Ionophilicity and Transport Dynamics of Concentrated Electrolytes in Sub-Nanometre Graphite Confinement

Fulu Zhou, and Paola Carbone

Supporting Information

1. Example of LAMMPS input file for the LiTFSI simulations

```
# LAMMPS input script

units           real
dimension       3
boundary        p p p

atom_style      full
bond_style      harmonic
angle_style     harmonic
dihedral_style  charmm

##------------------------------ Force field -----------------------------------------------##

pair_style      lj/cut/tip4p/long 1 2 1 1 0.1546 12.0
pair_modify     table 0
pair_modify     tabinner/disp 10
pair_modify     tail yes
kspace_style    pppm/tip4p 1.0e-4
comm_modify cutoff  15.5

##----------------------------- Build configuration ----------------------------------------##

region          box  block 0 50 -400 501 0 33
region          liq1 block 0 50 -105 -5  0 33
region          liq2 block 0 50  105 205  0 33

create_box      9 box &
                bond/types 5 &
                angle/types 8 &
                dihedral/types 6 &
                extra/bond/per/atom 4 &
                extra/angle/per/atom 12 &
                        extra/dihedral/per/atom 30 &
                extra/special/per/atom 30 &


molecule water tip3p.mol  offset 0 0 0 0 0 # this uses the TIP3P geometry
molecule TFSI  TFSI.mol  offset  3 1 1 0 0
```

```
create_atoms 0 random 100   52802 liq1 mol TFSI  25894 overlap 1.0 maxtry 500
create_atoms 0 random 5388  34564 liq1 mol water 25367 overlap 1.0
create_atoms 3 random 100   90182 liq1 overlap 0.5 maxtry 500

create_atoms 0 random 100   52802 liq2 mol TFSI  25894 overlap 1.0 maxtry 500
create_atoms 0 random 5388  34564 liq2 mol water 25367 overlap 1.0
create_atoms 3 random 100   90182 liq2 overlap 0.5 maxtry 500

read_data   channal.data add append offset 8 0 0 0 0
read_data   channal.data add append offset 8 0 0 0 0 shift 0 0 22.5

bond_coeff          1  450.0   0.9572  # O-H water
bond_coeff          2  493.0   1.466   # S-O TFSI
bond_coeff          3  257.1   1.752   # S-N TFSI
bond_coeff          4  248.9   1.782   # S-C TFSI
bond_coeff          5  363.8   1.344   # C-F TFSI

angle_coeff           1 55.00    104.52          #       H-O-H water
angle_coeff           2 45.30    121         #   O-S-O TFSI
angle_coeff           3 43.09    107.06          #       N-S-O  TFSI
angle_coeff           4 109.72  119.18           #       S-N-S  TFSI
angle_coeff           5 39.42    103.12         #       N-S-C  TFSI
angle_coeff         6    81.22    109.67          #       S-C-F  TFSI
angle_coeff           7 41.28    108.48         #       O-S-C  TFSI
angle_coeff           8 71.26    107.16          #       F-C-F  TFSI

dihedral_coeff    1    0.144000956   3        0       0       #       f-C3-Sy-O
dihedral_coeff    2    0.49999283    3        180     0       #       Sy-Ne-Sy-O
dihedral_coeff    3    6.799902008   3        180     0       #       Sy-Ne-Sy-O
dihedral_coeff     4   0.144000956   3        0       0       #       f-C3-Sy-Ne
dihedral_coeff    5    0.49999283    3        180     0       #       Sy-Ne-Sy-C3
dihedral_coeff    6    6.799902008   3        180     0       #       Sy-Ne-Sy-C3


##------------------------------ Set mass for atom ----------------------------------------##

mass 1 15.9994   # O_h2o
mass 2 1.008     # H
mass 3 6.94100   # Li
mass 4 16.00     # O_TFSI
mass 5 32.06     # S
mass 6 14.01     # N
mass 7 12.01     # C3
mass 8 19.00     # F
mass 9 12.0707   # C

##------------------------- must change charges for TIP4P ----------------------------------##


set       type     1         charge -1.1128
```

```
set       type    2       charge 0.5564
set       type    3       charge 0.85
set       type    4       charge -0.466
set       type    5       charge 0.911
set       type    6       charge -0.598
set       type    7       charge 0.3165
set       type    8       charge -0.1405
set       type    9       charge 0

##---------------------------------- Pair coeff ----------------------------------------##
##------------------------ eps ------ sigma ----------------------------------------------##

pair_coeff              1               1               0.1852          3.1589 #        O

pair_coeff              2               2               0               0       #       H

pair_coeff              3               3               0.10399                 1.4397 #        Li
                2019-Madrid
pair_coeff              4               4               0.21            2.9599          #       Ot

pair_coeff              5               5               0.25            3.5636          #       S

pair_coeff              6               6               0.17            3.25    #       N

pair_coeff              7               7               0.1094          3.3997 #        C3

pair_coeff              8               8               0.061           3.1182 #        F

pair_coeff              9               9               0.0000          3.3997 #        C
        0.0859 3.3997

pair_coeff              1               2               0                       1.57945 #       O
        H
pair_coeff              1               3               0.16746                 2.12    #       O
        Li
pair_coeff              1               4               0.197210547             3.0594 #        O
        Ot
pair_coeff              1               5               0.215174348             3.36125         #
        O       S
pair_coeff              1               6               0.177437313             3.20445         #
        O       N
pair_coeff              1               7               0.142340718             3.2793 #        O
        C3
pair_coeff              1               8               0.106288287             3.13855         #
        O       F
pair_coeff              1               9               0.11434                 3.275   #       O
        C       werder

pair_coeff              2               3               0               0.71985         #       H
        Li
```

```
pair_coeff      2       4       0       1.47995 #       H       Ot
pair_coeff      2       5       0       1.7818 #        H       S
pair_coeff      2       6       0       1.625   #       H       N
pair_coeff      2       7       0       1.69985 #       H       C3
pair_coeff      2       8       0       1.5591 #        H       F
pair_coeff      2       9       0       1.69985 #       H       C

pair_coeff      3       4       0.14777652      2.1998 #        Li      Ot
pair_coeff      3       5       0.161237403     2.50165 #       Li      S
pair_coeff      3       6       0.132959768     2.34485 #       Li      N
pair_coeff      3       7       0.106660705     2.4197 #        Li      C3
pair_coeff      3       8       0.079645402     2.27895 #       Li      F
pair_coeff      3       9       0.094513179     2.4197 #        Li      C

pair_coeff      4       5       0.229128785     3.26175 #       Ot      S
pair_coeff      4       6       0.188944436     3.10495 #       Ot      N
pair_coeff      4       7       0.151571765     3.1798 #        Ot      C3
pair_coeff      4       8       0.113181271     3.03905 #       Ot      F
pair_coeff      4       9       0.134309344     3.1798 #        Ot      C

pair_coeff      5       6       0.206155281     3.4068 #        S       N
pair_coeff      5       7       0.165378354     3.48165 #       S       C3
pair_coeff      5       8       0.12349089      3.3409 #        S       F
pair_coeff      5       9       0.146543509     3.48165 #       S       C

pair_coeff      6       7       0.136374484     3.32485 #       N       C3
pair_coeff      6       8       0.101833197     3.1841 #        N       F
```

```
pair_coeff          6          9          0.120842873      3.32485     #
        N       C

pair_coeff          7          8          0.081690881      3.25895     #
        C3      F
pair_coeff          7          9          0.096940497      3.3997 #    C3
        C

pair_coeff          8          9          0.072387154      3.25895     #
        F       C


##---------------------------------- Set group name ----------------------------------------##

group           Ox   type    1
group           Hy   type    2
group           Li   type   3
group           Ot   type    4
group           S    type    5
group           N    type    6
group           C3   type    7
group           F    type    8
group           gra  type   9

group           H2O  type   1 2
group           TFSI type  4 5 6 7 8
group           ele  type   1 2 3 4 5 6 7 8


##---------------------------------- Energy minimization -----------------------------------##



thermo            10
fix               freeze gra setforce 0.0 0.0 0.0
minimize           1.0e-4 1.0e-6 100 1000


write_data LiTFSIchannel1m.data


# ---------------------------------------- Initi Vel  ----------------------------------------##


velocity ele create 300 944588317
velocity ele zero linear
velocity ele zero angular
```

```
# ------------------------------------ Initi Vel  ------------------------------------##


velocity ele create 300 944588317
velocity ele zero linear
velocity ele zero angular

##---------------------- Run NVT at 298.15K correct every 200 timestep ----------------------##
##------------------------------- shake to fix bond and angle -------------------------------##

region            channel  block 0 50 0 100.6 10.2 22.5

variable Nh2o      equal count(H2O,channel)
variable Nli       equal count(Li,channel)
variable NOt       equal count(Ot,channel)
variable NS        equal count(S,channel)
variable NN        equal count(N,channel)
variable NC3       equal count(C3,channel)
variable NF        equal count(F,channel)


variable NTFSI     equal count(TFSI,channel)


fix       myat1 all ave/time 10 100 1000 v_Nh2o  file H2O.dat
fix       myat2 all ave/time 10 100 1000 v_Nli   file Nli.dat
fix       myat3 all ave/time 10 100 1000 v_NOt   file NOt.dat
fix       myat4 all ave/time 10 100 1000 v_NS    file NS.dat
fix       myat5 all ave/time 10 100 1000 v_NN    file NN.dat
fix       myat6 all ave/time 10 100 1000 v_NC3   file NC3.dat
fix       myat7 all ave/time 10 100 1000 v_NF    file NF.dat


timestep          2       #2fs
dump              mydmp all custom 1000 md.lammpstrj id type x y z
compute           eletemp ele temp

thermo            1000
thermo_style      custom step c_eletemp pe press v_Nh2o v_Nli v_NTFSI v_NOt v_NS
v_NN v_NC3 v_NF

fix               freeze gra setforce 0.0 0.0 0.0
fix               myshk H2O shake 1.0e-5 200 0 b 1 a 1
fix               mynvt ele nvt temp 298.15 298.15 400
#fix              mynvt2 gra nvt temp 0 0 400
fix               balance all balance 10000 1.05 shift y 10 1.05
fix               moment ele momentum 1 linear 1 1 1 rescale

restart           500000 restart/restart.*.equil
run               25000000   #50ns
```

```
write_data          LiTFSIchannel1M_final.data nocoeff


## --------------------------change the parameters for NaTFSI setup----------------------##
##
##   mass 3 22.98977   # Na
##
##
##   ##---------------------------------- Pair coeff ----------------------------------------##
##   ##------------------------- eps ------ sigma -----------------------------------------##
##
##   pair_coeff          1               1               0.1852          3.1589          #
         O
##   pair_coeff          2               2               0                 0         #       H

##   pair_coeff          3               3               0.3519          2.21737         #
         Na
##   pair_coeff          4               4               0.21            2.9599          #
         Ot
##   pair_coeff          5               5               0.25            3.5636          #
         S
##   pair_coeff          6               6               0.17            3.25        #       N

##   pair_coeff          7               7               0.1094          3.3997          #
         C3
##   pair_coeff          8               8               0.061           3.1182          #
         F
##   pair_coeff          9               9               0.0               3.3997        #
         C
##

##   pair_coeff          1               2               0                   1.57945       #
         O       H
##   pair_coeff          1               3               0.18962                 2.60838
         #       O       Na  2019-Madrid
##   pair_coeff          1               4               0.197210547     3.0594          #
         O       Ot
##   pair_coeff          1               5               0.215174348     3.36125         #
         O       S
##   pair_coeff          1               6               0.177437313         3.20445
         #       O       N
##   pair_coeff          1               7               0.142340718         3.2793      #
         O       C3
##   pair_coeff          1               8               0.106288287         3.13855
         #       O       F
##   pair_coeff          1               9               0.11434               3.275
         #       O       C       werder
##
```

```
## pair_coeff 2 3 0 1.108685 # H Na
## pair_coeff 2 4 0 1.47995 # H Ot
## pair_coeff 2 5 0 1.7818 # H S
## pair_coeff 2 6 0 1.625 # H N
## pair_coeff 2 7 0 1.69985 # H C3
## pair_coeff 2 8 0 1.5591 # H F
## pair_coeff 2 9 0 1.69985 # H C
##

## pair_coeff 3 4 0.271843705 2.588635 # Na Ot
## pair_coeff 3 5 0.296605799 2.890485 # Na S
## pair_coeff 3 6 0.244587408 2.733685 # Na N
## pair_coeff 3 7 0.196208715 2.808535 # Na C3
## pair_coeff 3 8 0.146512457 2.667785 # Na F
## pair_coeff 3 9 0.173862618 2.808535 # Na C
##

## pair_coeff 4 5 0.229128785 3.26175 # Ot S
## pair_coeff 4 6 0.188944436 3.10495 # Ot N
## pair_coeff 4 7 0.151571765 3.1798 # Ot C3
## pair_coeff 4 8 0.113181271 3.03905 # Ot F
## pair_coeff 4 9 0.134309344 3.1798 # Ot C
##

## pair_coeff 5 6 0.206155281 3.4068 # S N
## pair_coeff 5 7 0.165378354 3.48165 # S C3
## pair_coeff 5 8 0.12349089 3.3409 # S F
## pair_coeff 5 9 0.146543509 3.48165 # S C
```

```
##

## pair_coeff          6               7               0.136374484     3.32485
        #       N       C3
## pair_coeff          6               8               0.101833197     3.1841  #
        N       F
## pair_coeff          6               9               0.120842873     3.32485
        #       N       C
##

## pair_coeff          7               8               0.081690881     3.25895
        #       C3      F
## pair_coeff          7               9               0.096940497     3.3997  #
        C3      C
##

## pair_coeff          8               9               0.072387154     3.25895
        #       F       C
##
## ----------------------------------------------------------------------------------------------------
```

2. Example of LAMMPS input file for LiCl simulations

```
# LAMMPS input script

units           real
dimension       3
boundary        p p p

atom_style      full
bond_style      harmonic
angle_style     harmonic

##------------------------------ Force field -----------------------------------------------##

pair_style      lj/cut/tip4p/long 1 2 1 1 0.1546 12.0
pair_modify     table 0
pair_modify     tabinner/disp 10
pair_modify     tail yes
kspace_style    pppm/tip4p 1.0e-4
comm_modify cutoff   15.5

##------------------------------ Build configuration ---------------------------------------##

region          box  block 0 50 -400 501 0 33
region          liq1 block 0 50 -100 0   0 33
region          liq2 block 0 50 101 201 0 33

create_box      5 box &
                bond/types 1 &
                angle/types 1 &
                extra/bond/per/atom 2 &
                extra/angle/per/atom 1 &
                extra/special/per/atom 2 &


bond_coeff      1  450 0.9572
angle_coeff     1  55  104.52

molecule water tip3p.mol  # this uses the TIP3P geometry

create_atoms 0 random 5388  34564 liq1 mol water 25367 overlap 1.33
create_atoms 3 random 100   52802 liq1 overlap 1 maxtry 500
create_atoms 4 random 100   90182 liq1 overlap 1 maxtry 500

create_atoms 0 random 5388  34564 liq2 mol water 25367 overlap 1.33
create_atoms 3 random 100   52802 liq2 overlap 1 maxtry 500
create_atoms 4 random 100   90182 liq2 overlap 1 maxtry 500

read_data   channal.data add append offset 4 0 0 0 0
read_data   channal.data add append offset 4 0 0 0 0 shift 0 0 22.5
```

```
##------------------------------ Set mass for atom ----------------------------------------##

mass 1 15.9994    # O
mass 2 1.008      # H
mass 3 6.94100    # Li
mass 4 35.4530    # Cl
mass 5 12.0707    # C

##------------------------- must change charges for TIP4P ----------------------------------##
#
set type 1 charge -1.1128
set type 2 charge  0.5564
set type 3 charge  0.85
set type 4 charge -0.85
set type 5 charge  0

##---------------------------------- Pair coeff ----------------------------------------##

pair_coeff          1 1  0.18520    3.15890  # O
pair_coeff          2 *  0.00000    0.00000  # H
pair_coeff          3 3  0.10399    1.43970  # Li
pair_coeff          4 4  0.01834    4.69906  # Cl
pair_coeff          5 5  0.00000    0.00000  # C  0.08590 3.3997

pair_coeff          1 5  0.11434    3.27500  # O  C  werder
pair_coeff          1 3  0.16746    2.12000  # O  Li
pair_coeff          1 4  0.01481    4.23867  # O  Cl

pair_coeff          3 4  0.30663    2.70000  # Li Cl
pair_coeff          3 5  0.09451    2.41955  # C  Li
pair_coeff          4 5  0.03969    4.04938  # C  Cl


##---------------------------------- Set group name ----------------------------------------##

group               Ox type    1
group               Hy type    2
group               Li  type   3
group               Cl  type   4
group               gra type   5

group               H2O type   1 2
group               ele type   1 2 3 4

##---------------------------------- Energy minimization ----------------------------------##

fix                 freeze gra setforce 0.0 0.0 0.0
thermo              10
```

```
minimize 1.0e-4 1.0e-5 300 1000
write_data liclchannel1m.data

# ------------------------------------ Initi Vel  ----------------------------------------##


velocity ele create 300 944588317
velocity ele zero linear
velocity ele zero angular


##---------------------- Run NVT at 298.15K correct every 200 timestep ------------------------##
##------------------------------ shake to fix bond and angle -------------------------------##

##---------------------- Run NVT at 298.15K correct every 200 timestep ------------------------##
##------------------------------ shake to fix bond and angle -------------------------------##

region             channel  block 0 50 0 100.6 10.2 22.5

variable Nh2o       equal count(H2O,channel)
variable Nli        equal count(Li,channel)
variable Ncl        equal count(Cl,channel)


fix       myat1 all ave/time 10 100 1000 v_Nh2o  file H2O.dat
fix       myat2 all ave/time 10 100 1000 v_Nli   file Nli.dat
fix       myat3 all ave/time 10 100 1000 v_Ncl   file NCl.dat


timestep           2       #2fs
dump               mydmp all atom 1000 md.lammpstrj
compute             eletemp ele temp

thermo             1000
thermo_style        custom step c_eletemp pe press vol ly density v_Nh2o v_Nli v_Ncl
fix                freeze gra setforce 0.0 0.0 0.0
fix                myshk H2O shake 1.0e-5 200 0 b 1 a 1
fix                mynvt ele nvt temp 298.15 298.15 400
fix                balance all balance 10000 1.05 shift y 10 1.05
fix                moment all momentum 1 linear 1 1 1 rescale


restart             500000 restart/restart.*.equil
run                15000000 # 30ns

write_data          LiCl1Mequ.data nocoeff

##--------------------change the parameters for NaCl setup---------------------##
##                                                          ##
##  mass 3 22.98977   # Na                                        ##
```

```
##                                                    ##
##  #---------------------------------- Pair coeff -------------------------##
##                                                    ##
##  pair_coeff          1 1  0.18520    3.15890  # O                    ##
##  pair_coeff          2 *  0.00000    0.00000  # H                    ##
##  pair_coeff          3 3  0.35190    2.21737  # Na                    ##
##  pair_coeff          4 4  0.01834    4.69906  # Cl                   ##
##  pair_coeff          5 5  0.00000    3.3997  # C  0.08590 3.3997         ##
##                                                    ##
##                                                    ##
##  pair_coeff          1 5  0.11434    3.27500  # O  C  werder            ##
##  pair_coeff          1 3  0.18962    2.60838  # O  Na                  ##
##  pair_coeff          1 4  0.01481    4.23867  # O  Cl                  ##
##                                                    ##
##  pair_coeff          3 4  0.34390    3.00512  # Na Cl                  ##
##  pair_coeff          3 5  0.09451    2.41955  # C  Na                  ##
##  pair_coeff          4 5  0.03969    4.04938  # C  Cl                  ##
##-----------------------------------------------------------------------------##
```