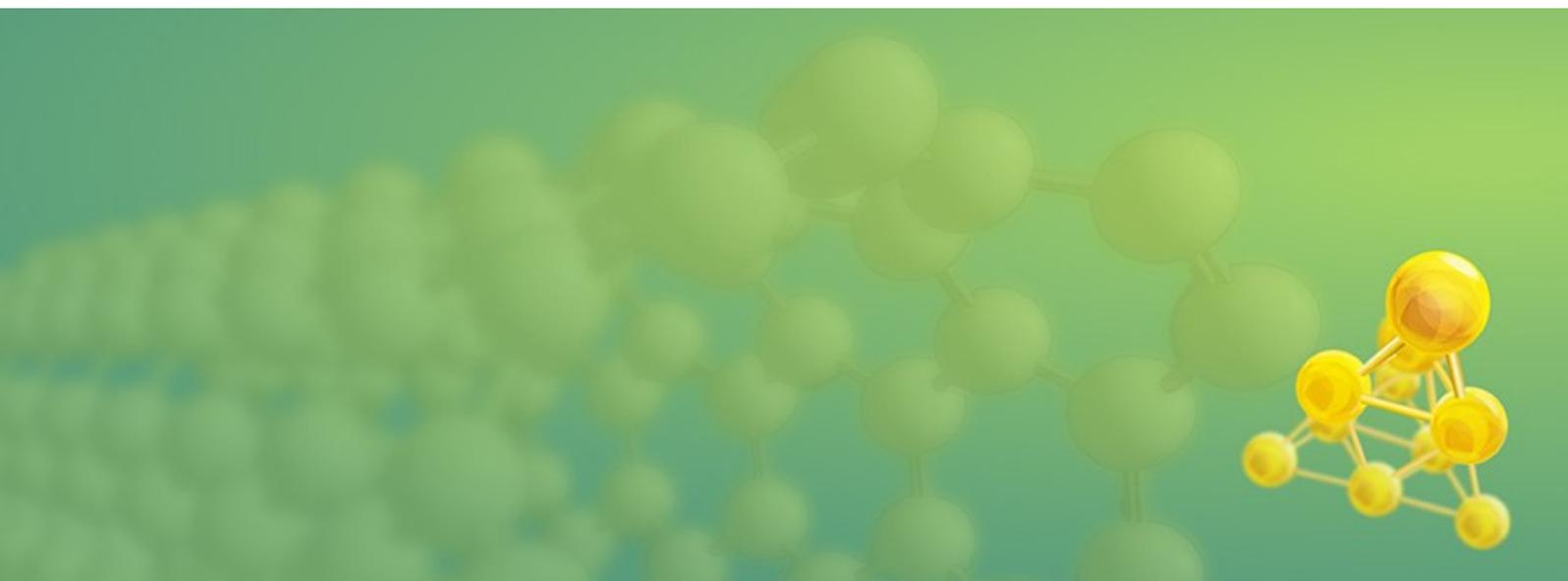


# ADF Modeling Suite

Powerful Computational Chemistry



**Discharge voltage profiles during lithiation  
using grand canonical monte carlo and  
ADF/ReaxFF**



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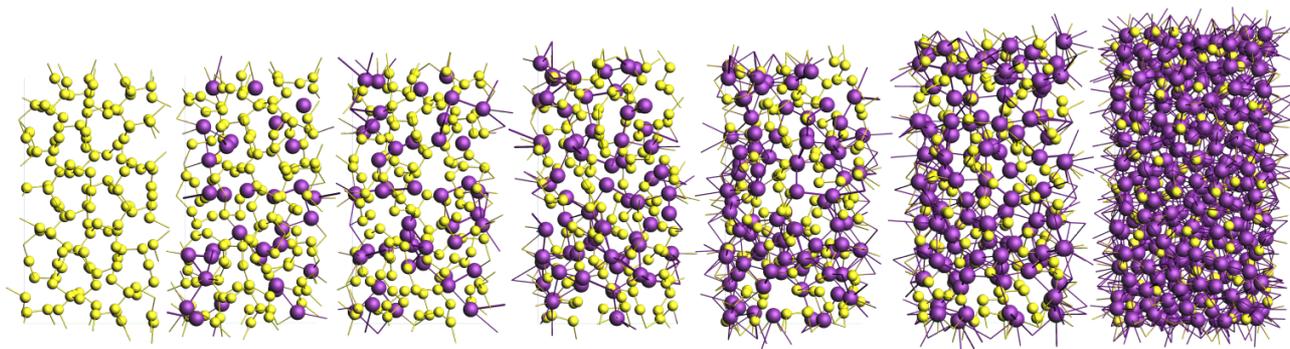
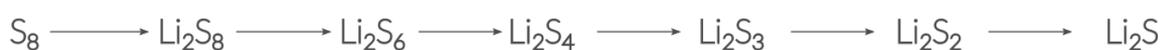
## Contents

This ReaxFF recipe will demonstrate the following techniques:

1. Importing a CIF file from an external database and equilibrating the structure
2. Calculating the chemical potential for Li
3. Setting up a grand canonical monte carlo (GCMC) simulation w. ReaxFF
4. Results: Discharge voltage profiles. etc...

## The System

The system employed throughout this tutorial uses an alpha-sulfur bulk structure of 128 atoms. Both the system and workflow are originally described in the publication “ReaxFF molecular dynamics simulations on lithiated sulfur cathode materials” by M. M. Islam and coworkers[1] (see [here](#)).



Reduction of polysulfides during the discharge process, simulated with GCMC and ADF/ReaxFF.

The discharge process is simulated using ReaxFF in a grand canonical monte carlo scheme. Volume changes upon lithiation are accounted for by using an  $N_{\text{SPT}}-\mu_{\text{Li}}$  scheme.

The discharge voltage can be calculated from the total energies of the lithiated compounds.

### 1. Importing the Sulfur( $\alpha$ ) 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  $\text{S}_8$  alpha Sulfur from the [American Mineralogist Crystal Structure Database](#).

The downloaded CIF can now directly be imported into ADFinput:

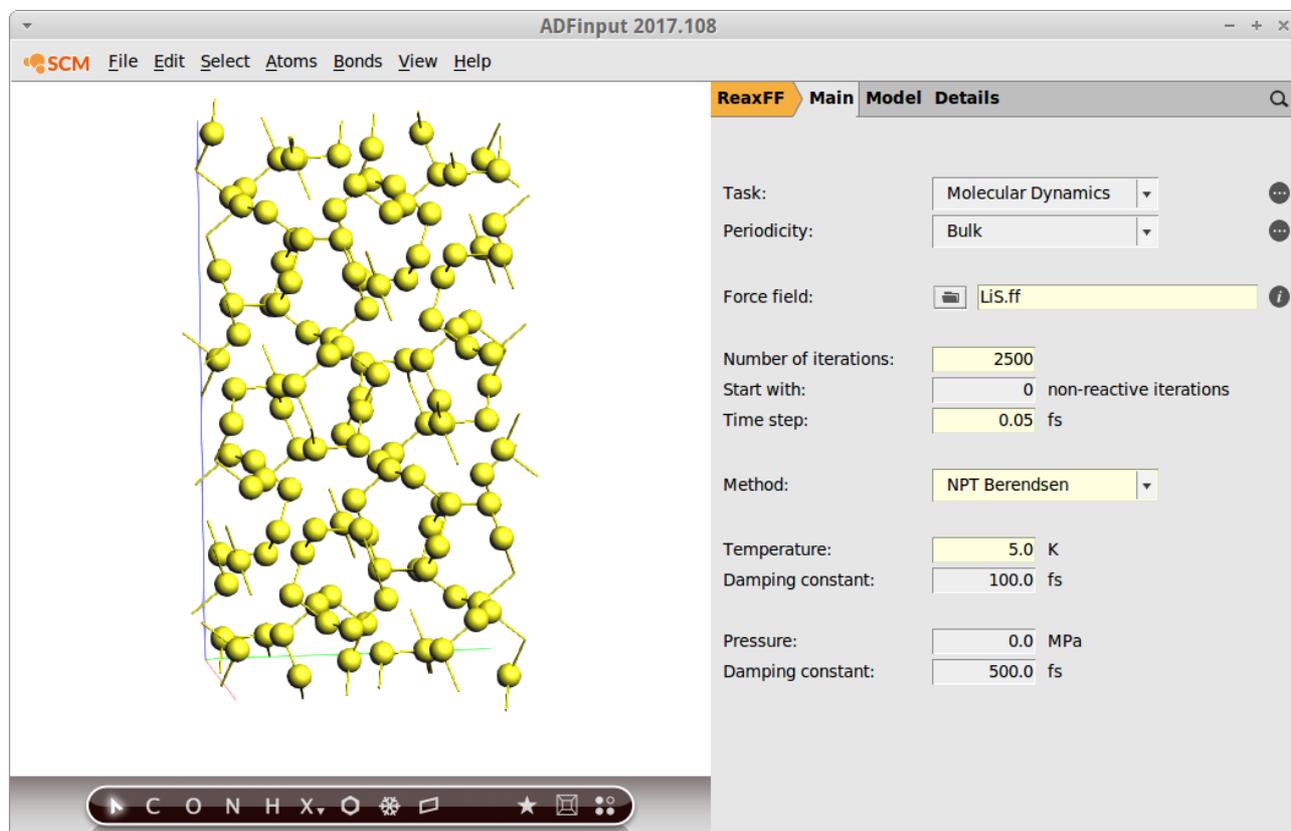
- File → Import Coordinates

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 geometry and cell 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<sup>1</sup> is sufficient as a relaxation or at least speed 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)

For this tutorial we need to calculate the total energy of the optimized  $S_8$  structure so we run a full cell geometry optimization with the following settings:

- Optimizer: Conjugate Gradient, 5000 steps, 1.0 (kcal/mol)/Å, full cell

which yields a total energy of

$$E_s = -8535.99 \text{ kcal/mol}$$

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<sup>1</sup> It should be noted that small unit cells with less than 10Å length in any direction are known to be problematic in NPT simulations and full cell geometry optimizations. Its only for the sake of computational speed that we don't create a supercell in this recipe.

## 2. Calculating the chemical potential for Li

Following the approach of M. M. Islam and coworkers[1], we fix the external chemical potential of Li at the total energy of a single lithium atom in body-centered cubic lithium.

The structure of bcc Lithium can be created easily via the crystal builder in ADFinput:

- Edit → Crystal → Cubic → bcc
- Select Li from the Presets and click OK
- Edit → Crystal → Generate Supercell
  - Generate an 8x8x8 supercell (512 atoms)
- Edit → Crystal → Map atoms to (0..1)

Optimize the resulting structure, including the lattice(!) with the following settings:

- Force field: LiS.ff
- Optimizer: Conjugate Gradient, 5000 steps, 1.0 (kcal/mol)/Å, full cell

After the optimization has finished successful, the chemical potential is calculated as the total energy / number of atoms. The value depends to some extent on the chosen force field and should be changed according to the following table if a different force field is used:

Force field	$\mu_{\text{Li}}$ [kcal/mol]
LiS.ff	-37.70
CHOLi_2.ff	-37.09
LiSi.ff	-37.69
HOSiAlLi.ff	-37.70
CHOLi.ff	-36.44
SiOAlLi.ff	-37.57
CHOSMoNiLiBFPN.ff	-37.70

Total energies of a single lithium atom in body-centered cubic lithium for various force fields included in the ADF modeling suite (see [list of included force fields](#) for a description of all available force fields).

Throughout this recipe LiS.ff is used and the chemical potential of Li will be fixed at

$$\mu_{\text{Li}} = -37.70 \text{ kcal/mol}$$

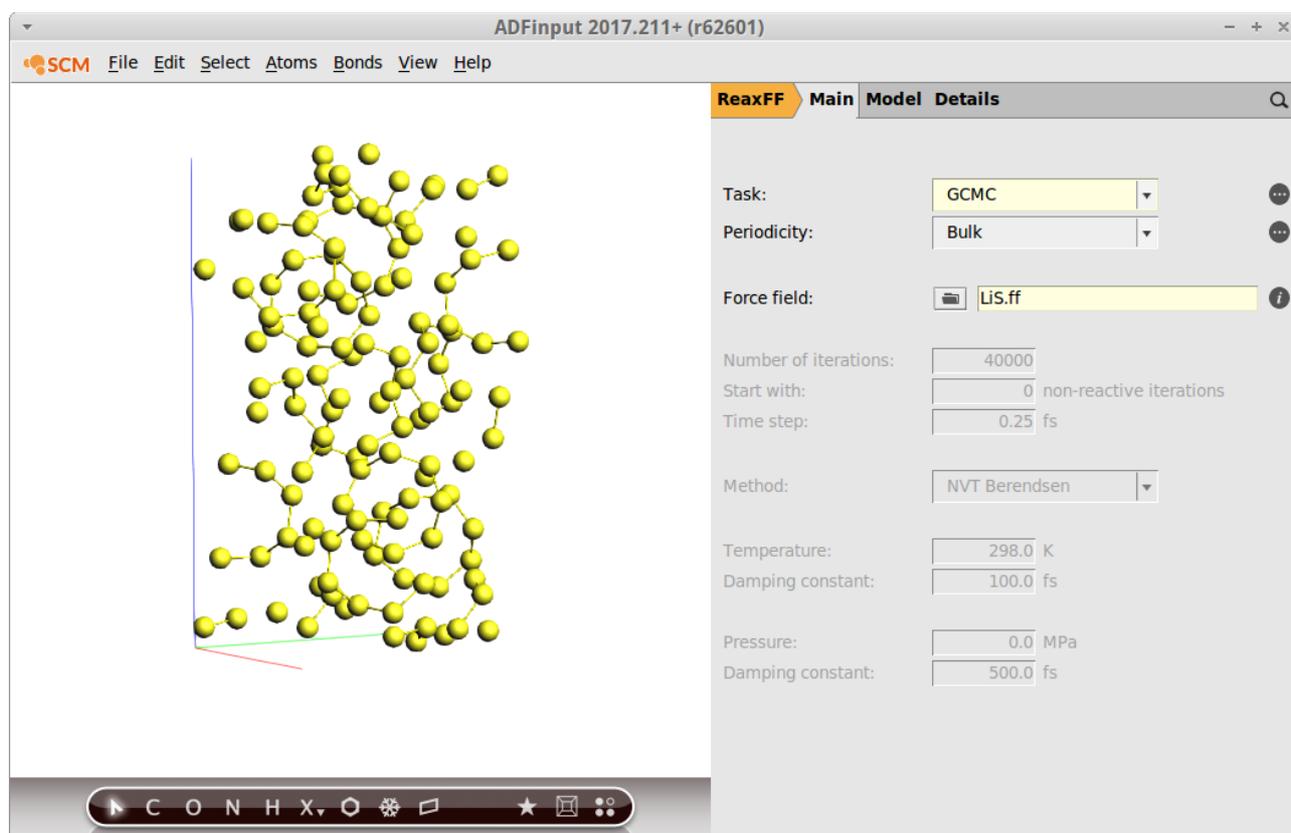
### 3. Setting up the GCMC-calculation

#### Note:

GCMC calculations are quite sensitive to the chosen settings. The main reason being the interplay of comparing small energy differences in the GCMC acceptance criteria and the optimization procedure carried out after each MC-trial move. Its therefore advised to try different optimizer settings (max. steps, convergence criteria, etc...). All GCMC settings are documented online ([here](#)).

#### GUI Setup

The current development version of ADF ( $\geq$  r62841) comes with GUI support for GCMC calculations. We use our previously optimized  $S_8$  structure as the system:



- Select the Task “GCMC” and click on the button “...” next to it

In the GCMC control panel we apply the following settings:

- MC ensemble =  $\mu$ PT
- Number of Iterations = 3000

This will be enough steps to converge the current system. However, this value is not known beforehand and one might want to choose a larger number of iterations for larger systems.

- Temperature = 300 K

- Add molecules between 1.2 and 6.0 Å

These fields correspond to the Rmax and Rmin values in the GCMC input. You can try different values here. As a complete empirical rule of thumb: setting Rmin to roughly  $\frac{1}{2}$  of the shortest expected bond and Rmax approx. half of the shortest lattice vector seems a good starting point.

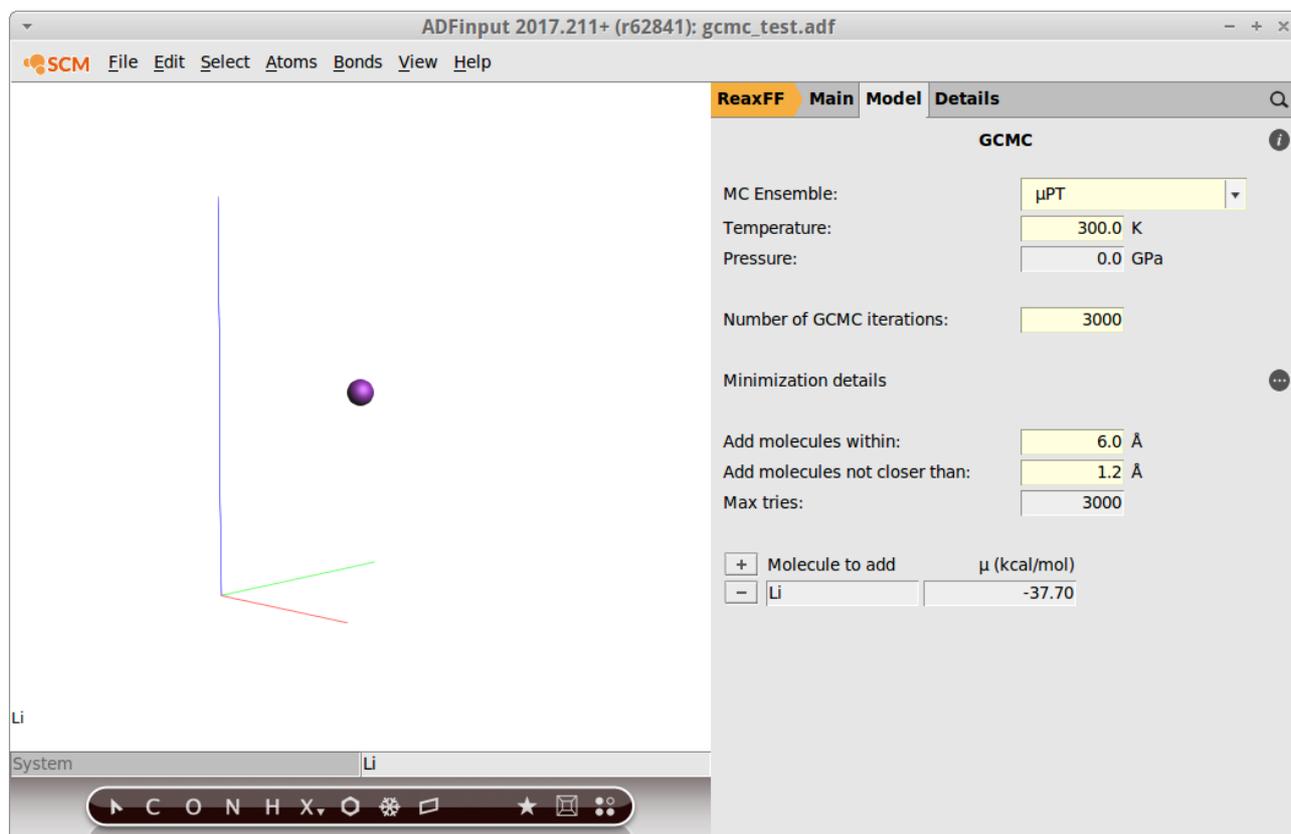
- Max tries = 3000

The number of attempted tries must be sufficiently large, if not the calculation will abort with an error message stating that number of max tries was exceeded.

- Molecule to add

Press the button labelled “+” and enter Li as the name. The name is generic, you will still need to draw a Lithium atom into the window labelled “Li” in the molecule view to the left. After placing the Li-atom, select it and

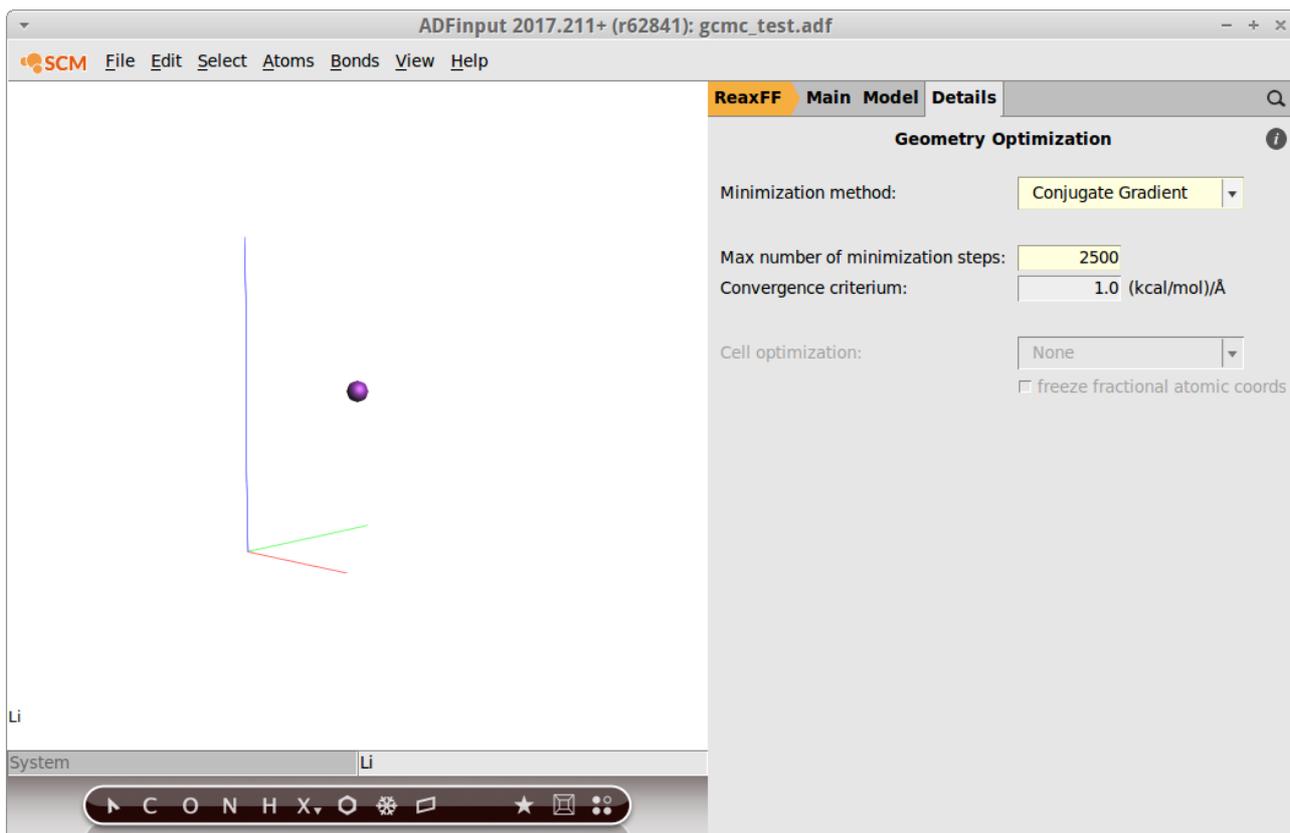
- Edit → Crystal → Set(0.5,0.5,0.5)



The optimizer settings can be found by clicking on the “...” button next to “Minimization details”.

Remember that the optimizer settings are most crucial for the GCMC algorithm:

- Select “Conjugate Gradient”, set the max number of iterations to 2500 and the convergence criterium to 1.0 (kcal/mol)/Å.



Save your changes and run the calculation. The initial stages of the calculation are reached quite fast and the progress can be followed in ADFmovie. However, it will typically take a bit less than one day until convergence.

### Troubleshoot

1. No MC moves are accepted:
  - Check if you set the correct chemical potential (remember to use the one calculated with your force field!)
  - Tighten the convergence criteria for the optimization
  - Change Rmax/Rmin settings
  - Try to optimize the system (here: the sulfur structure) with tighter optimization settings
  - Try a different force field
2. The calculation takes a lot of time:
  - Loosen the convergence criteria, e.g. less steps and a lower convergence criterium
  - The obvious: Try a smaller system.

## 4. Results

The discharge voltage profiles can be calculated as a function of Li intercalation content from

$$V(x) = - \left( \frac{G_{Li_xS} - x \cdot G_{Li} - G_S}{x} \right)$$

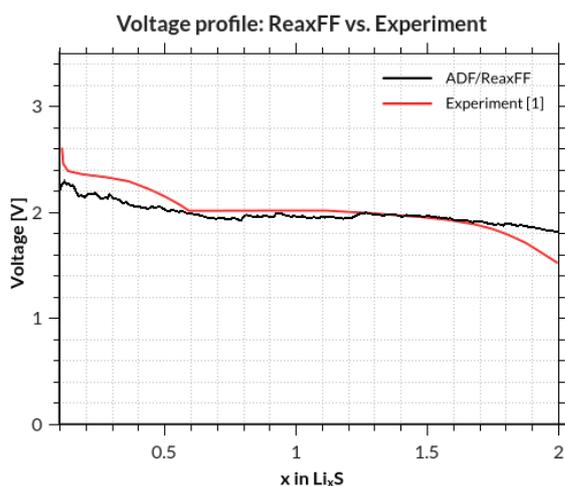
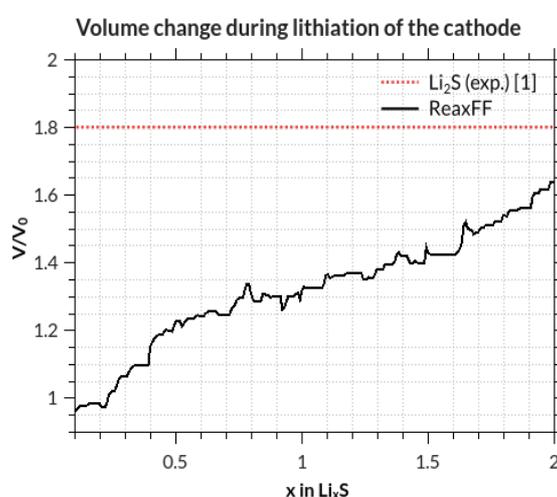
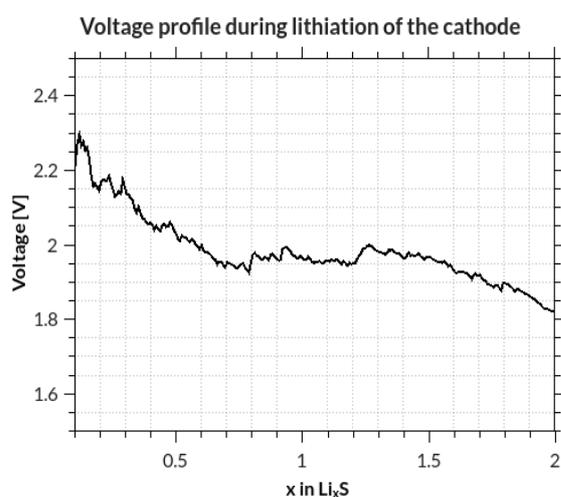
where  $G$  denotes the Gibbs free energy and  $x$  the concentration of Li-ions. The enthalpic (PT) and entropic (TS) contributions can be neglected [1] and thus the Gibbs free energy replaced by the ground state energy.

In this case and many other cases of non-standard trajectory analysis, writing a short Python script using the PLAMS library is the most efficient way to obtain results. Remember there is no need to take any further action than writing the script: Both Python and PLAMS are shipped with every copy of ADF/ReaxFF and are ready-to-use.

The script called LiVoltageProfile.py is available from [here](#) and can be run as follows from the command line:

```
$ADFBIN/startpython LiVoltageProfile.py gcmc_test.rxkf
```

assuming that your trajectory was called gcmc\_test.rxkf and that you used the same system and force field as explained in this recipe. The results are written to a file called voltage\_profile.out:



Results calculated for the small system in this recipe. The volume changes are calculated relative to the initial volume of sulfur and taken directly from the GCMC trajectory. Note that, significantly more accurate volume changes can be obtained by running NPT dynamics as discussed in [1].

## 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.* 2015, **17**.

Questions and comments: [support@scm.com](mailto:support@scm.com)