Volumetric expansion of Li_xS compounds and discharge voltage profile with larger polysulfides

MSE 6270: Introduction to Atomistic Simulations
Final Project

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April 17, 2018

1 Outline

Brief Description Using ReaxFF (bond order) potential study effect of volume expansion when introducing varying concentrations of Li into alpha-phase Sulfur using NPT simulation (previously published by van Duin) and extend to larger polysulfides (Li2Sy where y=1,2,3,4,5,8). Voltage profile relative to Li/Li+ can be calculated from ground state energy using heuristic optimization such as genetic algorithm for structure and phase prediction (GASP).

1.1 Project Plan

1. Abstract
2. Introduction/Motivation
3. Details on Building Systems (6 Li_xS systems) [Avogadro -> Packmol -> VMD -> LAMMPS]
4. Details on Building Systems (6 Li_xS_y systems) [Avogadro -> Packmol -> VMD -> LAMMPS]
5. Heating (annealing) Simulation to get amorphous structure (300K -> 1600K)
6. Discharge Voltage Profile (GC-MC/MD)
7. (If time:) Re-run 3-6 with OPLS-All instead of ReaxFF, compare results
8. Volume Expansion calculation and Comparison with Experiment
9. Diffusion Coefficient Calculation

1.2 Questions:

1. Is using LAMMPS in addition to-/insted of- the MSE627-MD code allowed?
2. Need to describe potential in report? To what detail?
3. van Duin uses dT = 0.25 fs, T = 1 ns (4M timesteps). On Rivanna single-node it will take ~18 hours. Ok to do this?
4. Cannot use GASP+DFT in time to find formation energies, ok to estimate values from figure in published paper? Needed to calculate voltage profile.

1.3 Buildling system

1. Build 1 molecule of α-S_8 (octocyclo...) in Avogardo export as PDB:

```
COMPND    UNNAMED
AUTHOR    GENERATED BY OPEN BABEL 2.3.90
HETATM    1  S   UNL     1       4.721   4.648   2.201  1.00  0.00           S
HETATM    2  S   UNL     1       5.762   3.681   3.640  1.00  0.00           S
HETATM    3  S   UNL     1       5.595   1.680   3.260  1.00  0.00           S
HETATM    4  S   UNL     1       4.151   0.975   4.541  1.00  0.00           S
HETATM    5  S   UNL     1       2.418   0.833   3.468  1.00  0.00           S
HETATM    6  S   UNL     1       1.300   2.475   3.950  1.00  0.00           S
HETATM    7  S   UNL     1       1.532   3.809   2.421  1.00  0.00           S
HETATM    8  S   UNL     1       2.911   5.181   3.045  1.00  0.00           S
CONECT    1    2    8
CONECT    2    1    3
CONECT    3    2    4
CONECT    4    3    5
CONECT    5    4    6
CONECT    6    5    7
CONECT    7    6    8
CONECT    8    7    1
MASTER        0    0    0    0    0    0    0    0    8    0    8    0
END
```

Listing 1: PDB file for Sulfur ring.

1. Build 1 molecule of Li in Avogardo export as PDB:

```
COMPND    Lithium
AUTHOR    GENERATED BY OPEN BABEL 2.3.90
HETATM    1 LI    UNL     1      -0.576   1.200   0.000  1.00  0.00          Li
MASTER        0    0    0    0    0    0    0    0    1    0    1    0
END
```

Listing 2: PDB file for Lithium atom.

1. Use Packmol to mix 2048 atoms of α-S_8 and Li in various ratios Li_xS:

```
#
# A mixture of Li and S 1:1
#

# All the atoms from diferent molecules will be separated at least 2.0
# Anstroms at the solution.

tolerance 2.0

# The file type of input and output files is PDB

filetype pdb

# The name of the output file

output Li1S.pdb
```

```
17
18 # 2048 S molecules and 2048 Li molecules will be put in a box
19 # defined by the minimum coordinates x, y and z = 0. 0. 0. and maximum
20 # coordinates 65.96 65.96 65.96 That is, they will be put in a cube of side
21 # 65.96 (the keyword "inside cube 0. 0. 0. 65.96") could be used as well.
22
23 structure S8.pdb
24   number 256
25   inside box 0. 0. 0. 65.96 65.96 65.96
26 end structure
27
28 structure Li.pdb
29   number 2048
30   inside box 0. 0. 0. 65.96 65.96 65.96
31 end structure
```

Listing 3: Packmol input file.

1. Open pdb file with VMD:
   - /Applications/VMD\ 1.9.3.app/Contents/vmd/vmd$_{\text{MACOSXX86}}$ Li1s.Pdb
   - Command: package require topotools
   - Command: topo writelammpsdata data.Li1S molecular

x	Atoms of S : Atoms of Li ratio	Square Box Size [A]
0.4	2048 S : 820 Li	41.32
0.8	2048 S : 1611 Li	44.42
1.0	2048 S : 2048 Li	45.96
1.2	2048 S : 2428 Li	47.22
1.6	2048 S : 3222 Li	49.66
2.0	2048 S : 1024 Li	52.09

- To calculate simulation box size:
  1. Molar Volume of Sulfur is 15.53 cm^3/mole = 25.78 Angstrom^3/atom
  2. Molar Volume of Lithium is 13.02 cm^3/mole = 21.62 Angstrom^3/atom
  3. Cube root of (Molar Volume (in Angstrom^3/atom) * # of atoms (Li,S))

1.4 Create amorphous structure

1. Slowly heat to T = 1600 K using NVT (V = ???)

see LAMMPS Tdamp in fix nvt doc page also Tstart Tstop

```
1 # LAMMPS Input file: ReaxFF potential for LiS sysstem
2
3 # Intialization
4 units           real
5 boundary        p p p
6 atom_style      charge
7 read_data       data.Li1S
8
9 # Atom Definition
10 #  reax args:
```

```
#             hbcut hbnewflag tripflag precision
pair_style     reax 6.0 1 1 1.0e-6
pair_coeff     * * ffield.reax 7 4

compute reax all pair reax

variable eb      equal c_reax[1]
variable ea      equal c_reax[2]
variable elp     equal c_reax[3]
variable emol    equal c_reax[4]
variable ev      equal c_reax[5]
variable epen    equal c_reax[6]
variable ecoa    equal c_reax[7]
variable ehb     equal c_reax[8]
variable et      equal c_reax[9]
variable eco     equal c_reax[10]
variable ew      equal c_reax[11]
variable ep      equal c_reax[12]
variable efi     equal c_reax[13]
variable eqeq    equal c_reax[14]

# Nieghbor list cutoff
# 2.5 Angstrom (2 is more typical?)
neighbor        2.5 bin

# Rebuild neighbor list:
#  delay value = N
#    N = delay building until this many steps since last build
#  every value = M
#    M = build neighbor list every this many steps
#  check value = yes or no
#    yes = only build if some atom has moved half the skin distance or more
#    no = always build on 1st step that every and delay are satisfied
neigh_modify    every 10 delay 0 check no

# Timestep of iteration [fs]
# van Duin paper uses 0.25 fs
timestep        1.0

dump            1 all custom 10 dump.Li1S.lmp id type q xs ys zs

dump            2 all image 25 image.*.jpg type type &
                axes yes 0.8 0.02 view 60 -30
dump_modify     2 pad 3

#dump            3 all movie 25 movie.mpg type type &
#                axes yes 0.8 0.02 view 60 -30
#dump_modify     3 pad 3

# Run for # of timesteps (NOT [fs])
# Example: with 0.25 fs timestep, 1 ns = 4,000,000 timesteps
run             100
```

Listing 4: Annealing simulation in LAMMPS

1. Quench heated structure to T = 300 K using NPT (P = 1 atm)

2 Reference values

Density of a-Si_8 = 2.07 g/cm^3 = 0.086 g/$Angstrom^3$

Volume of 1 S_8 = 0.086 $Angstorm^3$ Total volume = (2048 Atoms / 8 Atoms/Molecular) * Volume of 1 Molecular = 22.016

3 Changes to van Duin ReaxFF Force Field file

1. Had to remove off-diagonal parameters between irrelevant atoms (Rivanna compiles with max=20 off-diagonal elements, van Duin has 31 in his 11-atom potential. We only need to look at 2 atoms).

4 Notes

- Use $\$LD_{LIBRARYPATH}$ to find LAMMPS lib dir!
- **Library path on Rivanna**: /apps/software/standard/mpi/intel/16.0/openmpi/2.1.1/lammps/2017-08-11:/share/rci_{apps}/intel/2016.2/openmpi-2.1.1/lib:/share/rci_{apps}/intel/2016.2/openmpi-2.1.1/lib/openmpi:/share
- export above at $MYTEST
- find ${MYTEST//:/ } -name $reax_{inout}$.F -print -quit
- Rearrange Packmol output data file columns via: awk '{ print $1 " " $3 " " $2 " " $4 " " $5 " " $6}' test > new_{test}