SUPPORTING INFORMATION

Molecular Dynamics Simulation of LiTFSI – Acetamide Electrolytes: Structural Properties

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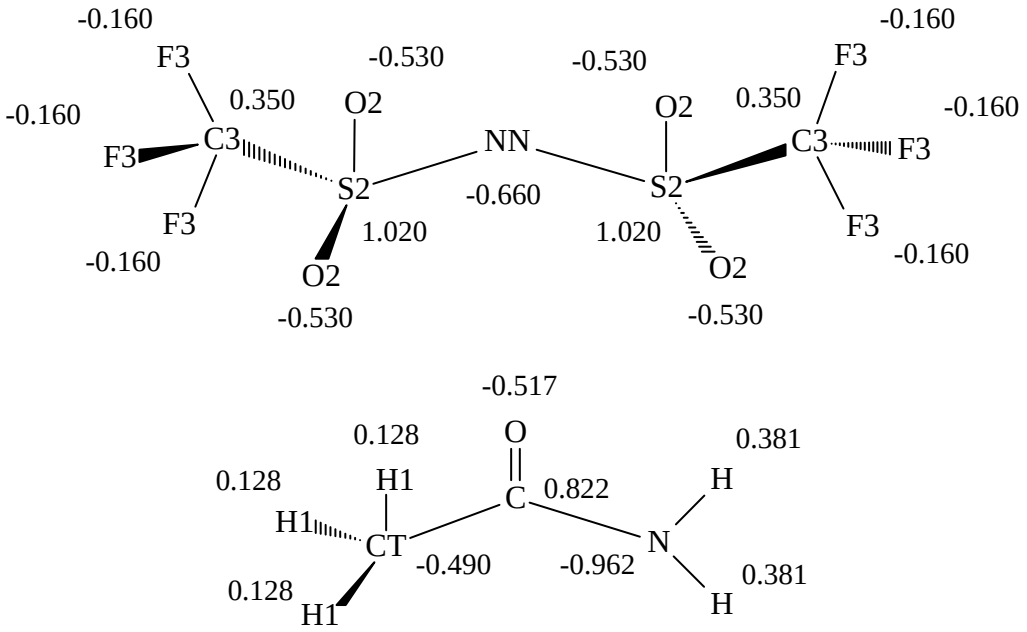
The potential energy function for the classical force field is written as,

$$V = \sum_{bonds} k_b (r - r_0)^2 + \sum_{angles} k_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} V_n [1 + \cos(n\phi - \delta)]$$
$$+ \sum_i \sum_{j>i} \left(4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} \right)$$

The partial charge of Li^+ is +1 and the RESP fitted partial charges (in elementary electron charge unit) for the $TFSI^-$ and acetamide are shown in the following figure.



The force field parameters are listed in the tables below.

Bond parameters [k_r in kcal/(mol Å^2) and r_{eq} in Å].

bond	k_r	r_{eq}	bond	k_r	r_{eq}	bond	k_r	r_{eq}
S2-NN	372.0	1.570	C3-F3	441.8	1.323	CT-H1	340.0	1.090
S2-O2	637.1	1.442	C-O	570.0	1.229	CT-C	317.0	1.522
S2-C3	235.4	1.818	C-N	490.0	1.335	N-H	434.0	1.010

Angle parameters [k_θ in kcal/(mol radian^2) and θ_{eq} in degree].

angle	k_θ	θ_{eq}	angle	k_θ	θ_{eq}
S2-NN-S2	80.2	125.60	C3-S2-O2	104.0	102.60
C3-S2-NN	97.5	100.20	NN-S2-O2	94.3	113.60
O2-S2-O2	115.8	118.50	F3-C3-F3	93.3	107.10
F3-C3-S2	82.9	111.80	O-C-N	80.0	122.90

C-N-H	30.0	120.0	O-C-CT	80.0	120.40
H-N-H	35.0	120.0	H1-CT-C	50.0	109.50
H1-CT-H1	35.0	109.50			

Dihedral angle parameters A (in kcal/mol) and δ (in degree) of acetamide.

dihedral	V	δ	n	dihedral	V	δ	n
CT-C-N-H	2.500	180	2	O-C-N-H	2.000	0	1
F3-C3-S2-O2	0.173	0	3	F3-C3-S2-NN	0.158	0	3
O2-S2-NN-S2	-0.002	0	3	C3-S2-NN-S2	[a]		

[a]The torsional function of $TFSI^-$ takes the form: $\sum_{n=1}^{3} V_n[1+(-1)^{n+1}\cos(n\varphi)]$, in which V_1=3.916, V_2=-1.245, and V_3=-0.382, in unit kcal/mol.

Van der Waals parameters [ε in kcal/mol and σ in Å].

pair	ε	σ	pair	ε	σ	pair	ε	σ
NN-NN	0.1700	3.250	NN-O2	0.1889	3.105	NN-S2	0.2062	3.400
NN-C3	0.1059	3.375	NN-F3	0.0949	3.100	NN-C	0.1209	3.325
NN-O	0.1889	3.105	NN-N	0.1700	3.250	NN-H	0.0517	2.160
NN-CT	0.1364	3.325	NN-H1	0.0517	2.861	NN-Li	0.0558	2.638
O2-O2	0.2100	2.960	O2-S2	0.2291	3.255	O2-C3	0.1177	3.230
O2-F3	0.1055	2.955	O2-C	0.1344	3.180	O2-O	0.2100	2.960
O2-N	0.1890	3.105	O2-H	0.0574	2.015	O2-CT	0.1516	3.180
O2-H1	0.0574	2.716	O2-Li	0.0620	2.493	S2-S2	0.2450	3.550

S2-C3	0.1285	3.525	S2-F3	0.1151	3.250	S2-C	0.1466	3.475
S2-O	0.2291	3.255	S2-N	0.2062	3.400	S2-H	0.0626	2.310
S2-CT	0.1654	3.475	S2-H1	0.0626	3.011	S2-Li	0.0676	2.788
C3-C3	0.0660	3.500	C3-F3	0.0591	3.225	C3-C	0.0753	3.450
C3-O	0.1177	3.230	C3-N	0.1059	3.375	C3-H	0.0322	2.285
C3-CT	0.0850	3.450	C3-H1	0.0322	2.986	C3-Li	0.0348	2.763
F3-F3	0.0530	2.950	F3-C	0.0675	3.175	F3-O	0.1055	2.955
F3-N	0.0949	3.100	F3-H	0.0288	2.010	F3-CT	0.0761	3.175
F3-H1	0.0288	2.711	F3-Li	0.0311	2.488	C-C	0.0860	3.400
C-O	0.1344	3.180	C-N	0.1209	3.325	C-H	0.0367	2.234
C-CT	0.0970	3.400	C-H1	0.0367	2.936	C-Li	0.0397	2.713
O-O	0.2100	2.960	O-N	0.1889	3.105	O-H	0.0574	2.015
O-CT	0.1516	3.180	O-H1	0.0574	2.716	O-Li	0.0620	2.493
N-N	0.1700	3.250	N-H	0.0517	2.160	N-CT	0.1364	3.325
N-H1	0.0517	2.861	N-Li	0.0558	2.638	H-H	0.0157	1.069
H-CT	0.0414	2.234	H-H1	0.0157	1.770	H-Li	0.0170	1.548
CT-CT	0.1094	3.400	CT-H1	0.0414	2.936	CT-Li	0.0447	2.713
H1-H1	0.0157	2.471	H1-Li	0.0170	2.249	Li-Li	0.0183	2.026

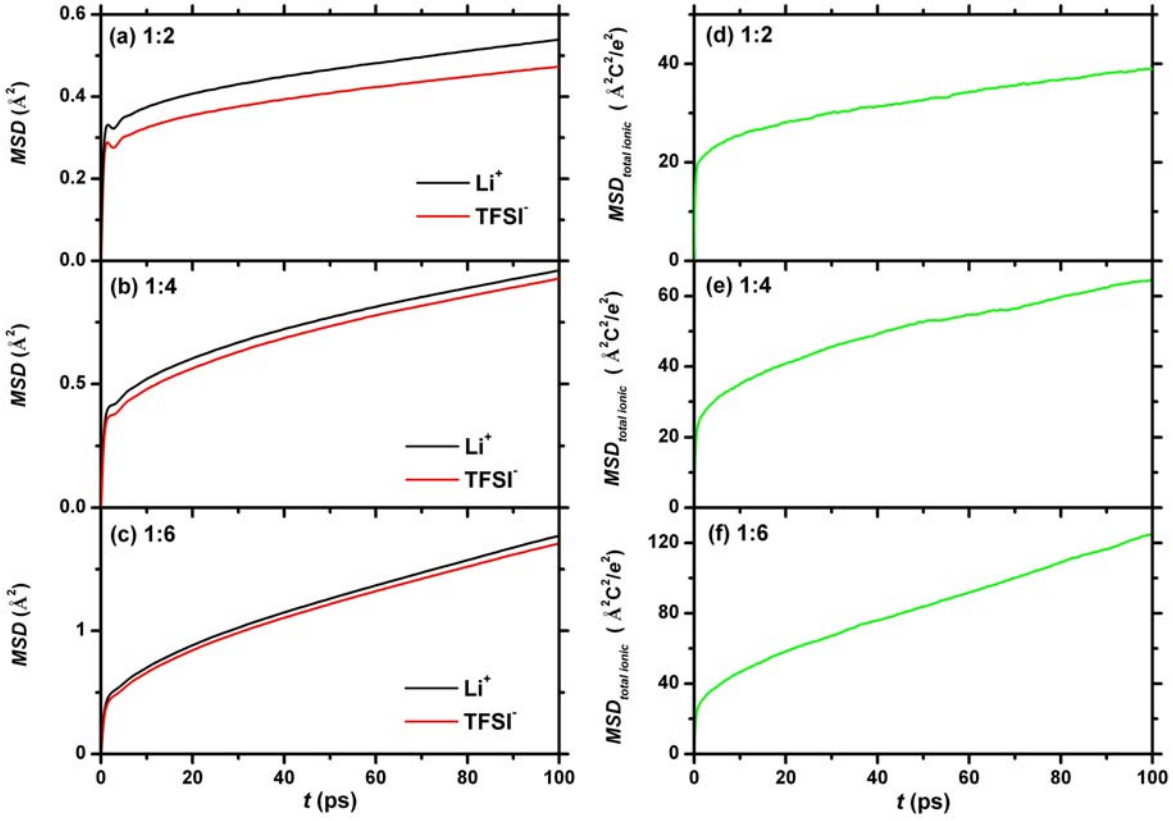


Fig. 11. Ionic mean square displacement (MSD) (left column) and total ionic MSD (right column), respectively, for (a), (d) LiTFSI1-ACE_2; (b), (e) LiTFSI1-ACE_4; and (c), (f) LiTFSI1-ACE_6; black for the Li^+ ion, red for the $TFSI^-$ ion, and green for the total ionic MSD. In the right colume, e=1.6022×10^{-19} C, i.e. unit electron charge.