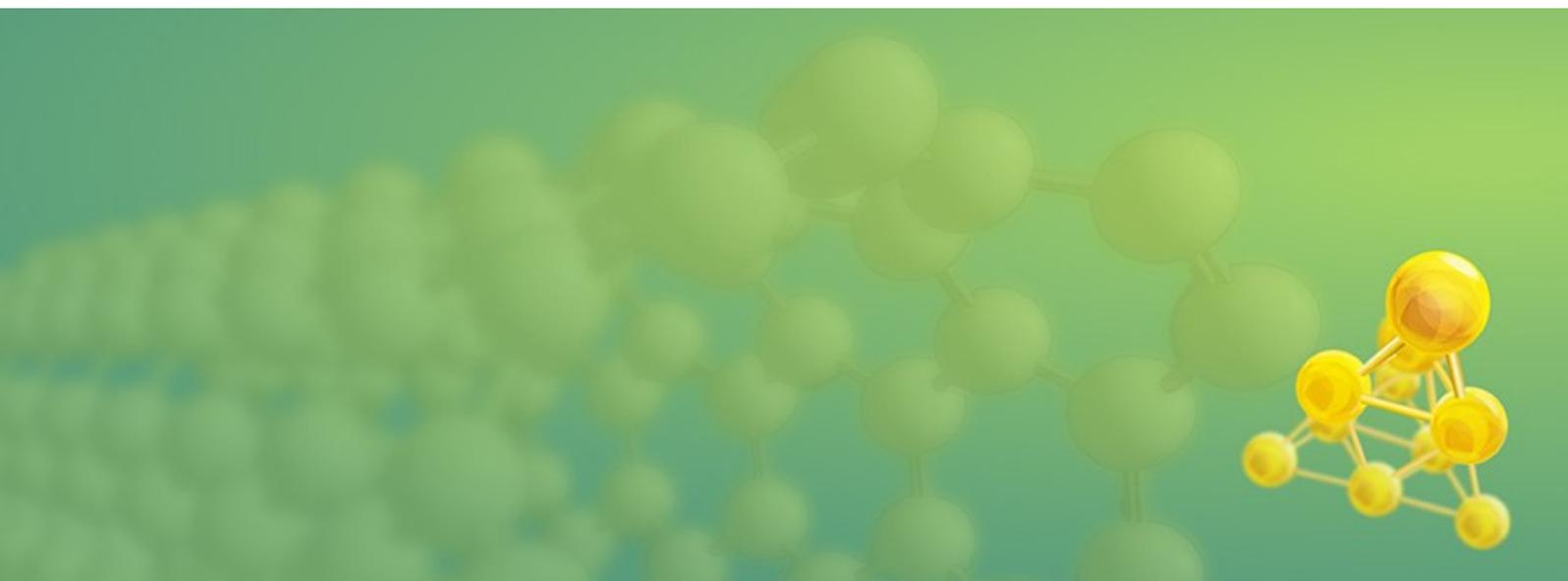


ADF Modeling Suite

Powerful Computational Chemistry



**Li-Ion Diffusion Coefficients
in cathode materials with ADF/ReaxFF**



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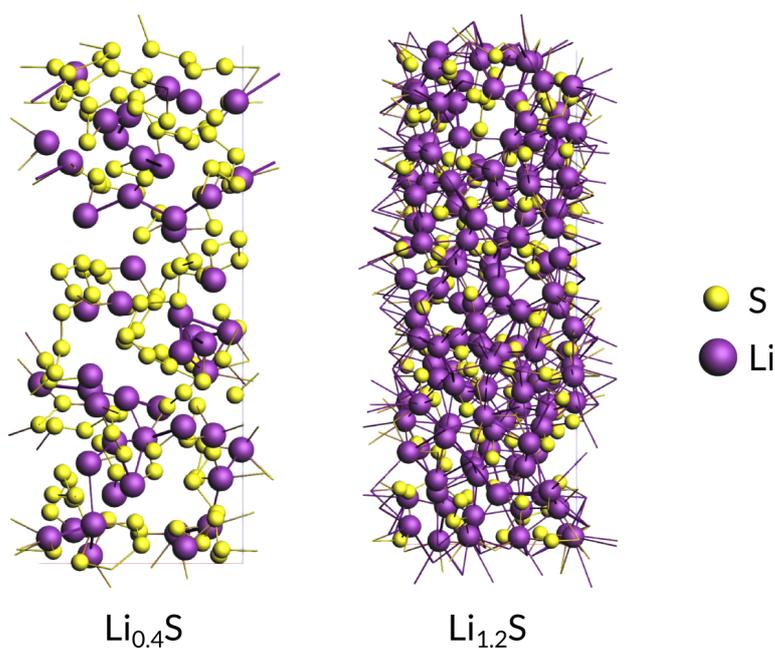
This ReaxFF recipe will demonstrate the following techniques:

1. Importing a CIF file from an external database and equilibrating the structure
2. Manipulating the structure, e.g. inserting particles
3. Creating an amorphous structure by running an annealing program
4. Calculate Diffusion Coefficients directly from trajectories
5. Calculate low temperature Diffusion Coefficients indirectly by means of extrapolation

The System

This tutorial will be using two representative Li x S systems. The systems and workflows presented here are originally described in the publication “ReaxFF molecular dynamics simulations on lithiated sulfur cathode materials” by van Duin and coworkers[1] (see [here](#)).

To speed up the calculations, we will use downsized Li_xS systems consisting of only 177 and 281 atoms respectively.



Starting from an experimental structure of Sulfur(α), Li-atoms were added at random positions followed by an annealing run to create the above amorphous structures.

1. Importing the Sulfur(α) crystal structure

The crystal structure can be directly imported from a CIF file. There are several resources for crystallographic data available online and you can choose according to your liking. Here we used the structure of S₈ alpha Sulfur from the [American Mineralogist Crystal Structure Database](#).

The downloaded CIF can now directly be imported into ADFinput:

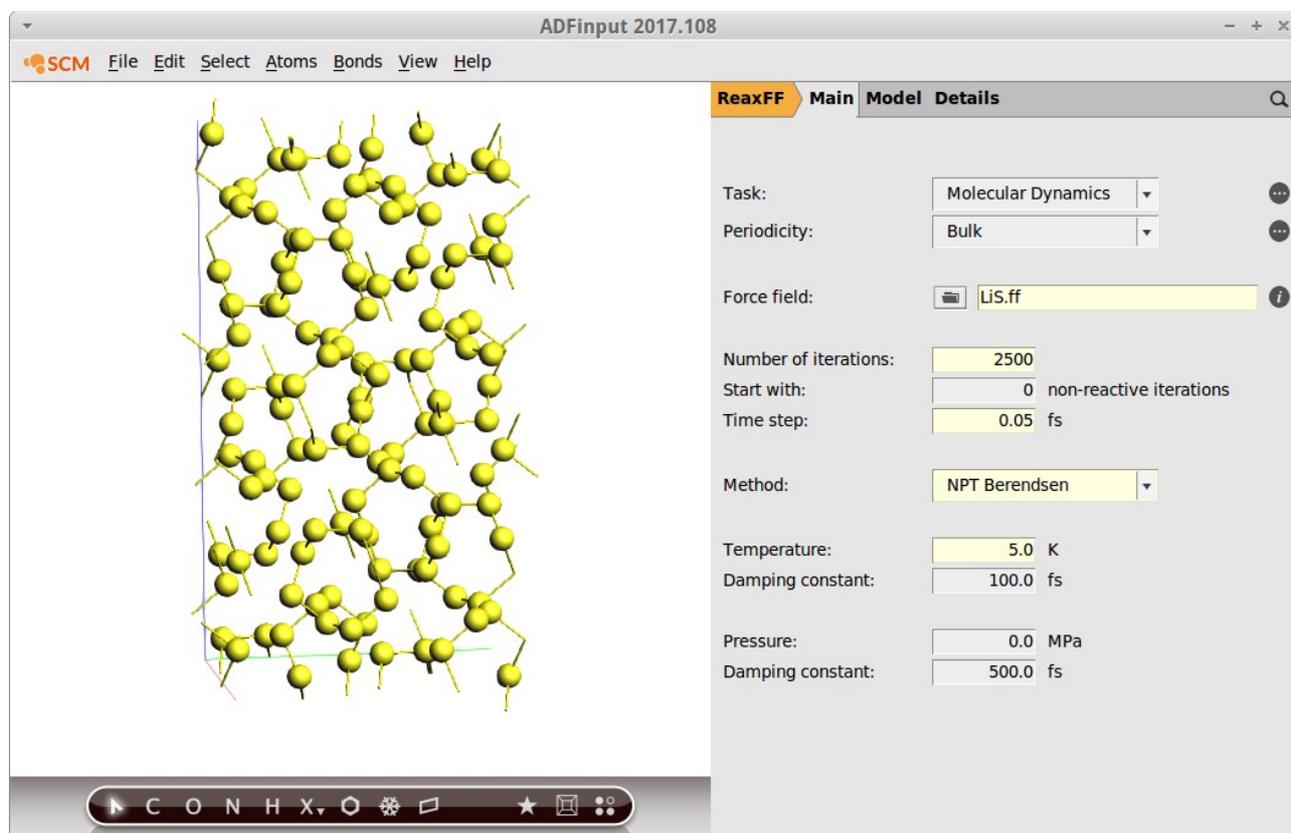
- File → Import Coordinates

Next, map the coordinates into the ReaxFF unit cell and display the lattice vectors:

- Edit → Crystal → Map atoms to (0..1)
- View → Periodic → Show lattice vectors

Before adding any Li-ions to the system, we need to relax the structure using a full geometry optimization, i.e. including the optimization of lattice vectors.

Tip: Most of the time we find that running a couple of hundred steps NPT dynamics at low temperature and 0.0 pressure using a small timestep is sufficient as a relaxation or at least speeds up a subsequent geometry optimization significantly. Try the following settings:



- Save and Run this calculation

You can inspect the trajectory with ADFmovie and look at the total Energy and pressure, both will drop dramatically already during the very first MD steps.

- Click “yes” when asked if the structure in ADFinput should be updated
- Edit → Crystal → Map atoms to (0..1)

2.1 Generating the Li_{0.4}S system

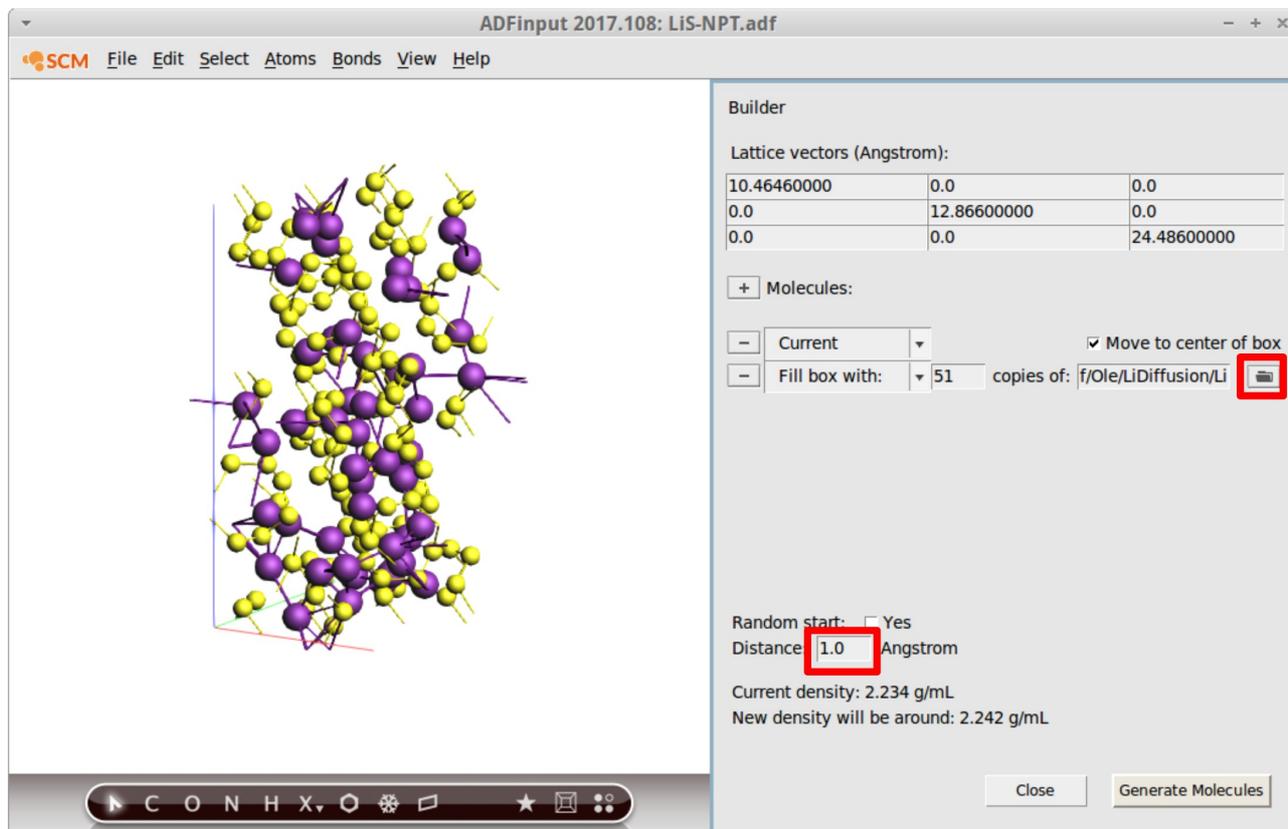
Preparation

Open up a new ADFinput draw a single Li-atom and export the geometry to a file called `Li.xyz`

- File → Export Coordinates

Adding atoms

We use the builder functionality of ADFinput to randomly insert 51 Li-atoms into our equilibrated Sulfur system:



- Import your previously saved Li-atom by clicking on the folder icon
- Set the Distance to 1.0

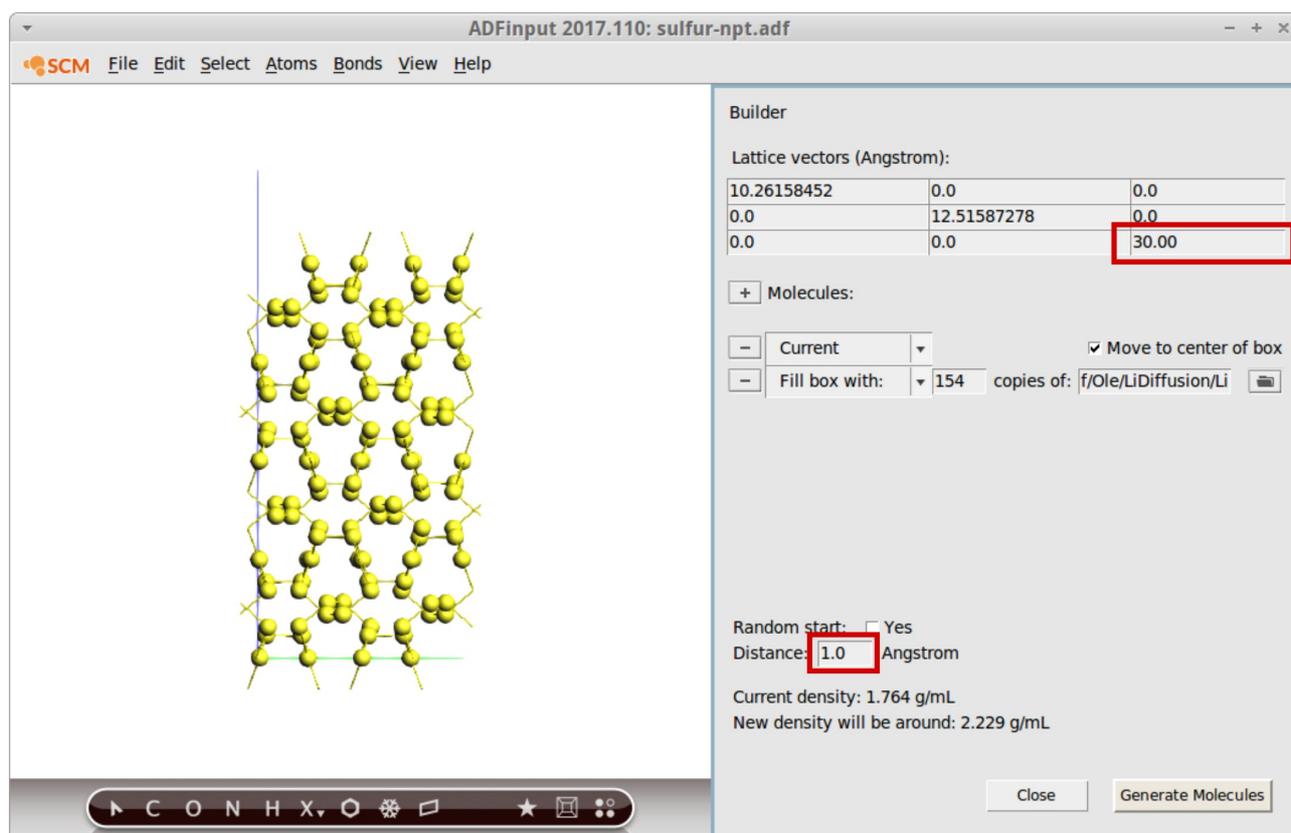
Relax this structure by running a geometry optimization or low-T NPT dynamics as with the plain sulfur system.

2.2 Generating the $\text{Li}_{1.2}\text{S}$ system

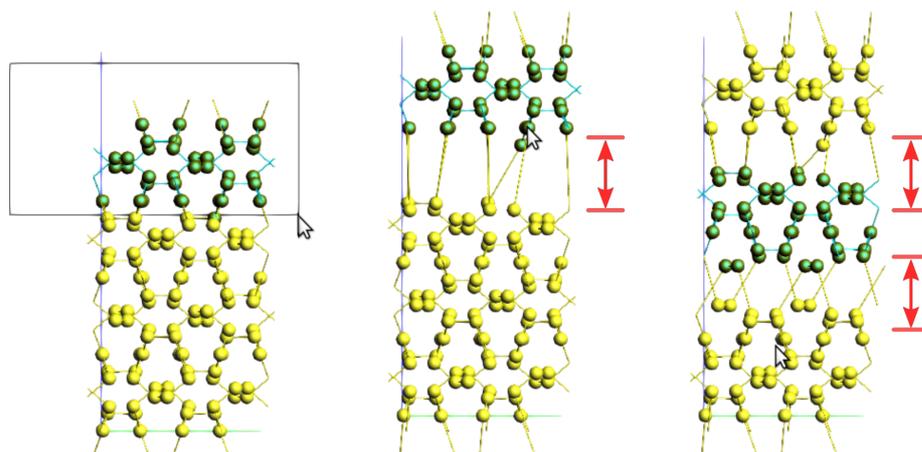
We'll follow the same strategy for the $\text{Li}_{1.2}\text{S}$ system but since now we'll have to add 154 Li-atoms we need a bigger unit cell to be able to fit all atoms.

We are creating an amorphous system later on, so we can just enlarge the unit cell in a rather crude way by increasing the z-lattice vector and manually moving part of the sulfur atoms up:

- Edit → Builder
- Set the z-vector to 30.0 Angstrom
- Reduce the Distance to 1.0 Angstrom



- Manually drag the sulfur atoms further apart. Insert the Li-atoms and relax the system as before.

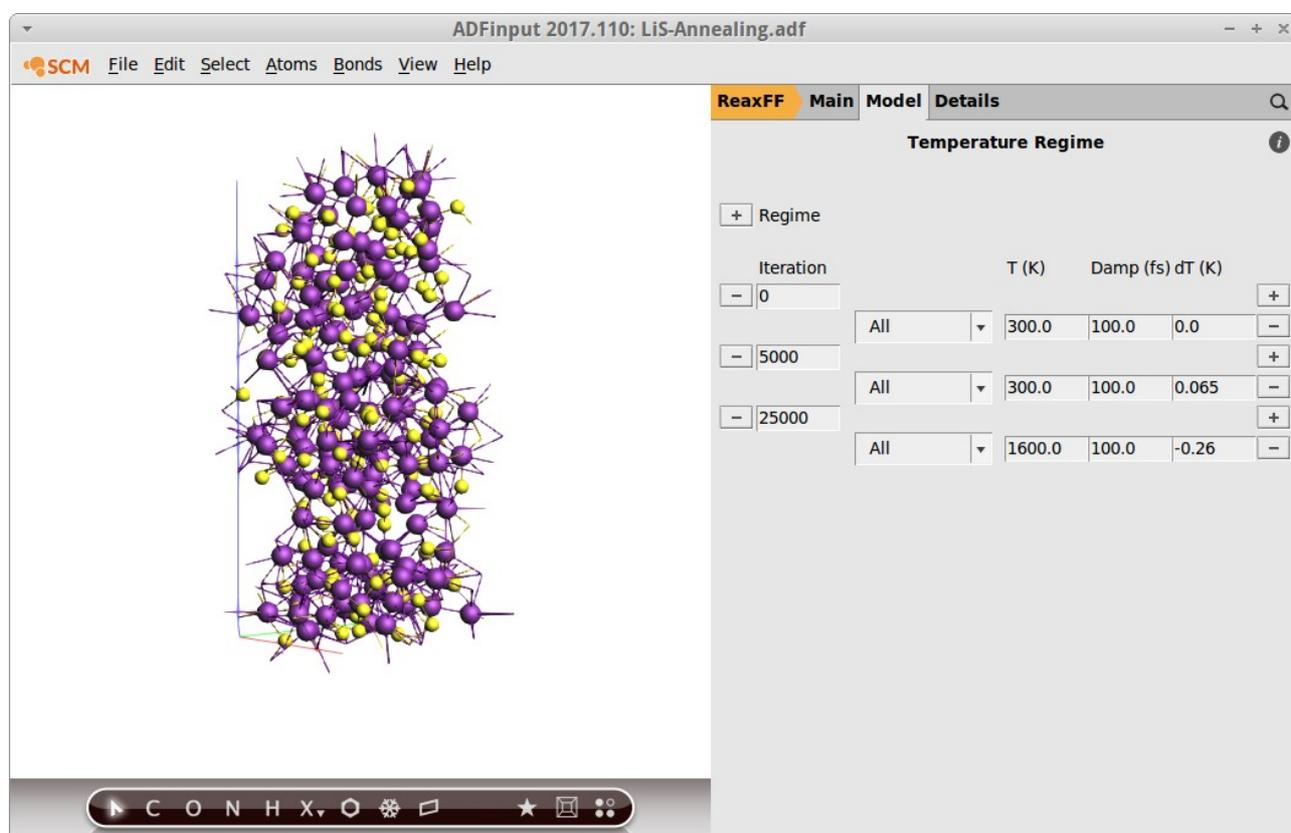


3. Creating the amorphous systems

Amorphous systems can be created by slowly annealing up to certain temperature followed by a rapid cooling down.

As in the publication [1] we will anneal up to 1600 K followed by a rapid cool down to room temperature. In order to speed up the calculation, only 30 000 steps are calculated here using the following temperature program:

1. From start until step 5000: $T = \text{const.} = 300 \text{ K}$
2. From step 5000 – 25 000: $T = T + dT$, $dT = 0.065 \text{ K/step}$ → Heating up.
3. From step 25 000 – 30 000: $T = T + dT$, $dT = -0.26 \text{ K/step}$ → Rapid cooling.



The screenshot shows the ADF software interface for a simulation. The main window displays a 3D ball-and-stick model of a molecular structure, likely a lithium-ion battery component, with atoms represented by purple and yellow spheres. The interface includes a menu bar (File, Edit, Select, Atoms, Bonds, View, Help) and a toolbar at the bottom. On the right side, the 'Temperature Regime' panel is open, showing a table of simulation parameters for different stages of the run.

Iteration	T (K)	Damp (fs)	dT (K)
0	300.0	100.0	0.0
5000	300.0	100.0	0.065
25000	1600.0	100.0	-0.26

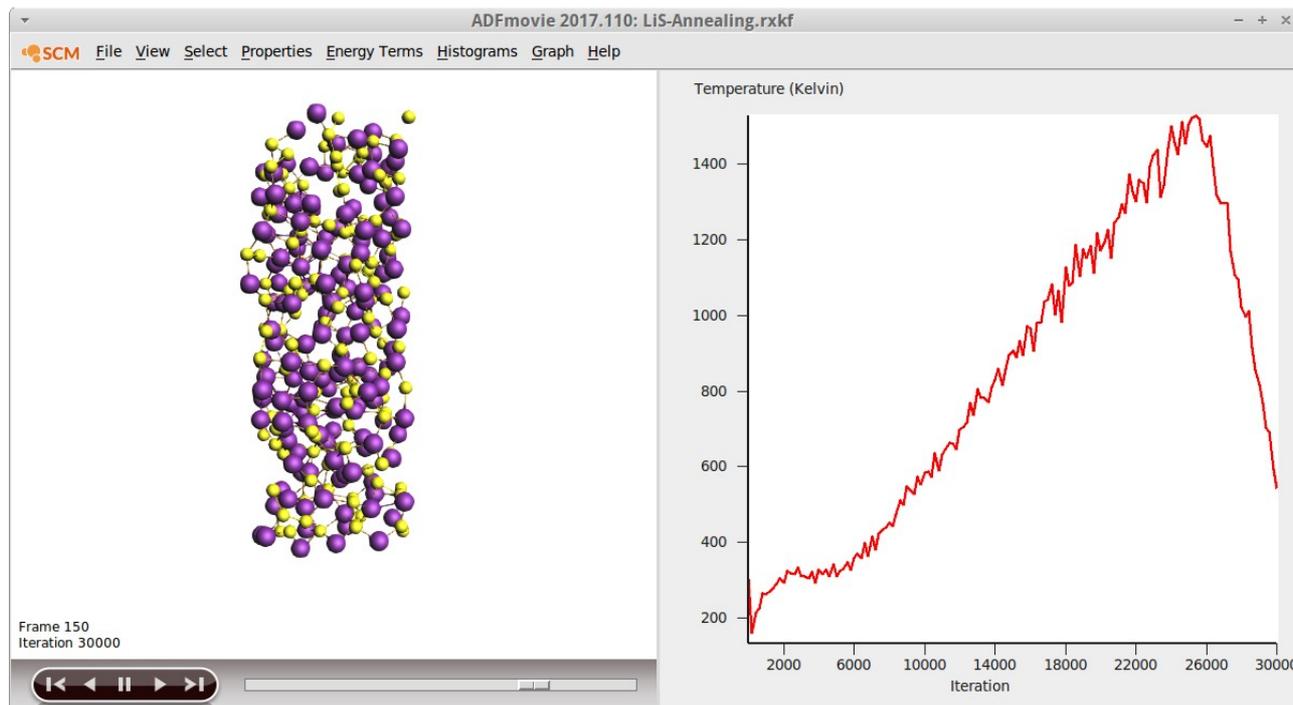
Use the following settings for the MD run:

- NVT Berendsen, 300K, 30 000 steps

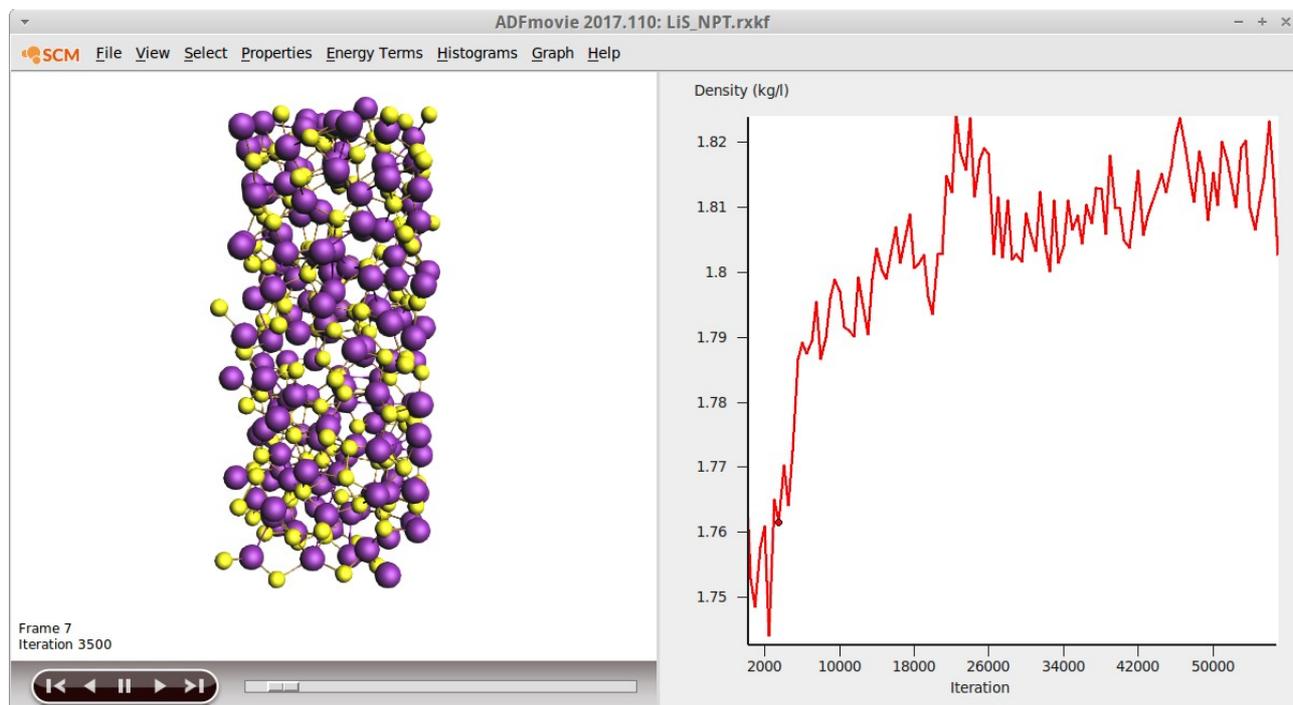
After the annealing run has finished:

- Accept the new structures
- Equilibrate with the following settings NPT (Berendsen), 300 K, 0.1 MPa, 40 000 steps

You can check the temperature during the annealing run with ADFmovie



The density of the system should at least be somewhat equilibrated for the following calculations of the diffusion coefficients:



4.1 Calculating the diffusion coefficients - ReaxFF

In order to calculate a diffusion coefficient with the TRAVIS program[2] an additional keyword needs to be set in the ReaxFF control file. This keyword will cause ReaxFF to calculate a non-backtranslated trajectory from which the mean square displacements are calculated.

We will use a minimal proof-of-principle setup of 10 000 equilibration steps followed by only 100 000 production steps. The settings are:

- NVT, 1600K, 110 000 steps, 10 000 non-reactive steps, timestep 0.25 fs
- The framerate can be set to 50 fs:

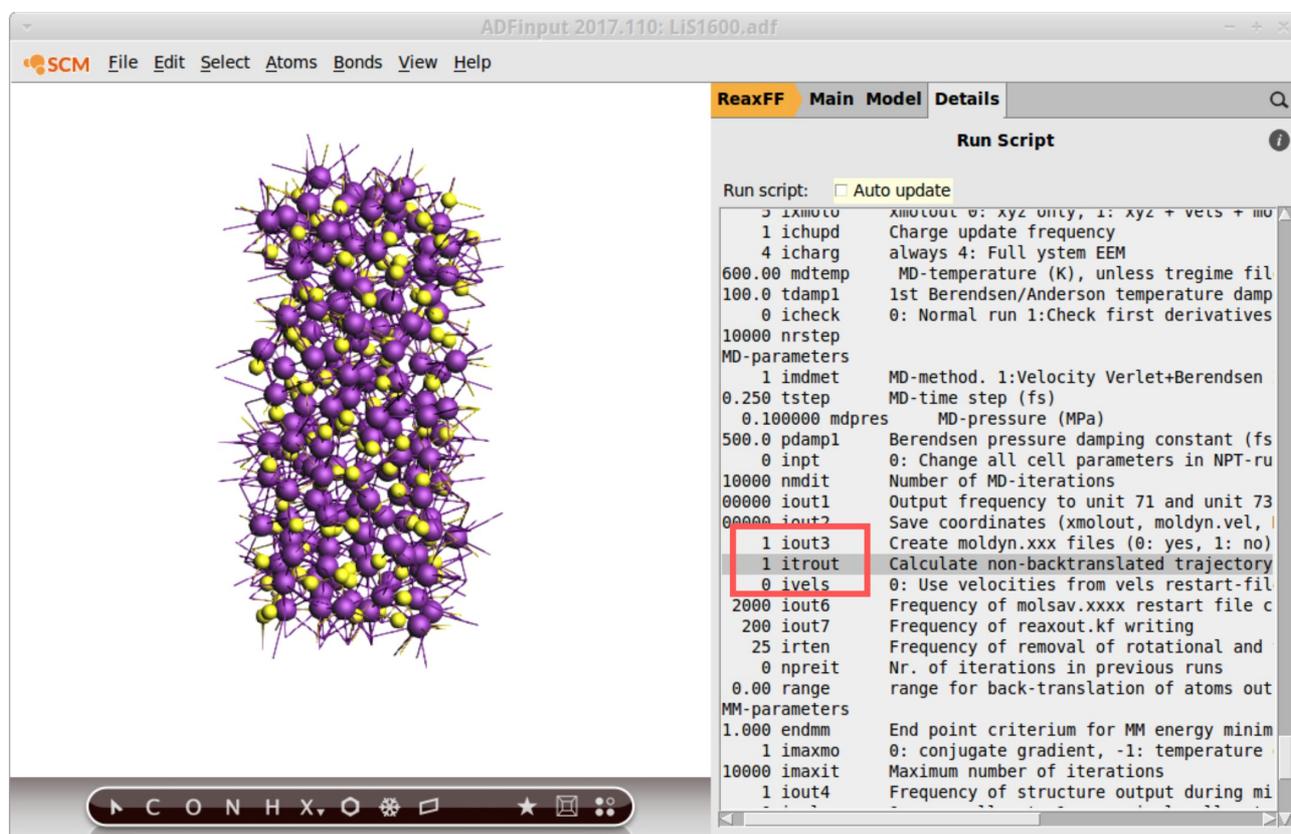
Details → Molecular Dynamics → KF result file: 200

Finally, edit the run file that is about to be created from the GUI.

- Details → Run Script

Use the scroll bar on the right to scroll past the definition of the geometry to the MD settings found at the end of the file. In the section starting with #MD-Parameters add the following (new!) line:

```
1 iout3      Create moldyn.xxx files (0: yes, 1: no)
1 itrout     Calculate a not-back translated trajectory
0 ivels      0: Use velocities from vels restart-file;
```



The screenshot shows the ADFInput 2017.110: LiS1600.adf GUI. The main window displays a 3D molecular model of a lithium-sulfur system. The right-hand panel is titled 'Run Script' and contains a list of parameters for the ReaxFF simulation. The line '1 itrout Calculate non-backtranslated trajectory' is highlighted with a red box. Other parameters include '1 iout3 Create moldyn.xxx files (0: yes, 1: no)', '0 ivels 0: Use velocities from vels restart-file;', and various MD parameters like '1 imdmet MD-method. 1:Velocity Verlet+Berendsen', '0.250 tstep MD-time step (fs)', '0.100000 mdpres MD-pressure (MPa)', '500.0 pdamp1 Berendsen pressure damping constant (fs)', '0 inpt 0: Change all cell parameters in NPT-ru', '10000 nmdit Number of MD-iterations', '00000 iout1 Output frequency to unit 71 and unit 73', '00000 iout2 Save coordinates (xmout, moldyn.vel, i', '1 iout3 Create moldyn.xxx files (0: yes, 1: no)', '1 itrout Calculate non-backtranslated trajectory', '0 ivels 0: Use velocities from vels restart-fil', '2000 iout6 Frequency of molsav.xxxx restart file c', '200 iout7 Frequency of reaxout.kf writing', '25 irten Frequency of removal of rotational and', '0 npreit Nr. of iterations in previous runs', '0.00 range range for back-translation of atoms out', 'MM-parameters', '1.000 endmm End point criterium for MM energy minim', '1 imaxmo 0: conjugate gradient, -1: temperature', '10000 imaxit Maximum number of iterations', '1 iout4 Frequency of structure output during mi

Save and run the calculation.

4.2 Calculate the Diffusion Coefficients - TRAVIS

Open a terminal and navigate to the folder you ran your calculations in. Just use your default Linux shell or – when on Windows – follow [these steps](#) to get into a Unix-like shell shipped with ADF.

First convert the binary rxkf file into a non-backtranslated xyz trajectory for usage with TRAVIS. Assuming your calculation was called LiS-1600, run the following command *on a single line*:

```
$ADFBIN/startpython
$ADFHOMe/scripting/trajectory_analysis/kf_to_xyz.py
LiS-1600.rxf -itout
```

This will create a file named LiS-1600_travis.xyz which can be processed by TRAVIS.

Open the interactive settings dialogue of TRAVIS by running the following command:

```
$ADFBIN/travis.exe -p LiS-1600_travis.xyz
```

Enter the following settings in the TRAVIS dialogue:

- Use the advanced mode [...] → yes
- Use periodic boundary conditions? → no
- Execute molecule recognition for which time step (-1 = disable)? [0] → -1
- Accept the defaults until you reach the “List of functions”

```
>>> List of functions <<<
*** Static (time independent) Functions
cdf - Combined Distribution Function
rdf - Radial Distribution Function
rdf - Radial Distribution Function
ddf - Dihedral Distribution Function
pddf - Point-Plane Distance Distribution
lddf - Point-Line Distance Distribution
plproj - Plane Projection Distribution
dens - fixed plane density profile
dens - Density Distribution Function
sdf - Spatial Distribution Function
psdf - Pseudo SDF (only 2 ref. atoms)
ddf - Dipole Distribution Function
cond - Evaluate structural condition
sfac - Compute Structure Factor

*** Dynamic (time dependent) Functions
vdf - Velocity Distribution Function
fdf - Force Distribution Function
msd - Mean Square Displacement / Diffusion Coefficients
acf - Velocity Autocorrelation Functions
rdyn - Vector Reorientation Dynamics
vccf - Van Hove Correlation Function
aggr - Aggregation Functions (DAF, DLF, DDISP)

*** Spectroscopic Functions
power - Calculate Power Spectrum
ir - Calculate IR Spectrum
raman - Calculate Raman Spectrum
nc - Normal coordinate analysis
vcd - Calculate VCD Spectrum
drest - Save dipole restart file
mrest - Save magnetic moment restart file
pol - Set up polarizability calculation

*** Miscellaneous Functions
env - Save trajectory of RR environment / TDD Plot
proc - Save processed Trajectory
clt - Cut Clusters
reg - Region-specific Analysis
chi - Chirality Analysis
ask - Transform to Eckart Frame
swan - Sort Wannier Centers
voro - Basic Voronoi Analysis
dona - Domain Analysis
vori - Voronoi Integration Functions

(You may specify multiple analyses at once, but
the safe way is to perform only one kind of analysis at a time.)
Which functions to compute (comma separated)? █
```

- Select the Mean Square Displacement / Diffusion Coefficients → msd
- Use advanced mode for the main part? → no
- Enter the length of one trajectory time step in fs? → 50
- Which molecule should be observed? → Choose Li
- Which atom(s) to take from OM Li (e.g. "C1,C3-5,H", "*" = all)? [#2] → ENTER
- Enter the resolution (=depth) for this MSD (in time steps): [601] → 60
- Accept defaults until asked at which timestep to start the analysis → 50
- Accept all defaults until the calculation starts.

TRAVIS will write a logfile (`travis.log`) it's settings (`input.txt`) and resultfiles called `msd_Li_#2.csv` the latter one contains three columns:

(1) Time [ps] (2) MSD [pm²] (3) Derivative of the MSD

Plotting either column 1 against column 2/3 will give the graphs shown below.

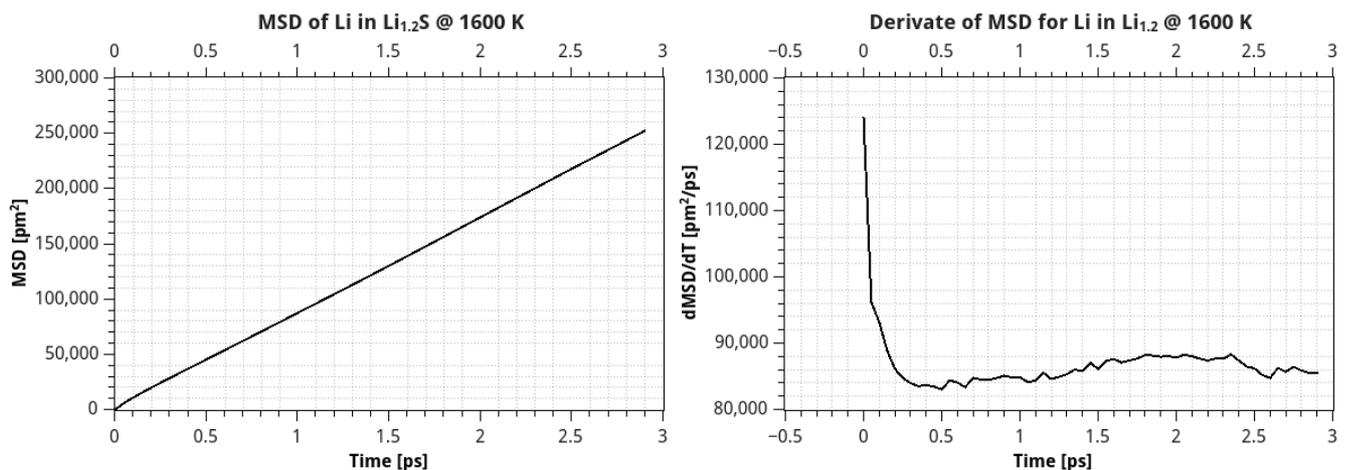
The Diffusion coefficients are calculated from a linear regression and are printed on the screen as well as in the logfile `travis.log`. With the described settings the Diffusion Coefficient for the Li_{1.2}S system at 1600 K is calculated as:

```
Diffusion coefficient D = 50680.522077 pm^2/ps
                        =      5.06805E-08 m^2/s.
```

If you want to re-run the exact same analysis, e.g. on a trajectory at a different temperature, you can ask TRAVIS to re-use the settings from a previous inputfile as follows:

```
$ADFBIN/travis.exe -p Lis-1600_travis.xyz -i input.txt
```

The MSD for Li in Li_{1.2}S system at 1600 K looks as follows:



The same analysis can also be applied to the sulfur atoms, yielding a Diffusion Coefficient of $D = 3.16567E-08 \text{ m}^2/\text{s}$.

6. Extrapolate to Diffusion Coefficients at room temperature

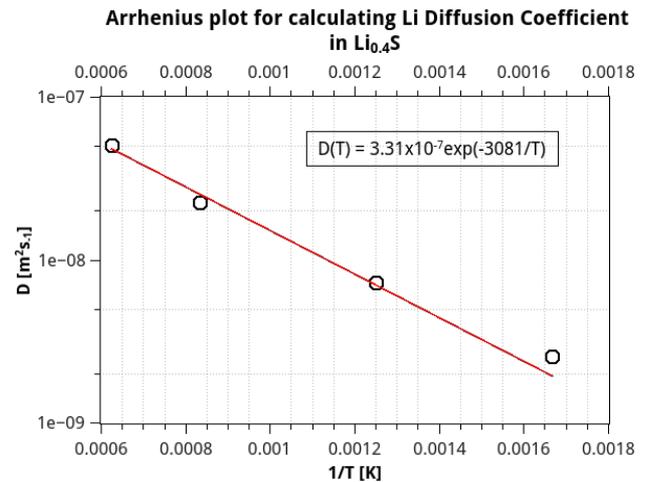
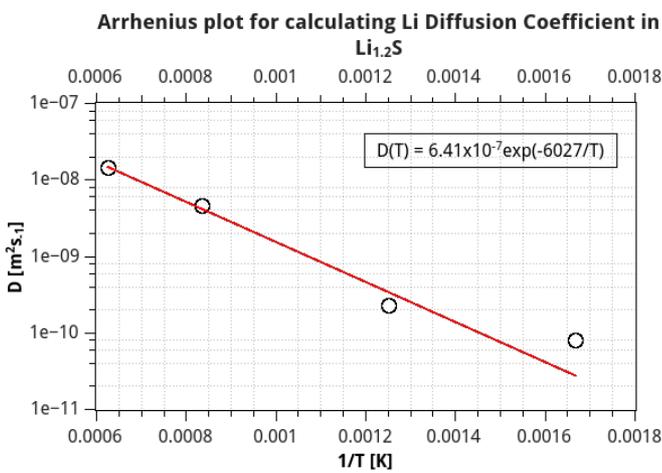
Since the Diffusion Coefficients are very small for the Li_xS systems calculating the Diffusion Coefficient at 300K would require a very, very long trajectory. However, it is possible to provide an upper bound to the Li diffusion by means of extrapolation from elevated temperatures using the following Arrhenius equation^[1].

$$D(T) = D_0 \exp\left(\frac{-E_a}{T}\right)$$

where D_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant, and T is the temperature. The activation energy and pre-exponential factors can then be obtained from an Arrhenius plot of $D(T)$ against $1/T$.

In order to extrapolate the Diffusion Coefficients for $\text{Li}_{0.4}\text{S}$ and $\text{Li}_{1.2}\text{S}$ we calculate trajectories for at least four different temperatures (600K, 800K, 1200K, 1600K) for each system summing to eight trajectories in total using the exact same settings discussed above:

x in Li_xS	$D(T = 600\text{K})$	$D(T = 800\text{K})$	$D(T = 1200\text{K})$	$D(T = 1600\text{K})$
0.4	2.5684e-09	7.27756e-09	2.25917e-08	5.06805e-08
1.2	8.1066e-11	2.28662e-10	4.68517e-09	1.45497e-08



We used a Levenberg-Marquardt algorithm w. statistical weighting from QtiPlot to fit the Arrhenius equation and obtained the following Diffusion Coefficients:

$$\text{Li}_{0.4}\text{S}: D(T = 300\text{K}) = 3.31 \times 10^{-7} \exp(-3081/300) = 1.15 \times 10^{-11} \text{ m}^2\text{s}^{-1}$$

$$\text{Li}_{1.2}\text{S}: D(T = 300\text{K}) = 6.41 \times 10^{-7} \exp(-6072/300) = 1.04 \times 10^{-15} \text{ m}^2\text{s}^{-1}$$

When comparing these values with the Diffusion Coefficients presented in publication by A. van Duin and coworkers [1] it becomes clear that the Diffusion Coefficient of the dense $\text{Li}_{1.2}\text{S}$ system is one or two orders of magnitude too high. Clearly this is due to the minimal setup (small systems and short trajectories). Nonetheless, the $\text{Li}_{0.4}\text{S}$ system as well as the overall trend are already nicely reproduced.

References

1. M. M. Islam, A. Ostadhossein, O. Borodin, A. T. Yeates, W. W. Tipton, R. G. Hennig, N. Kumar, and A. C. T. van Duin, *ReaxFF molecular dynamics simulations on lithiated sulfur cathode materials*, *Phys. Chem. Chem. Phys.* **17**, [3383-3393 \(2015\)](#).

2. TRAVIS is commandline tool for analyzing and visualizing trajectories from all kinds of Molecular Dynamics or Monte Carlo simulations initiated by Kirchner, written and developed by Brehm and Thomas ([J. Chem. Inf. Model. 51\(8\) \(2011\)](#)).

TRAVIS is included as a commandline tool from on ADF2017.

Questions and comments: support@scm.com