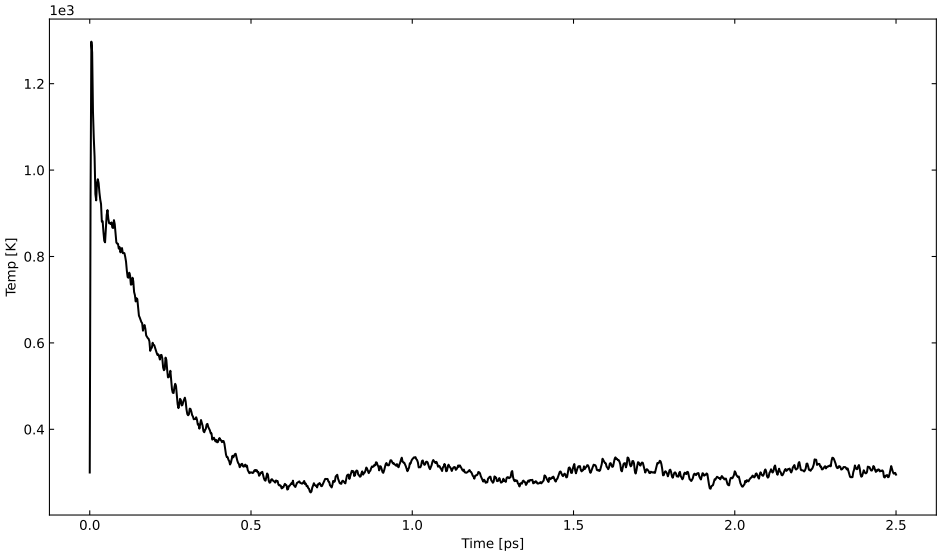


Figure 2: Time-course changes of temperature obtained from MD equilibration of silica.

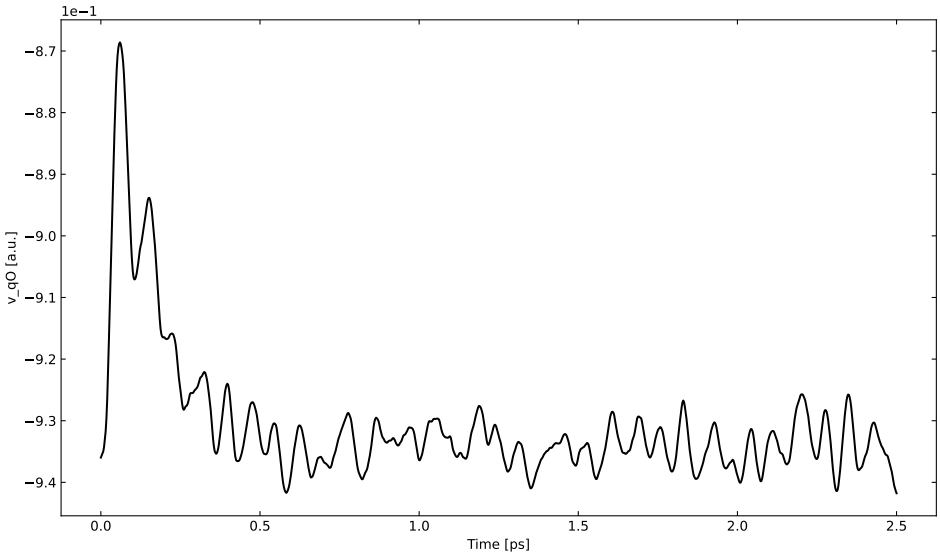


Figure 3: Time-course changes of oxygen charges obtained from MD equilibration of silica.

Delete the lines below the cursor by typing:

```
d600
```

and then press enter. Save and quit the vi text editor by typing:

```
:wq
```

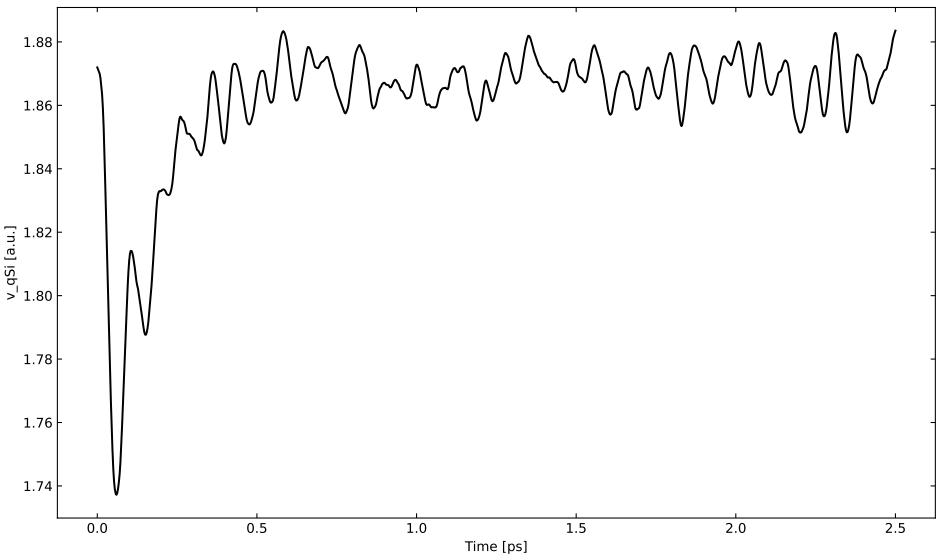


Figure 4: Time-course changes of silicon charges obtained from MD equilibration of silica.

3. Exit the current directory by typing:

```
cd ../
```

Make a new directory, namely, `Deform` by typing:

```
mkdir Deform
```

Enter the created directory:

```
cd Deform
```

4. Copy the example input file by typing:

```
cp /home/ssc/SSC_Workshop/Day5/Materials/Deform/in.lammps .
```

5. Copy the running script by typing:

```
cp /home/ssc/SSC_Workshop/Day5/Materials/Deform/run.sh .
```

In this case, since you will read the data and force field files from the `Equil` directory, you will not need to copy them.

6. Submit your simulation by typing:

```
sbatch run.sh
```

7. As usual, check your job status by typing:

```
squeue
```

   The simulation will finish in 30-40 minutes. Thus, you will need to wait until the end of this workshop. I will explain in detail about the input file during the workshop.

8. Once the simulation is finished, split the output file by typing:

```
vi log.lammps
```

9. Go to the last line of the file by pressing **SHIFT + G** button.

10. Search upward the line beginning with **Step** by typing:

```
?Step
```

   Press the upper arrow button on your keyboard one time as such that you are in the line containing `Per MPI rank memory ....` Delete all lines above by typing:

```
d2000
```

   then press **upper arrow button**. Note that this step is important; **do not press enter** because the enter button will delete the lines below the cursor instead. Save the file by typing:

```
:w log_deform.lammps
```

   Quit from vi editor by typing:

```
:q!
```

11. Plot the time course changes of the printed properties from the `log_deform.lammps` by typing:

```
../Equil/plot_loglammps.py log_deform.lammps -dt 0.5
```

This will give you the pdf files containing the time course changes of the printed properties during the silica deformation.

12. Download all simulation results, including the dump file and pdf files into your computer. The time-course changes of the oxygen and silicon charges should appear as the ones shown in Fig. 5 and 6.

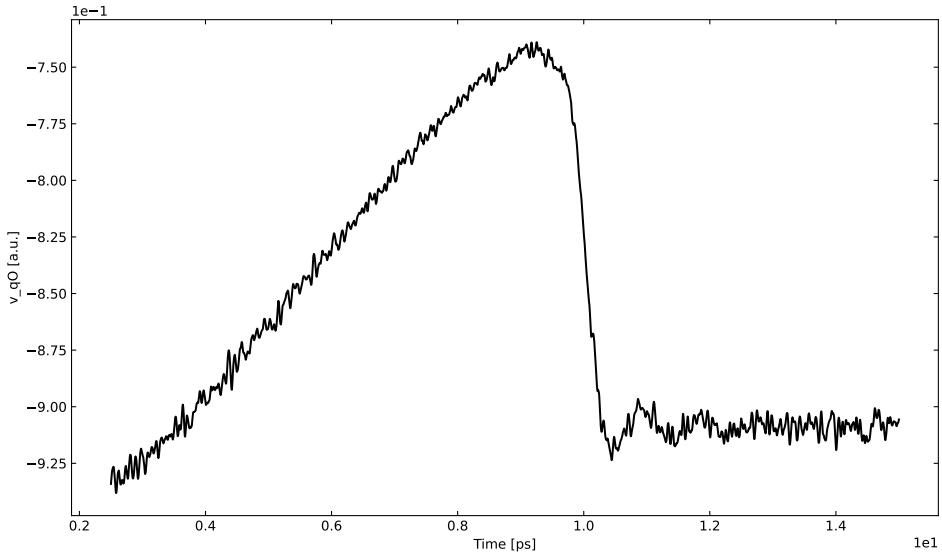


Figure 5: Time-course changes of the oxygen charges during the deformation of the amorphous silica structure.

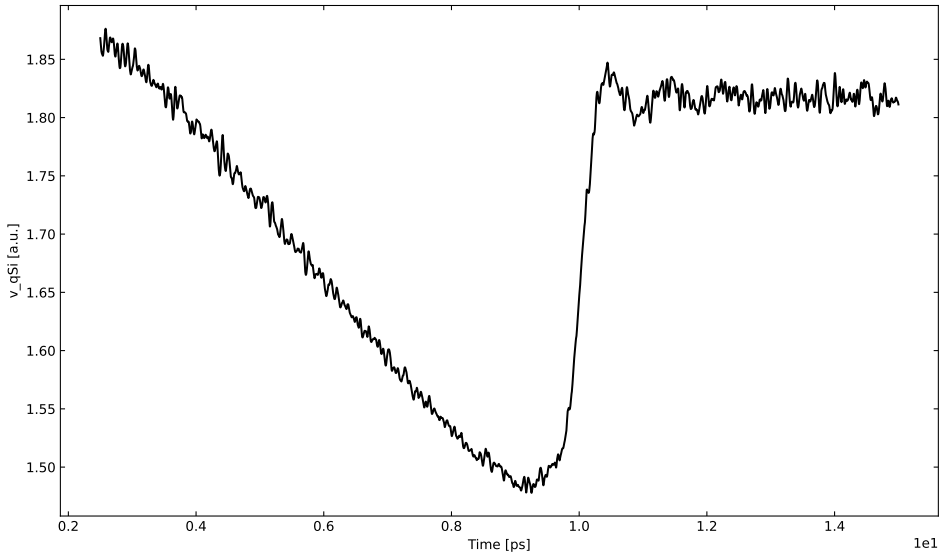


Figure 6: Time-course changes of the silicon charges during the deformation of the amorphous silica structure.

13. Visualize the deformation trajectory (`deform.dump` file) by using Ovito. The snapshot of the deformed structure is shown in Fig. 7.

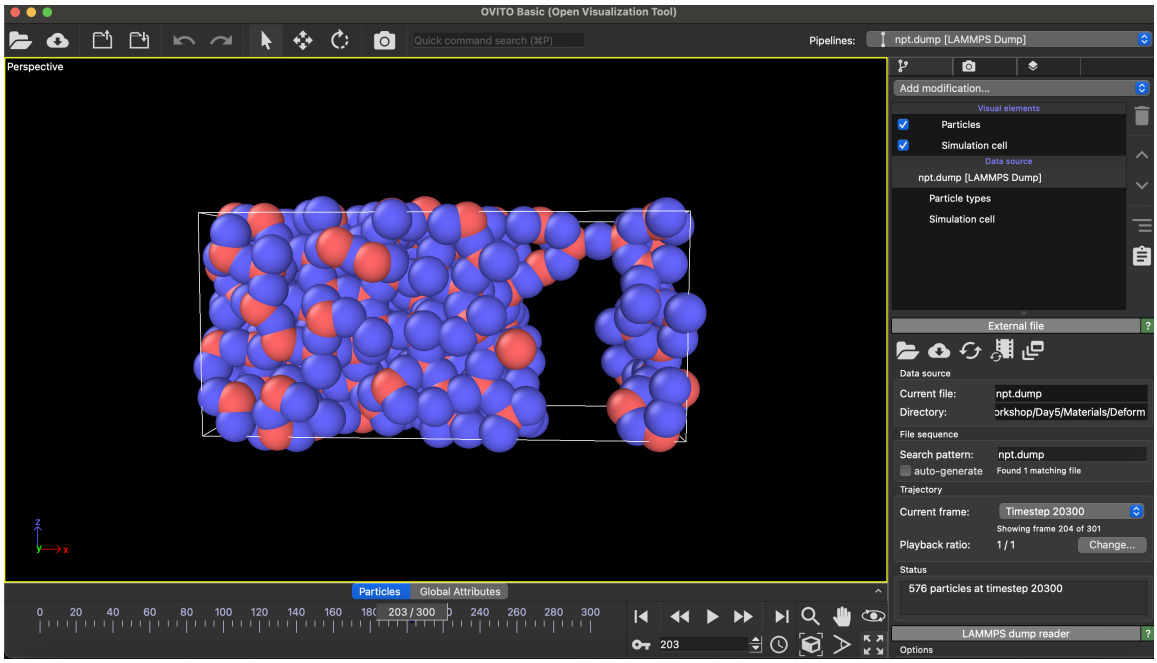


Figure 7: Snapshot of the deformed amorphous silica structure obtained from the MD simulation by adding the force upon the x-axis of the bulk silica crystal. The red and blue colors represent the silicon and oxygen atoms, respectively.

References

[1] Thomas P. Senftle et al. "The ReaxFF reactive force-field: development, applications and future directions". en. In: *npj Computational Materials* 2.1 (Mar. 2016), pp. 1–14. ISSN: 2057-3960. DOI: 10.1038/npjcompumats.2015.11. URL: https://www.nature.com/articles/npjcompumats201511 (visited on 09/22/2024).

[2] Adri C. T. van Duin et al. "ReaxFF: A Reactive Force Field for Hydrocarbons". In: *The Journal of Physical Chemistry A* 105.41 (Oct. 2001), pp. 9396–9409. ISSN: 1089-5639. DOI: 10.1021/jp004368u. URL: https://doi.org/10.1021/jp004368u (visited on 07/26/2018).

[3] Weiwei Zhang and Adri C. T. van Duin. "ReaxFF Reactive Molecular Dynamics Simulation of Functionalized Poly(phenylene oxide) Anion Exchange Membrane". In: *The Journal of Physical Chemistry C* 119.49 (Dec. 2015), pp. 27727–27736. ISSN: 1932-7447. DOI: 10.1021/acs.jpcc.5b07271. URL: http://dx.doi.org/10.1021/acs.jpcc.5b07271 (visited on 09/13/2016).

[4] Kimberly Chenoweth, Adri C. T. van Duin, and William A. Goddard. "ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation". In: *The Journal of Physical*

Chemistry A 112.5 (Feb. 2008), pp. 1040–1053. ISSN: 1089-5639. DOI: 10.1021/jp709896w. URL: https://doi.org/10.1021/jp709896w (visited on 10/07/2024).