Supplementary Information

Atomistic description of ionic diffusion in PEO-LiTFSI: Effect of temperature, molecular weight, and ionic concentration

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1. Ionic Charges on PEO_4-LiTFSI

Simulations of ionic diffusion require charges less[1] than the purely ionic charge of ±1 in order to account for shielding effects. The choice of charge is, in general, non-unique and requires a QM-based simulation on a representative system.

Here, a PEO_4-LiTFSI cluster (Figure S1) was built and a lithium charge of +0.70 was obtained using the electrostatic potential (ESP) method at the B3LYP/6-31G** level of theory (Table S1).

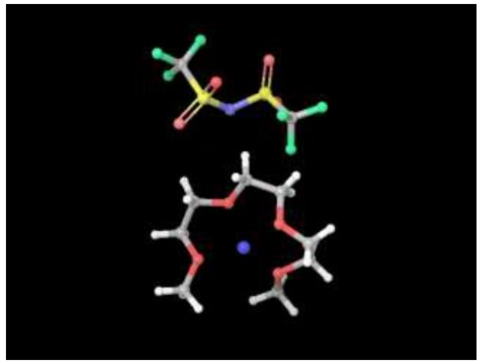


Figure S1. Representative PEO_4-LiTFSI cluster used for charge calculations.

Thus, we elected to use ionic charges of ±0.7. The TFSI charges were taken from ESP charges on an isolated $TFSI^-$ molecule, scaled by a factor of 0.7 in order to maintain a neutral system. Charges on the polymer were taken directly from the OPLS2005FF.[2]

Table S1. Molecular dynamics charges on PEO and LiTFSI. Polymer charges are from the OPLS2005 FF and LiTFSI charges are determined from ESP charges obtained from DFT calculations.

PEO

Atom	FF
C	+0.14
H	-0.03
O	-0.40

Li^+

Atom	FF
Li	+0.70

$TFSI^-$

Atom	FF
O	-0.34
S	+0.61
N	-0.45
C	+0.22
F	-0.09

These charges are also in reasonable agreement with Mulliken charges and a set of charges later developed using the PQEq method.[3]

2. Computational Procedure for Building Polymer Structures

After construction, each polymer cell was equilibrated using a standard procedure based on the Scaled-Effective-Solvent (SES) method,[4,5] which allows relaxation of the polymer chains. The steps in the initial equilibration procedure are as follows:

1. Construct a PEO-LiTFSI structure at 60% of the experimental density in an amorphous builder
2. Minimize for 300 steps to avoid clashes
3. Run NVT at 10 K for 20 ps to give the system an initial velocity
4. Run NPT at 300 K for 200 ps to equilibrate the lattice parameters
5. Minimize for 300 steps to avoid clashes
6. 500 ps of NVT at 300 K with non-bond (Coulomb, van der Waals) interactions scaled down to 20% of their original value to allow the polymer chains to relax
7. Minimize for 300 steps to avoid clashes
8. Run NPT at 300 K for 100 ps to re-equilibrate the lattice parameters

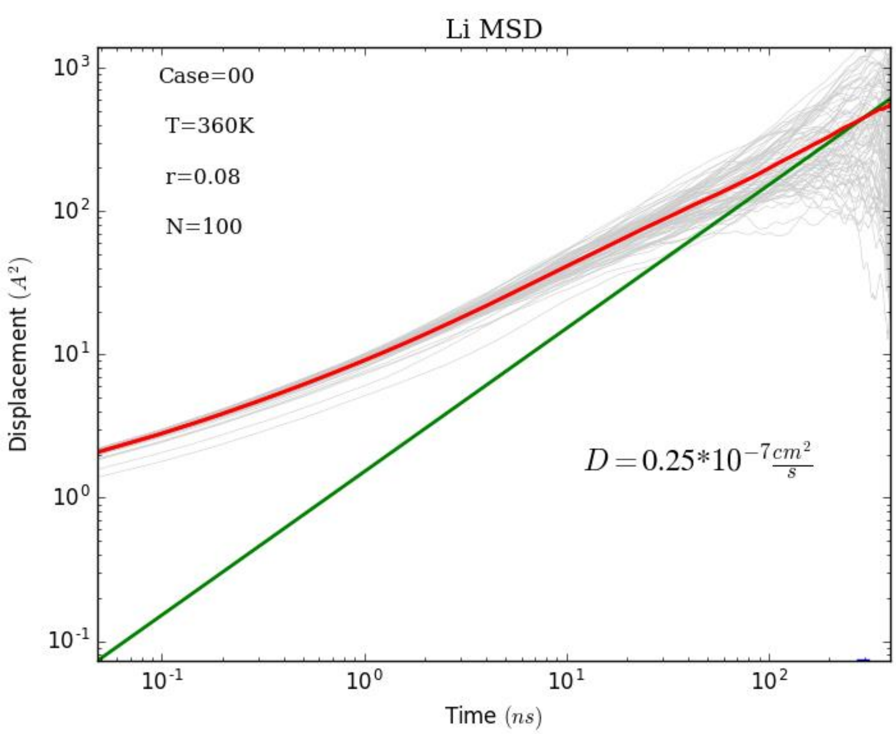
The equilibrated structure from step 8 is then used as the initial structure for simulations at 360, 400, 440 and 480K. To account for the higher temperature, two additional steps of equilibration are performed.

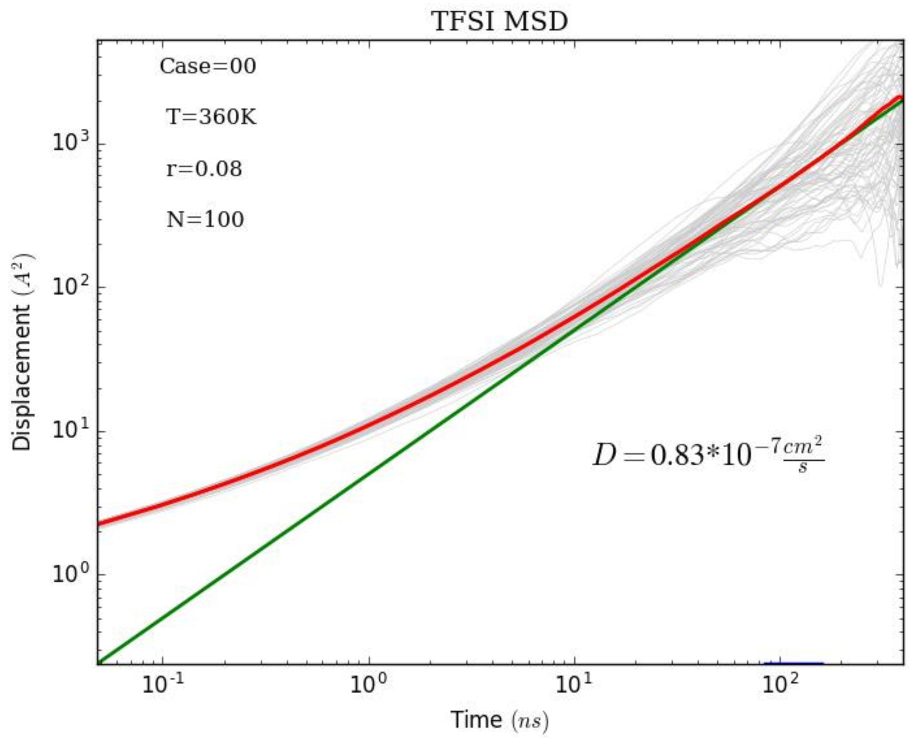
9. Run 1 ns of NPT at the target temperature to equilibrate lattice parameters
10. Run 10 ns of NVT at the target temperature to equilibrate polymer.

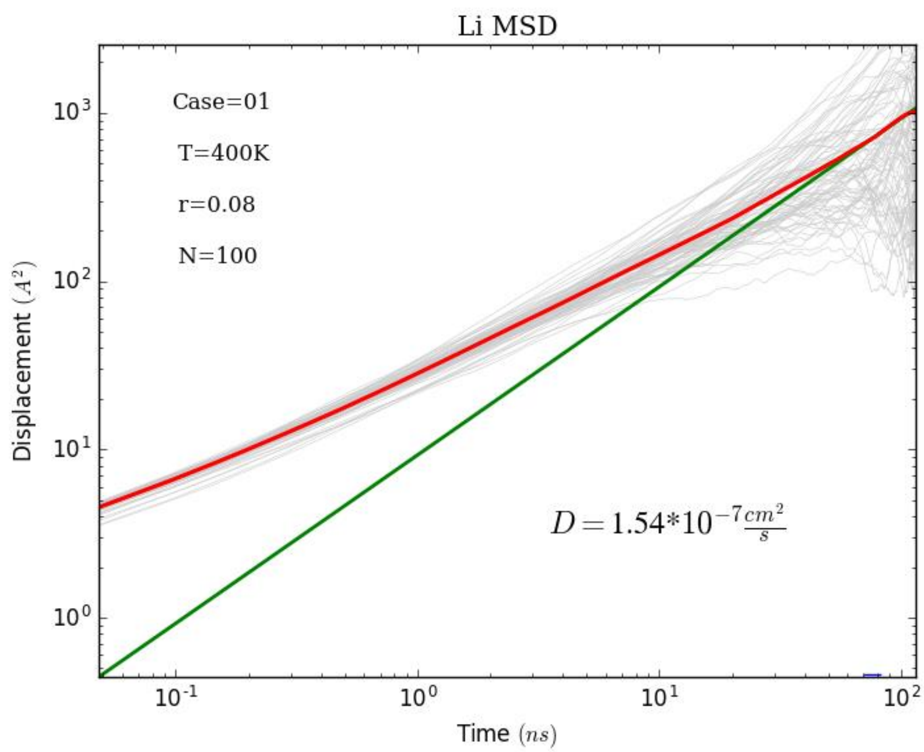
After the equilibration process is completed, a production simulation is run for 115-400 ns.

3. Mean-Squared-Displacement (MSD) Plots for All Simulations

The MSD (Å^2) is defined as the average squared displacement of the center of mass of the ion over all points in the trajectory separated by the corresponding time (ns). The MSD curves for individual ions are shown as grey lines and the average of the collection of ions is shown as a red curve. The Fickian regime of the MSD is identified as largest continuous group of times where the loglog slope is with 0.1 units of 1.0. To ensure a robust fit, if the Fickian regime (shown in blue) is less than 10% of the totally trajectory length, it is evenly extended to 10% of the trajectory in the ±t directions. This method yielded results in agreement with other fitting schemes, such as apparent diffusion coefficient,[5] while ensuring that diffusion coefficients are obtained from truly Fickian diffusion.




TFSI MSD
Case=00
T=360K
r=0.08
N=100
$D = 0.83*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)


Li MSD
Case=01
T=400K
r=0.08
N=100
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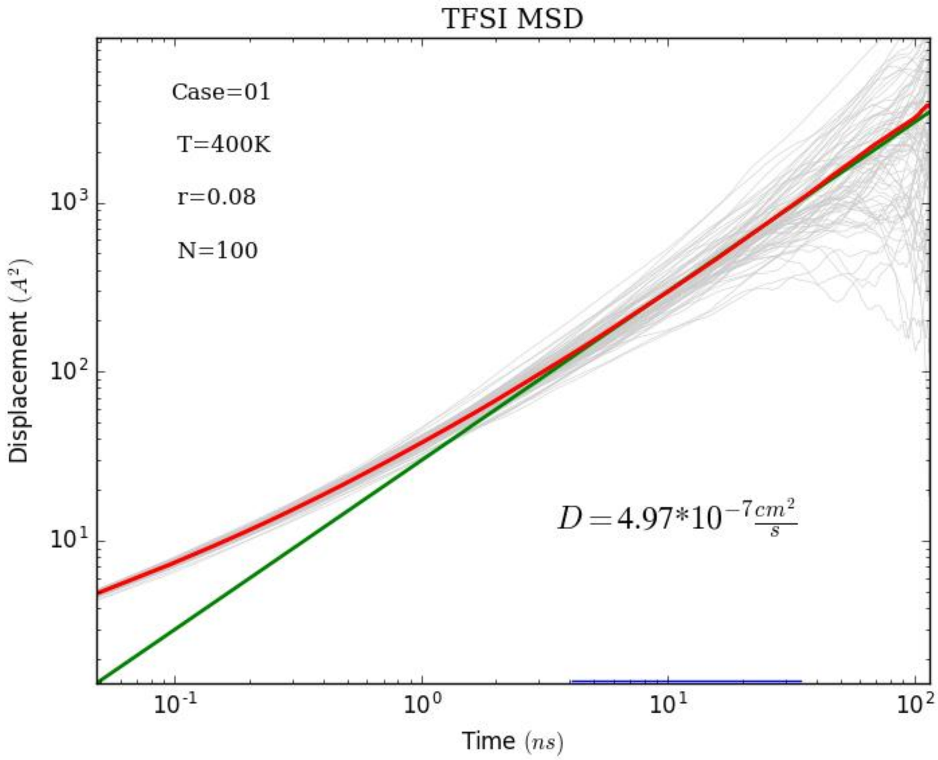
Displacement (A^2)
Time (ns)


TFSI MSD
Case=01
T=400K
r=0.08
N=100
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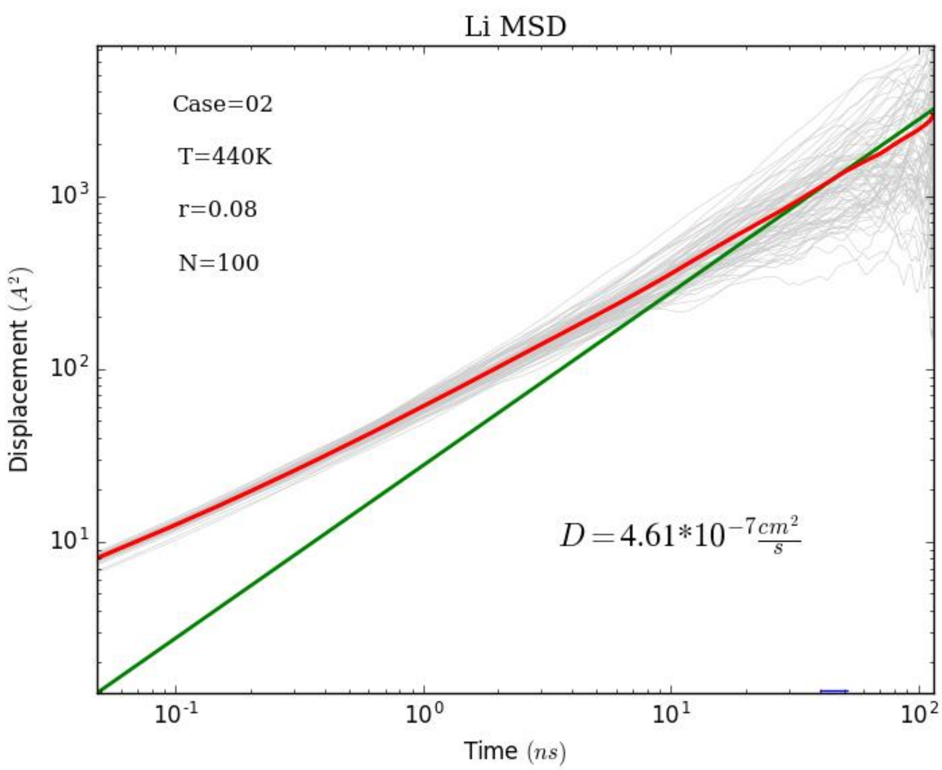
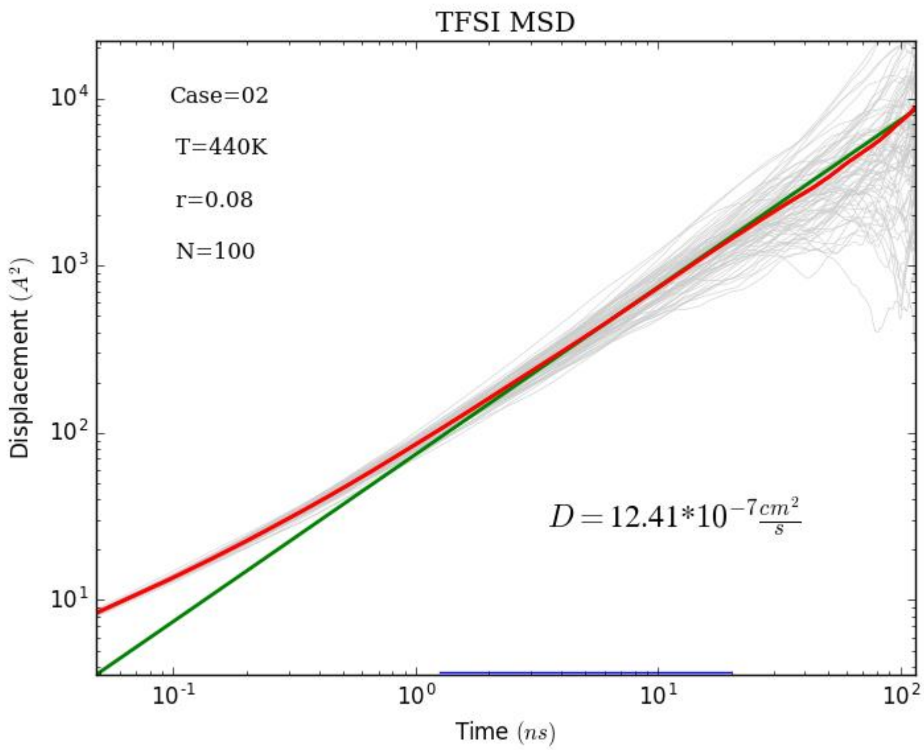
Displacement (A^2)
10^3
10^2
10^1
10^{-1}
10^0
10^1
10^2
Time (ns)


Li MSD
Case=02
T=440K
r=0.08
N=100
$D = 4.61*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
10^3
10^2
10^1
10^{-1}
10^0
10^1
10^2
Time (ns)


TFSI MSD
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r=0.08
N=100
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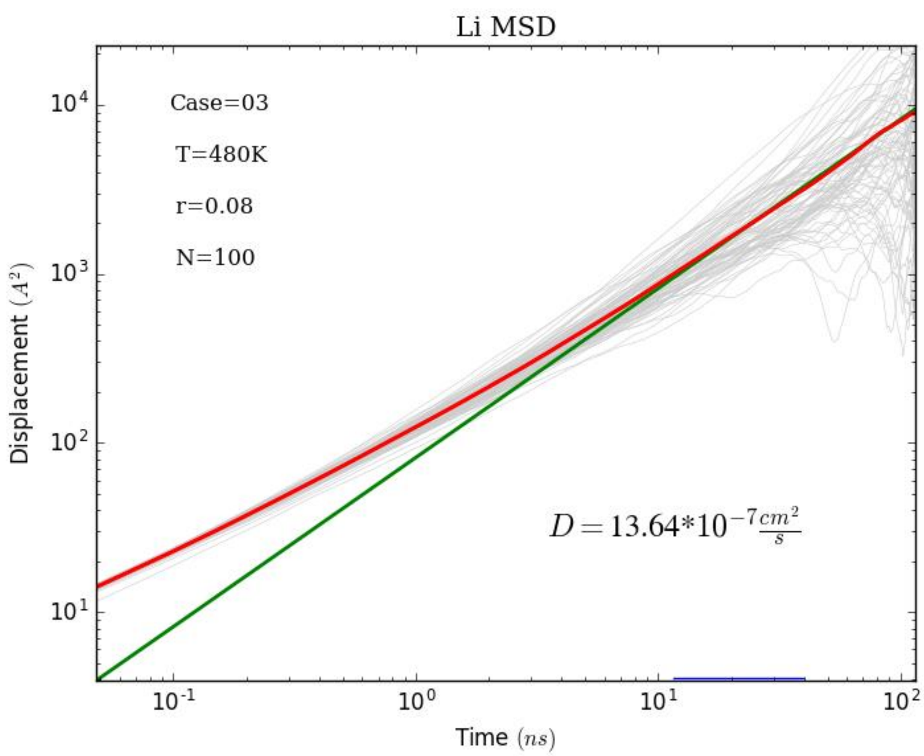
Displacement (A^2)
Time (ns)


Li MSD
Case=03
T=480K
r=0.08
N=100
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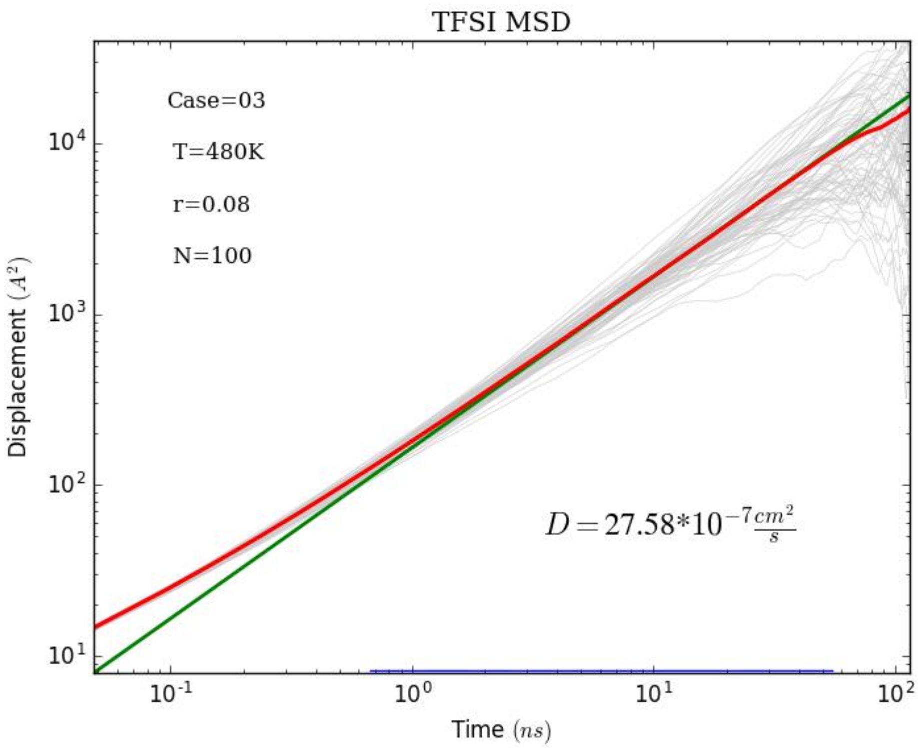
Displacement (A^2)
Time (ns)


TFSI MSD
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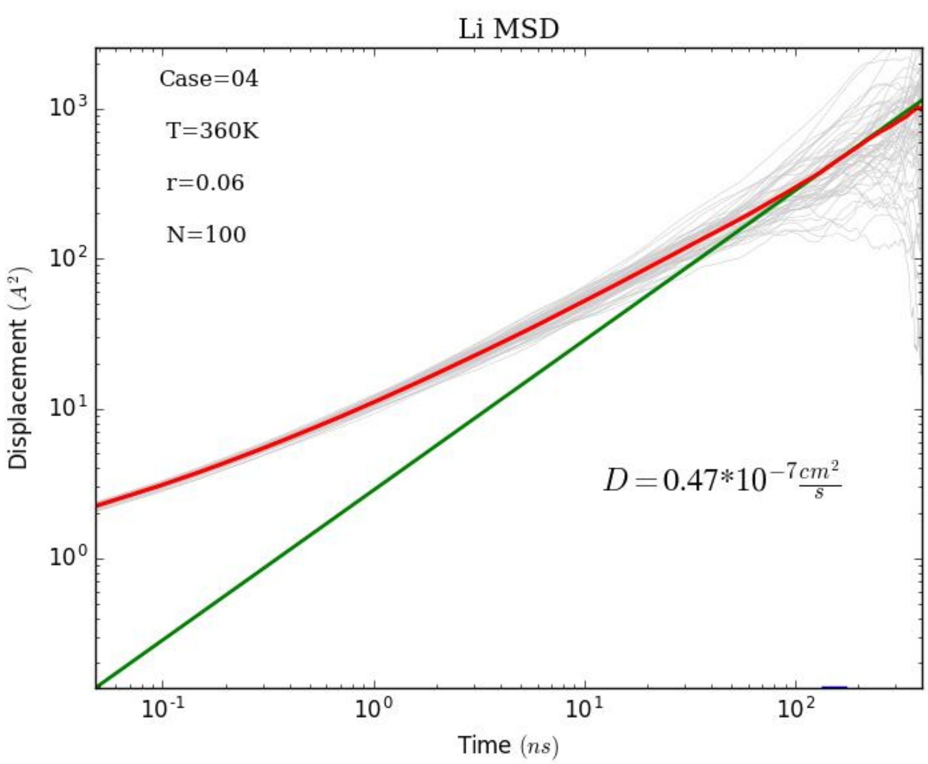
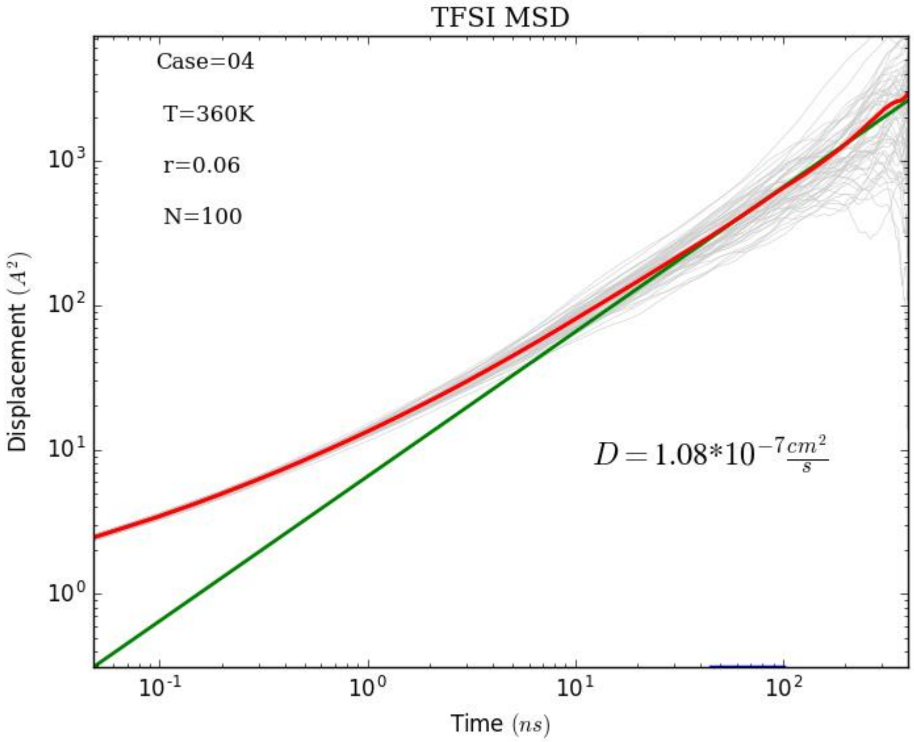
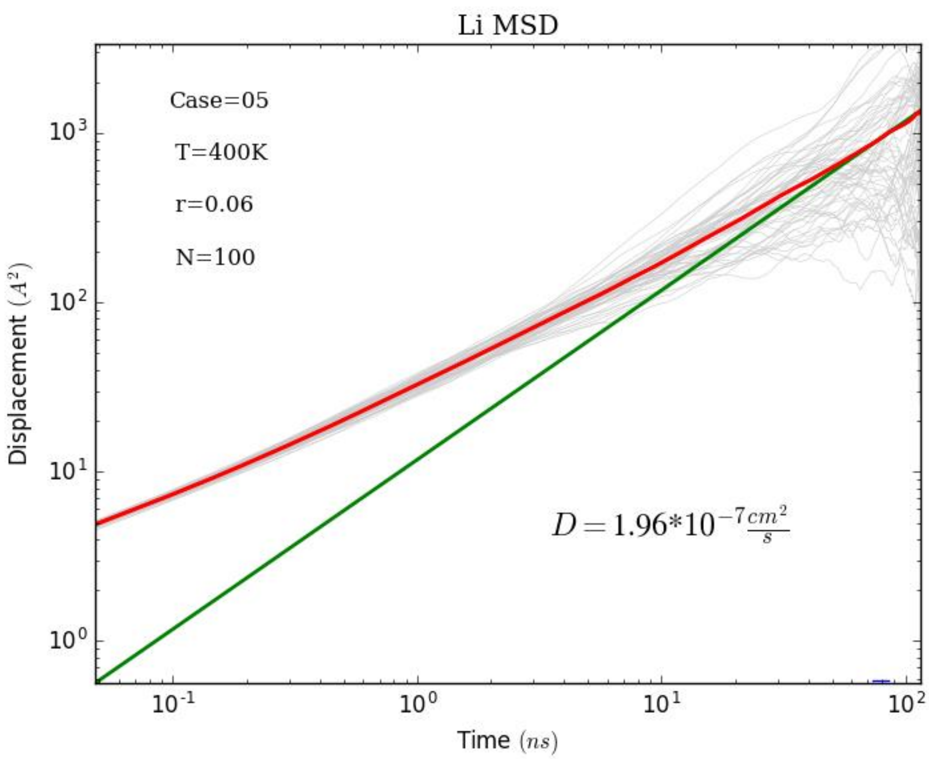
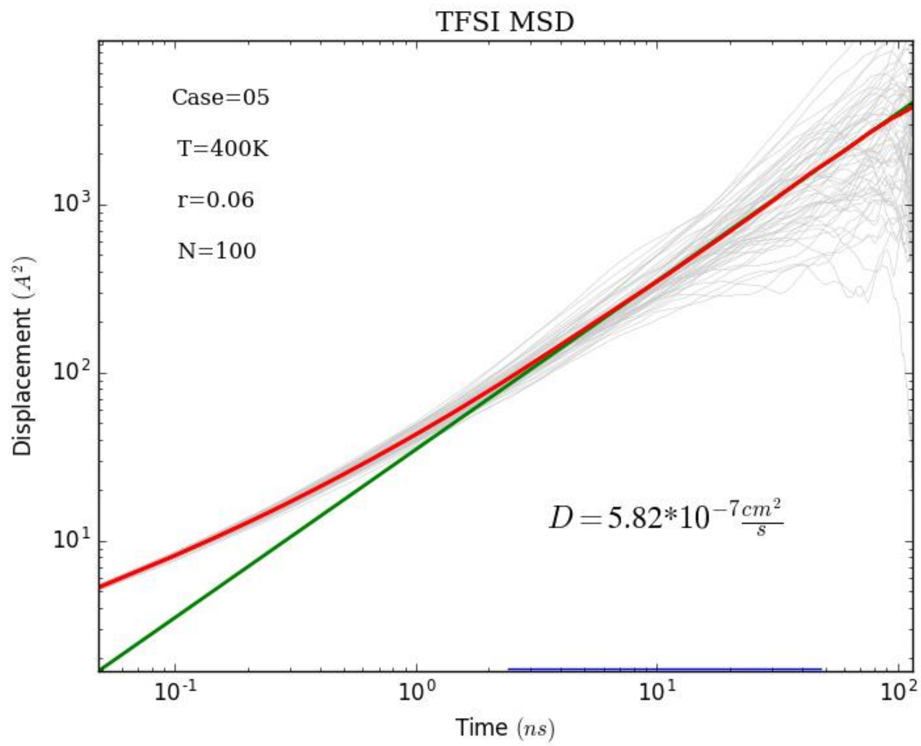
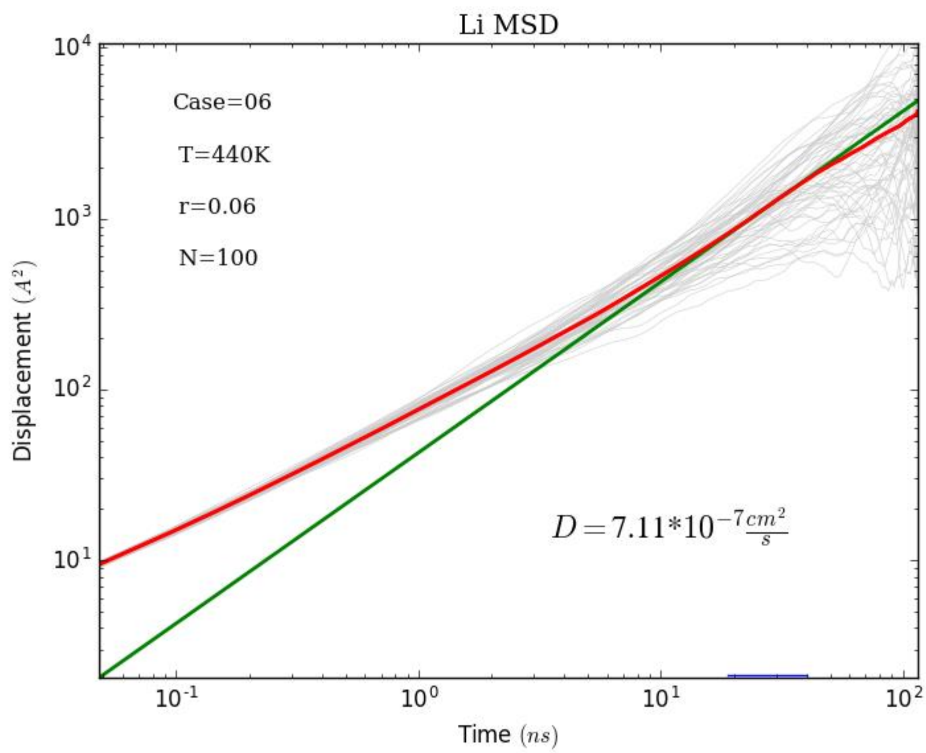
Displacement (A^2)
Time (ns)

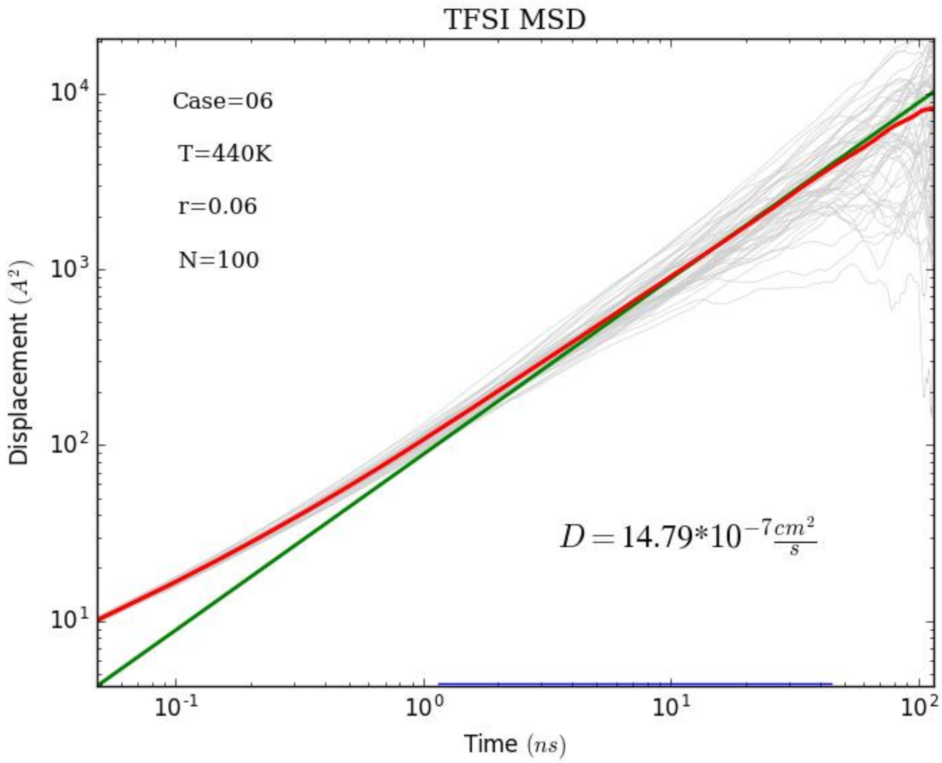

Li MSD
Case=04
T=360K
r=0.06
N=100
$D = 0.47*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

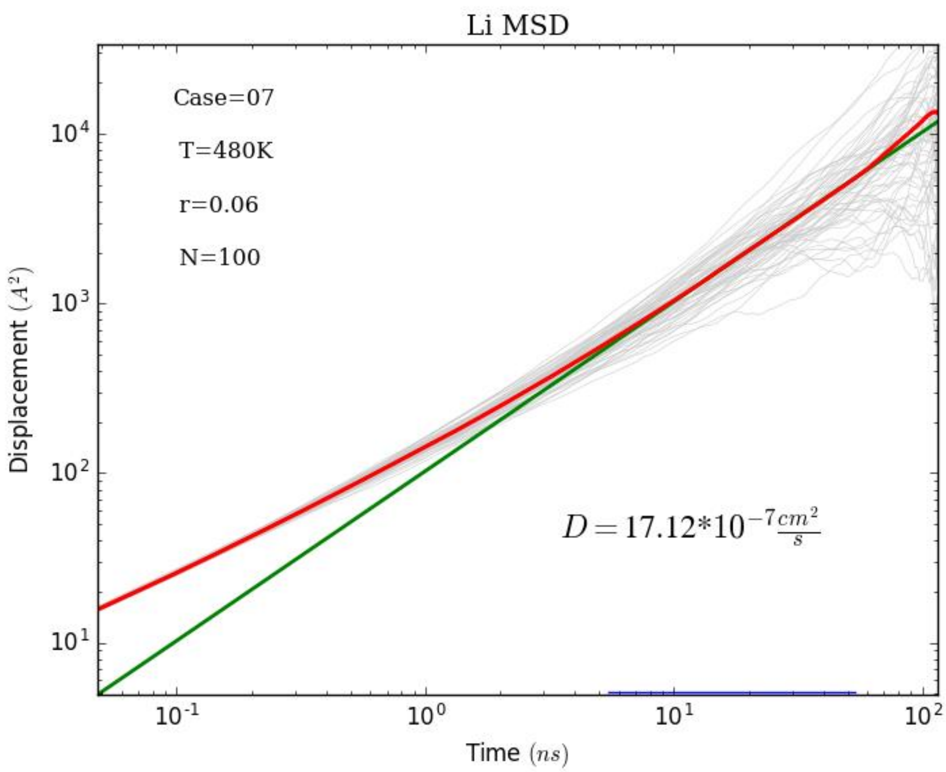

TFSI MSD
Case=04
T=360K
r=0.06
N=100
$D = 1.08*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

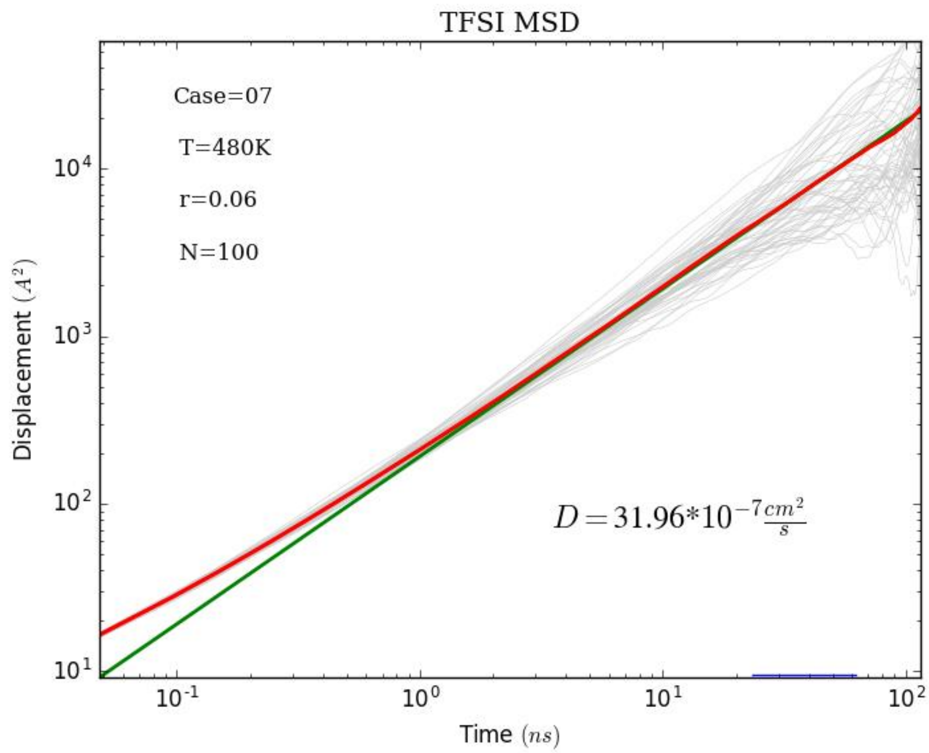

Li MSD
Case=05
T=400K
r=0.06
N=100
$D = 1.96*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

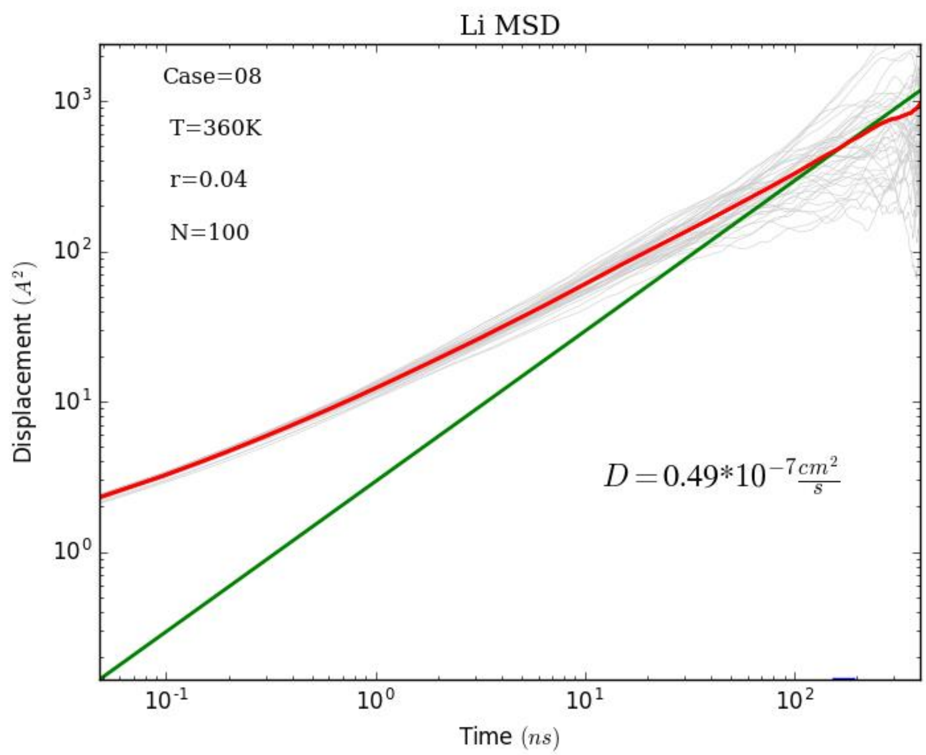

TFSI MSD
Case=05
T=400K
r=0.06
N=100
$D = 5.82*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}

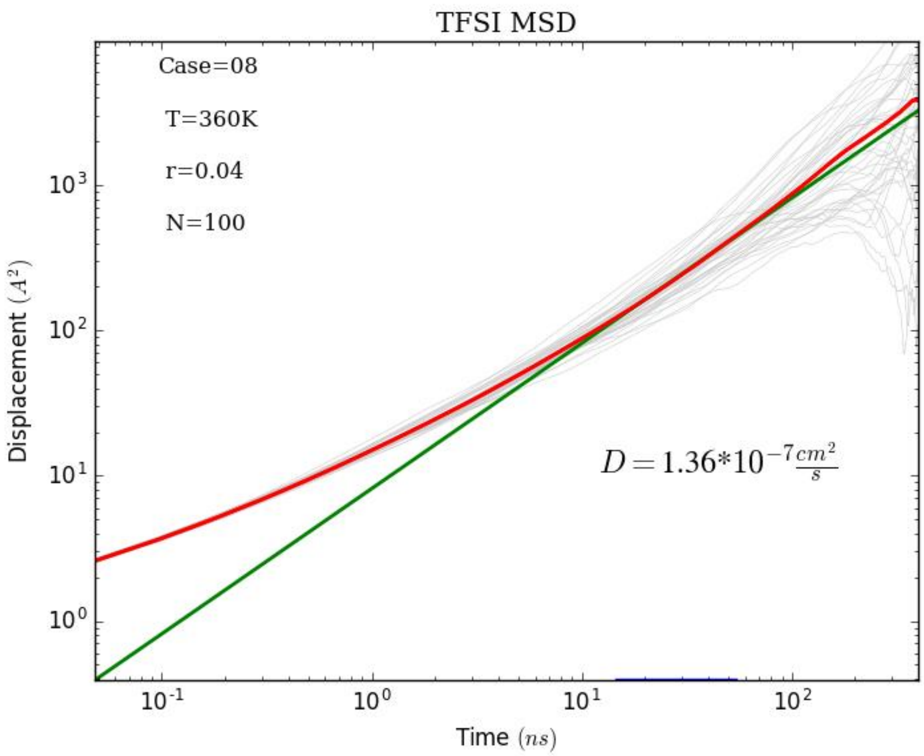

Li MSD
Case=06
T=440K
r=0.06
N=100
$D = 7.11*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}

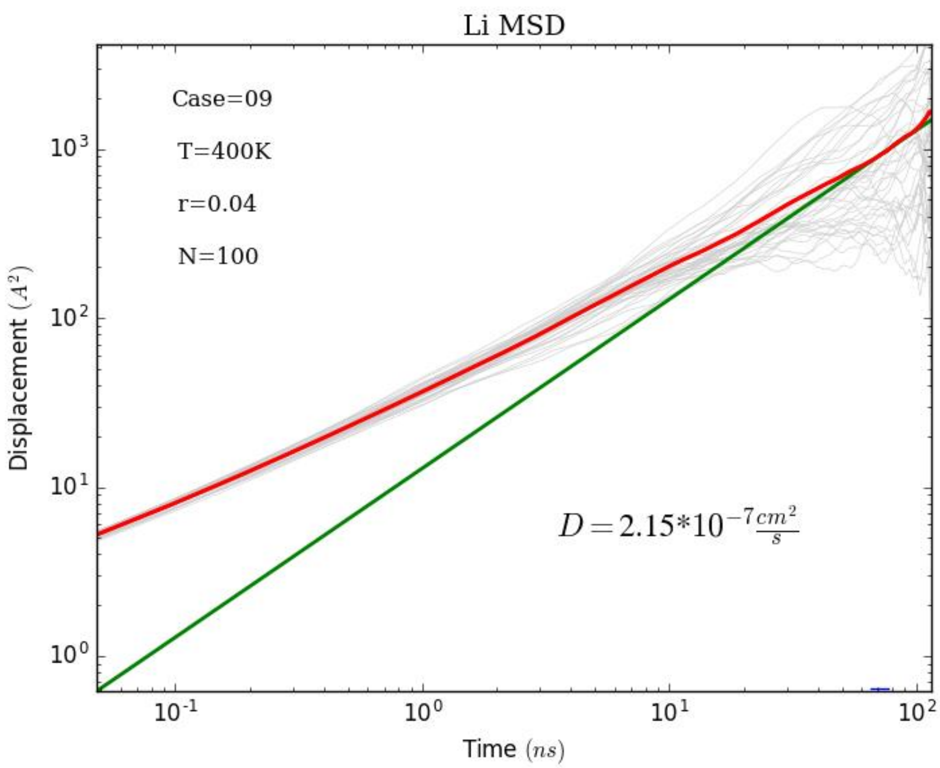

TFSI MSD
Case=06
T=440K
r=0.06
N=100
$D = 14.79*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

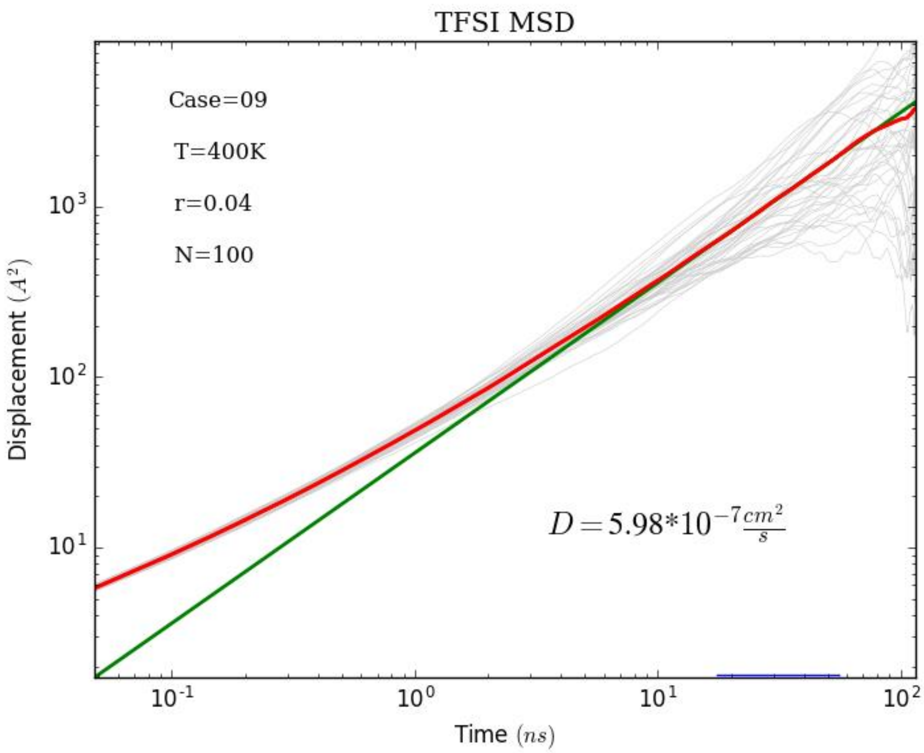

Li MSD
Case=07
T=480K
r=0.06
N=100
$D = 17.12*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

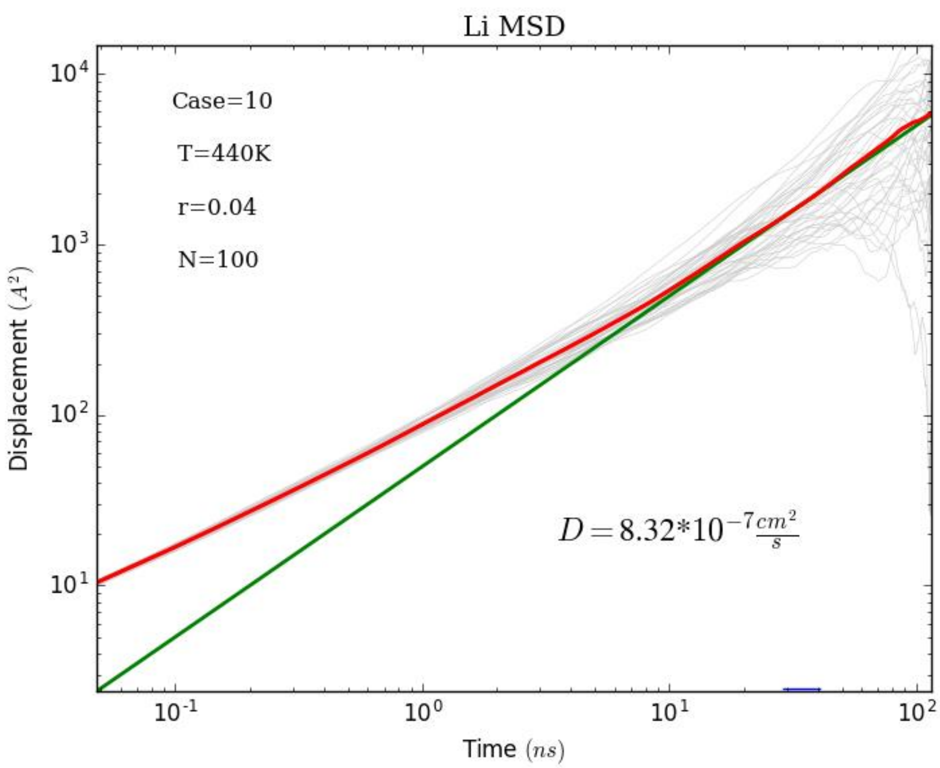

TFSI MSD
Case=07
T=480K
r=0.06
N=100
D = 31.96*10^-7 cm^2/s
Displacement (A^2)
Time (ns)
10^4
10^3
10^2
10^1
10^-1
10^0
10^1
10^2

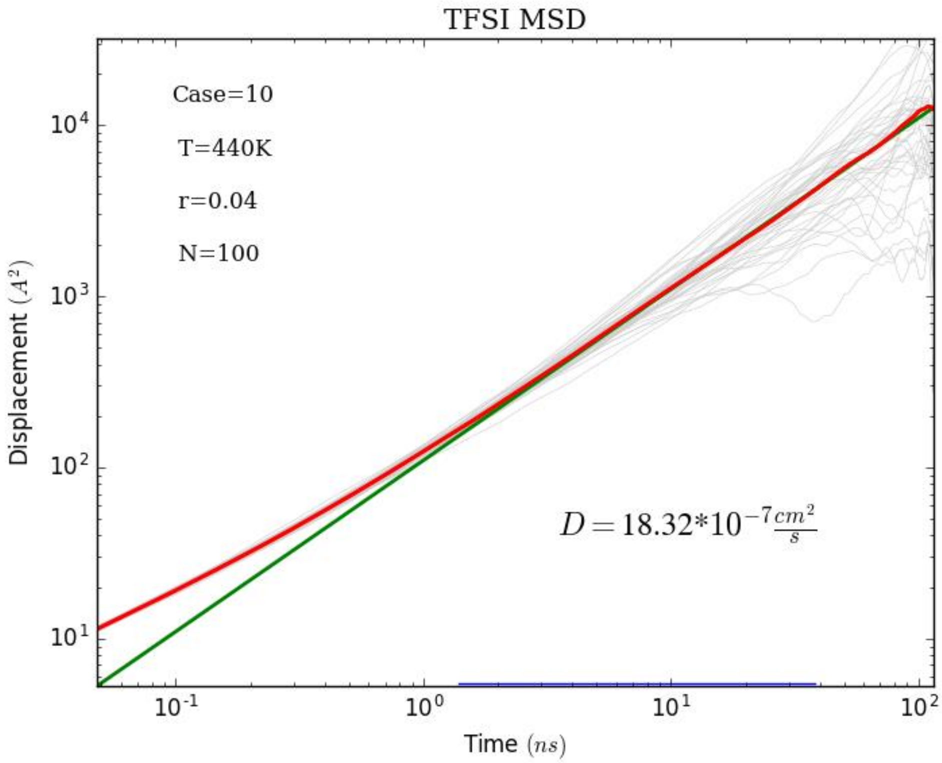

Li MSD
Case=08
T=360K
r=0.04
N=100
D = 0.49*10^-7 cm^2/s
Displacement (A^2)
Time (ns)
10^3
10^2
10^1
10^0
10^-1
10^0
10^1
10^2


TFSI MSD
Case=08
T=360K
r=0.04
N=100
$D = 1.36*10^{-7} \frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^0
10^1
10^2
10^3
10^{-1}


Li MSD
Case=09
T=400K
r=0.04
N=100
$D = 2.15*10^{-7} \frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^0
10^1
10^2
10^3
10^{-1}


TFSI MSD
Case=09
T=400K
r=0.04
N=100
Displacement (A^2)
10^3
10^2
10^1
$D = 5.98*10^{-7}\frac{cm^2}{s}$
10^{-1}
10^0
10^1
10^2
Time (ns)


Li MSD
Case=10
T=440K
r=0.04
N=100
Displacement (A^2)
10^4
10^3
10^2
10^1
$D = 8.32*10^{-7}\frac{cm^2}{s}$
10^{-1}
10^0
10^1
10^2
Time (ns)


TFSI MSD
Case=10
T=440K
r=0.04
N=100
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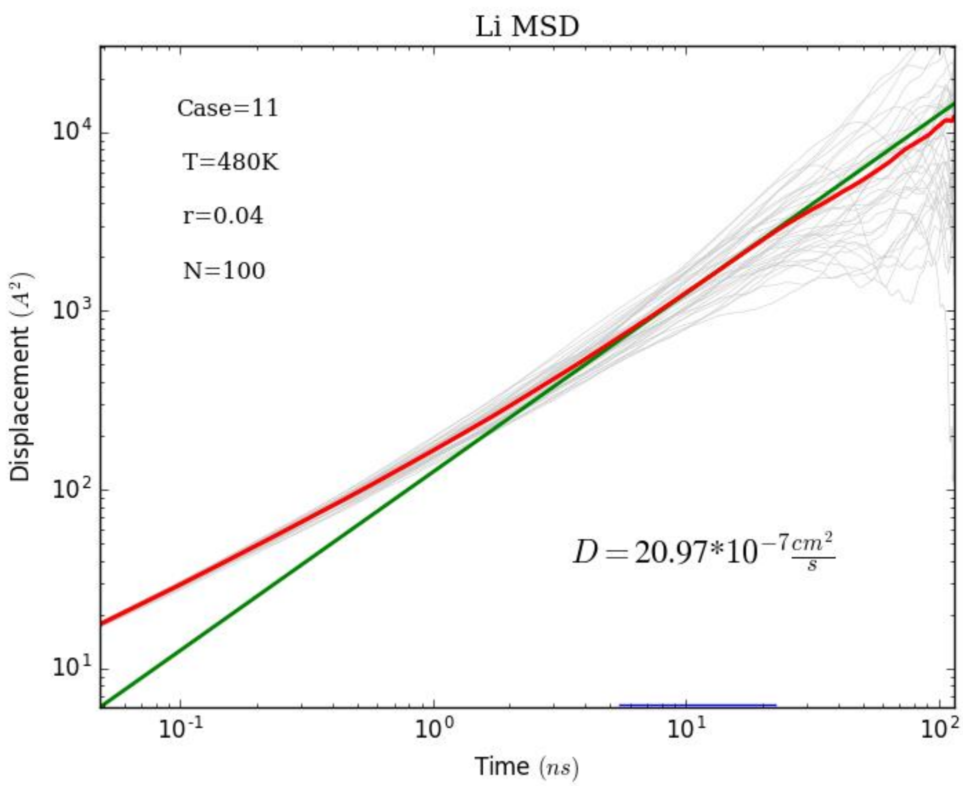
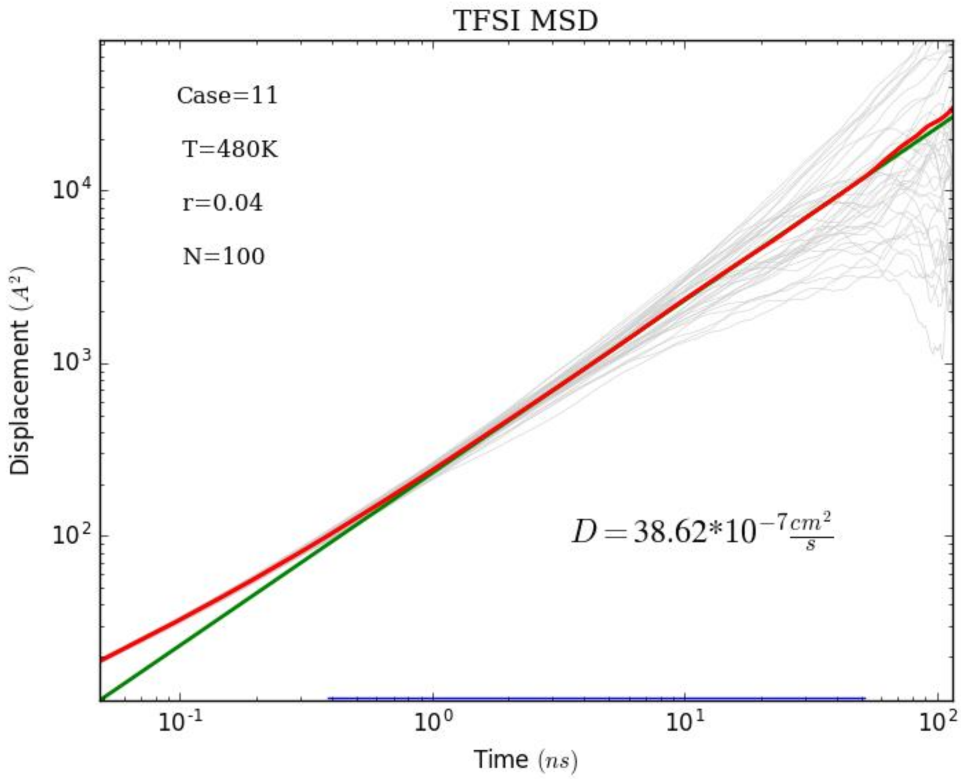
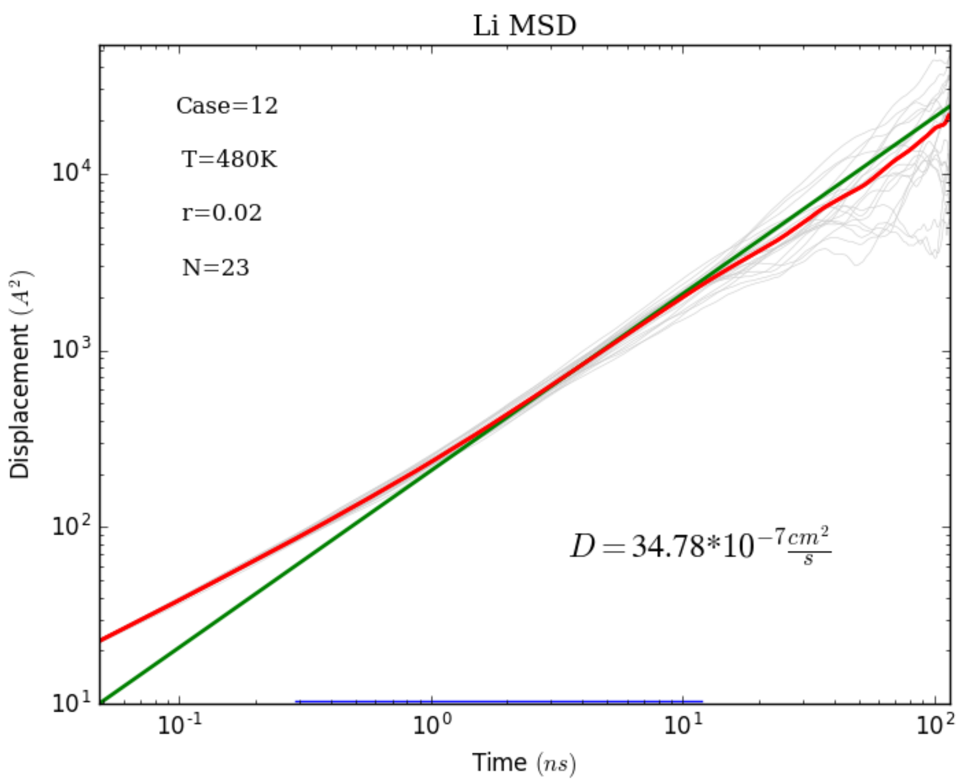
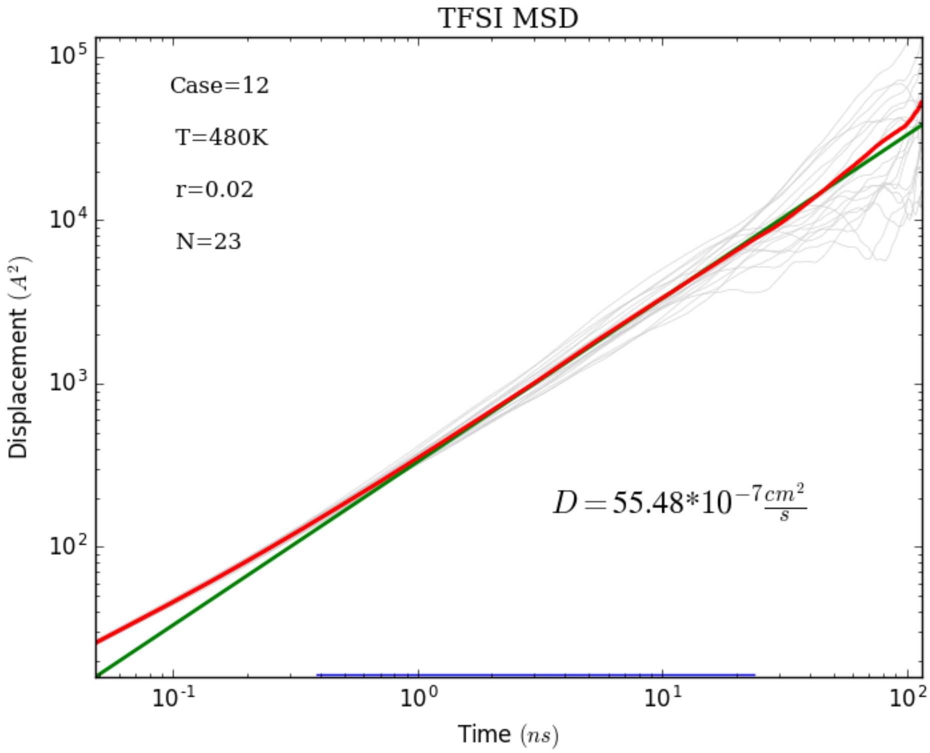
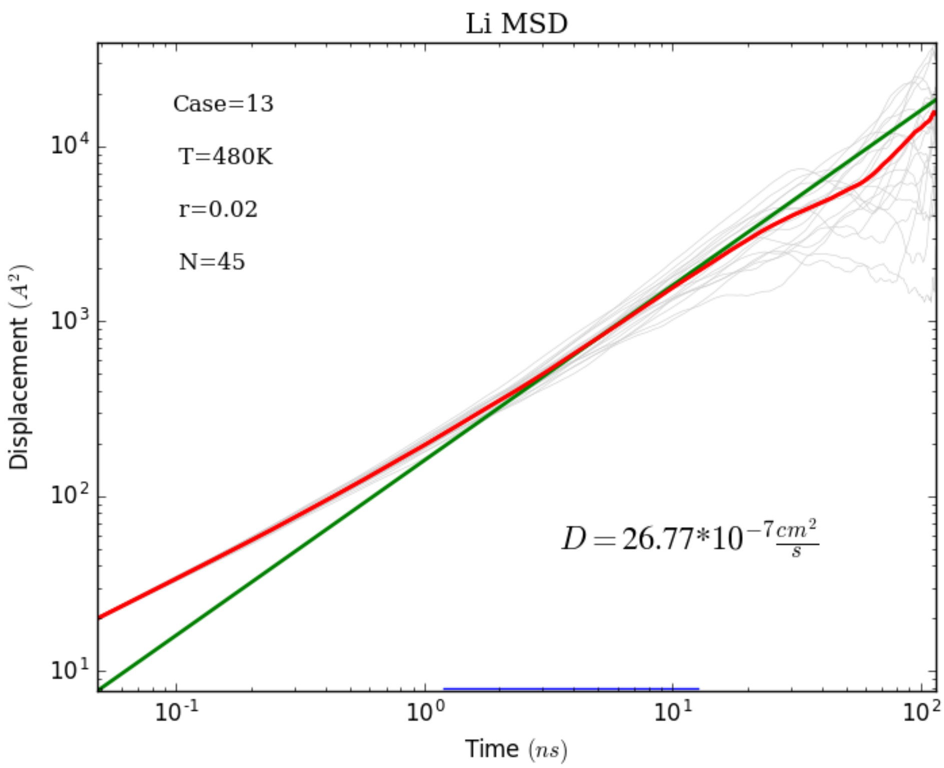
Displacement (A^2)
Time (ns)


Li MSD
Case=11
T=480K
r=0.04
N=100
$D=20.97*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)


TFSI MSD
Case=11
T=480K
r=0.04
N=100
$D = 38.62*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
10^2
10^3
10^4
Time (ns)
10^{-1}
10^0
10^1
10^2


Li MSD
Case=12
T=480K
r=0.02
N=23
$D = 34.78*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
10^1
10^2
10^3
10^4
Time (ns)
10^{-1}
10^0
10^1
10^2


TFSI MSD
Case=12
T=480K
r=0.02
N=23
$D = 55.48*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^{-1}
10^{0}
10^{1}
10^{2}
10^{2}
10^{3}
10^{4}
10^{5}


Li MSD
Case=13
T=480K
r=0.02
N=45
$D = 26.77*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^{-1}
10^{0}
10^{1}
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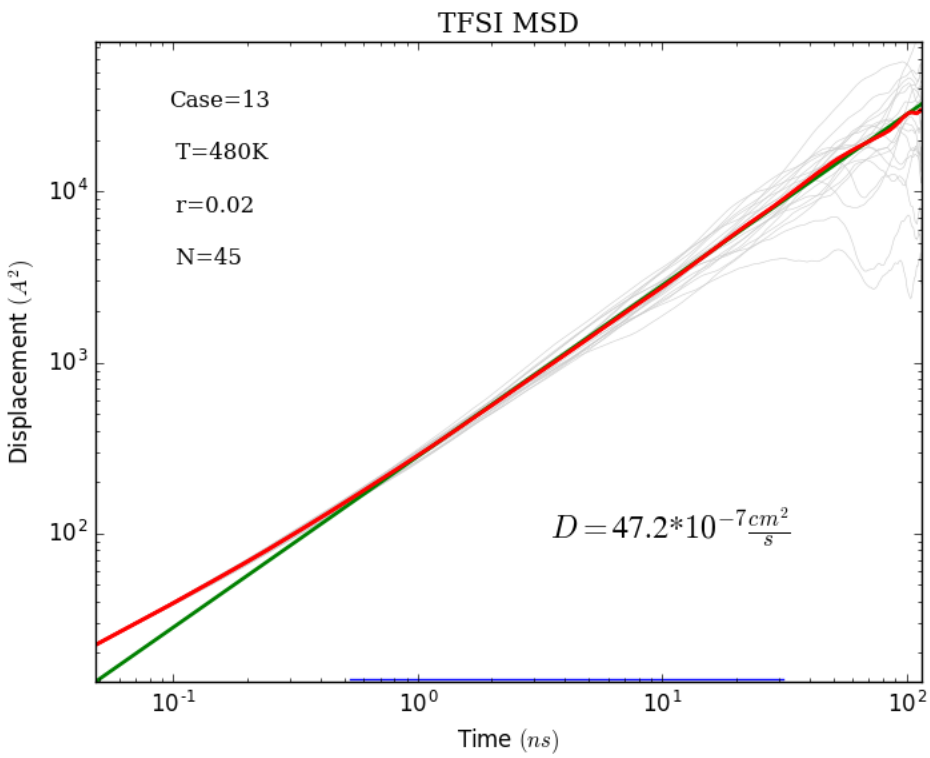
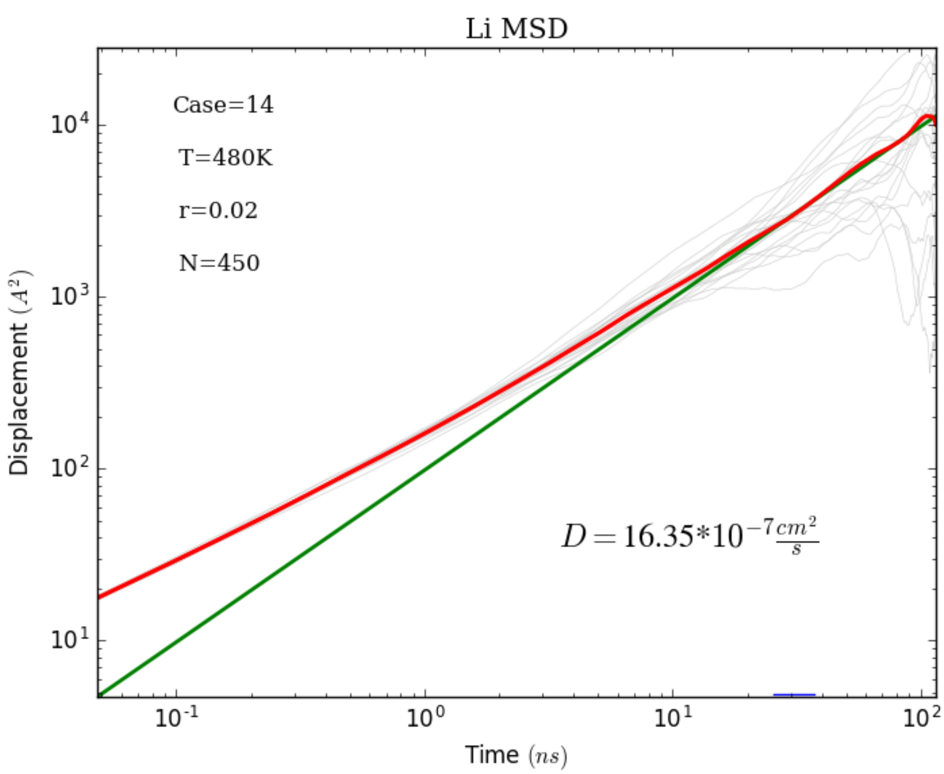
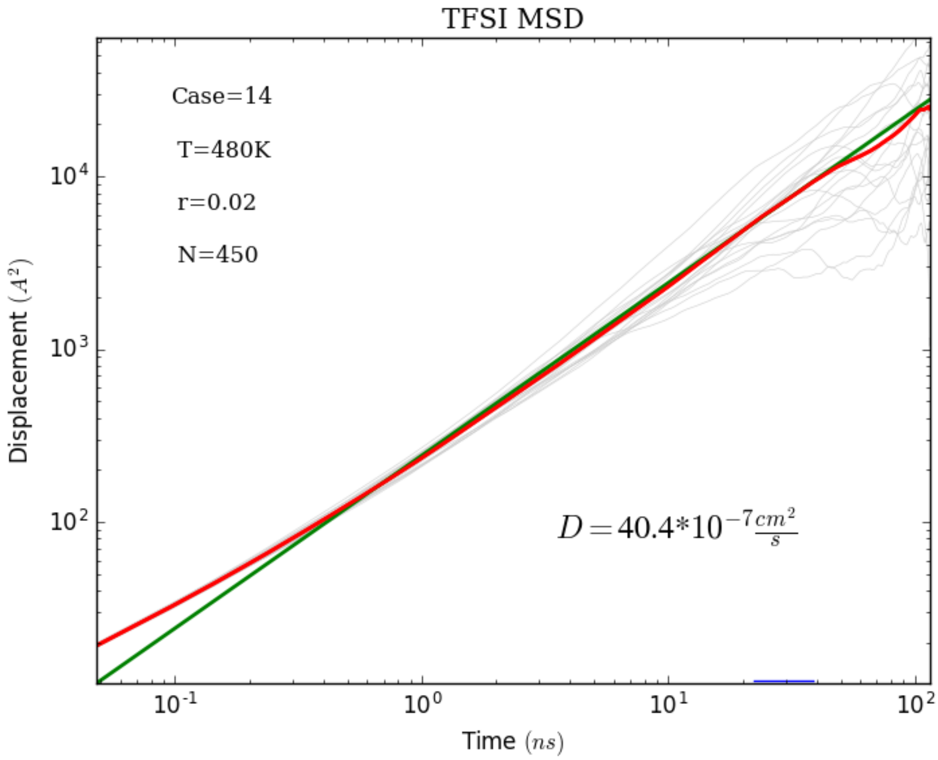
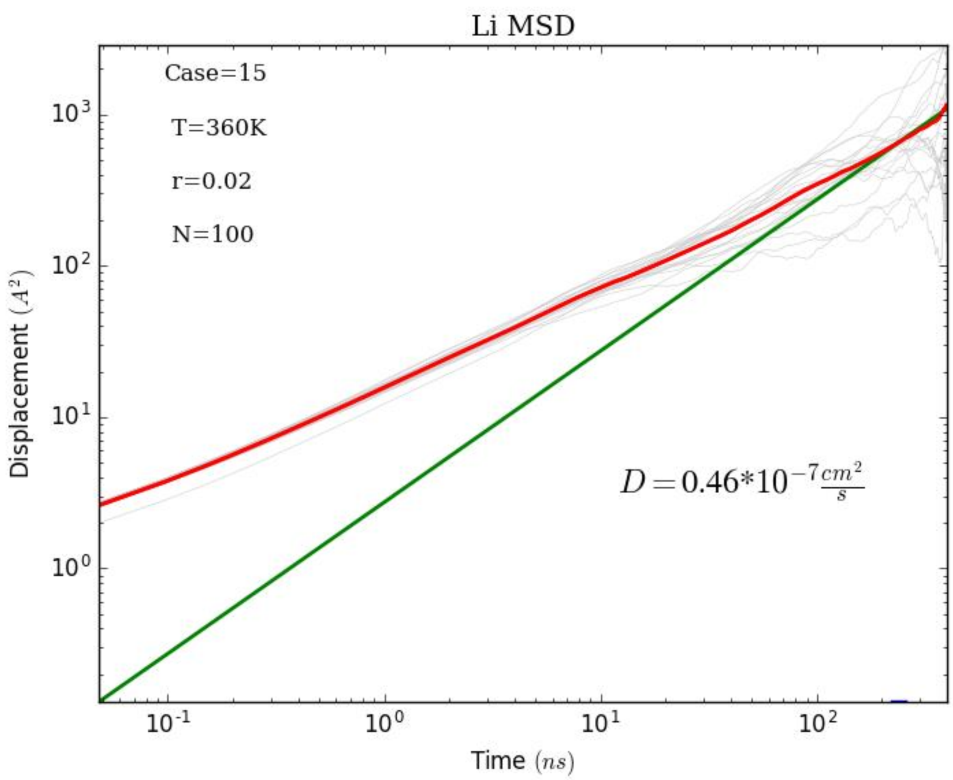
10^{1}
10^{2}
10^{3}
10^{4}


TFSI MSD
Case=13
T=480K
r=0.02
N=45
$D = 47.2*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

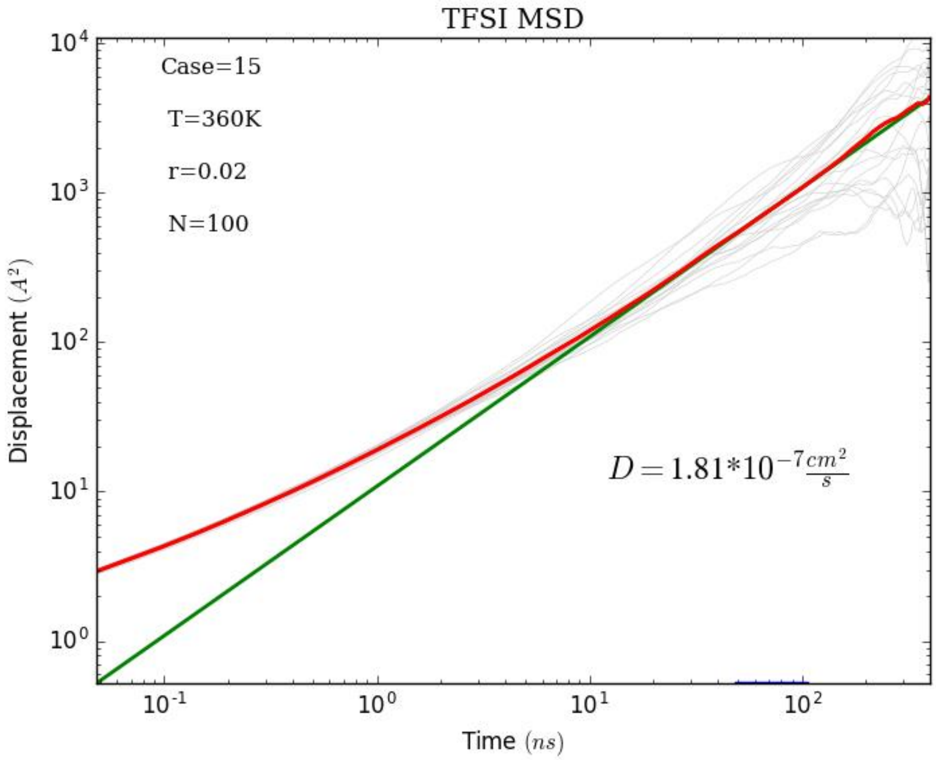

Li MSD
Case=14
T=480K
r=0.02
N=450
$D = 16.35*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

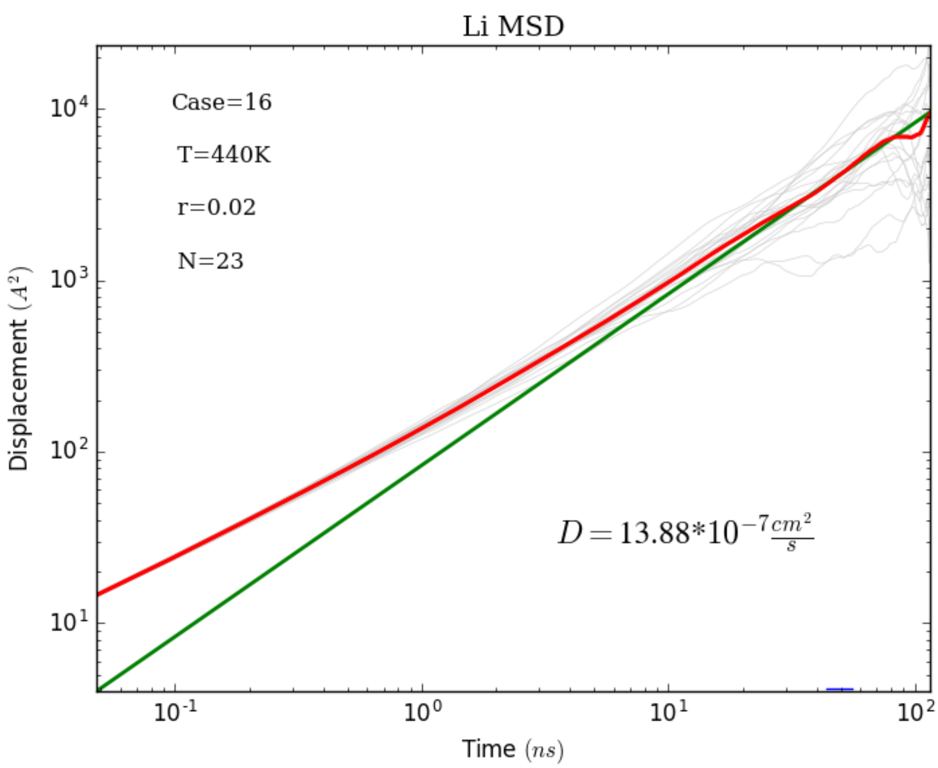


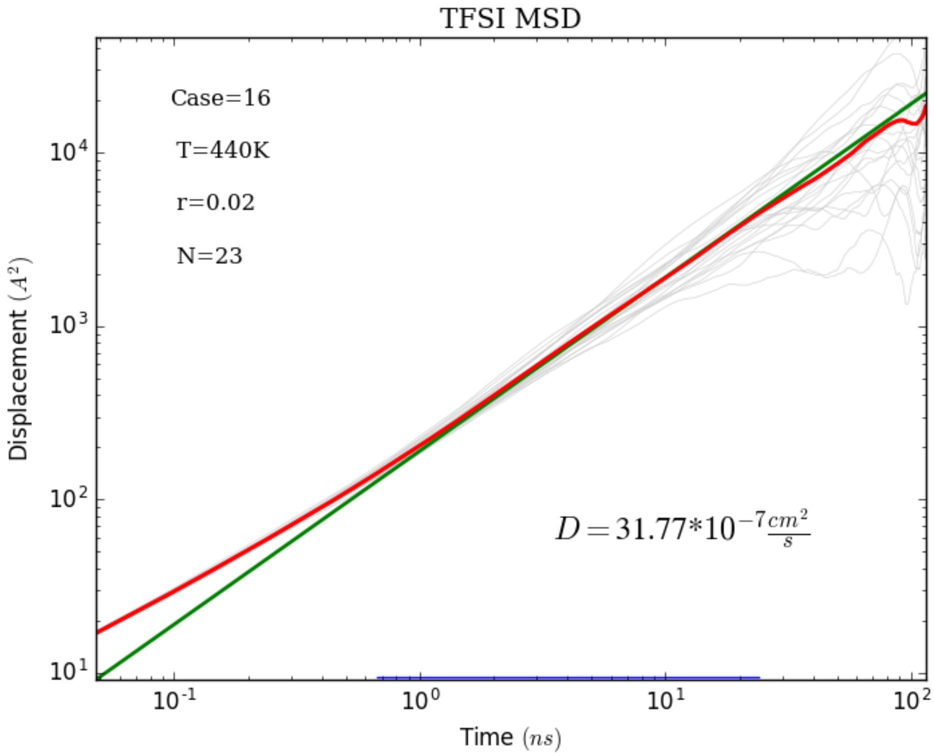
TFSI MSD
Case=14
T=480K
r=0.02
N=450
$D = 40.4*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

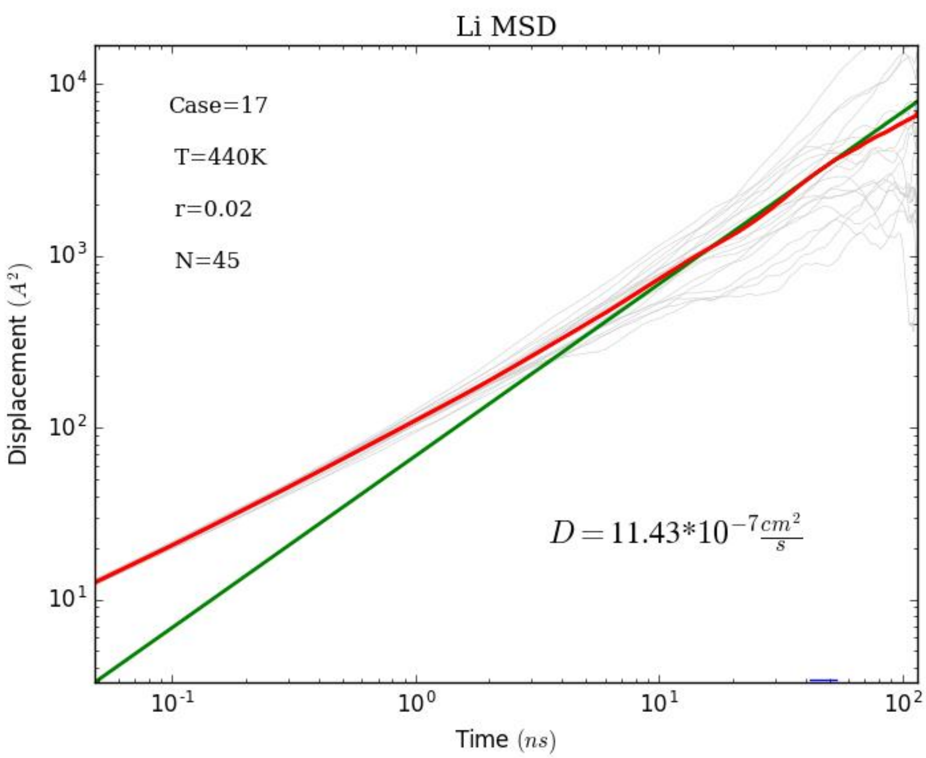


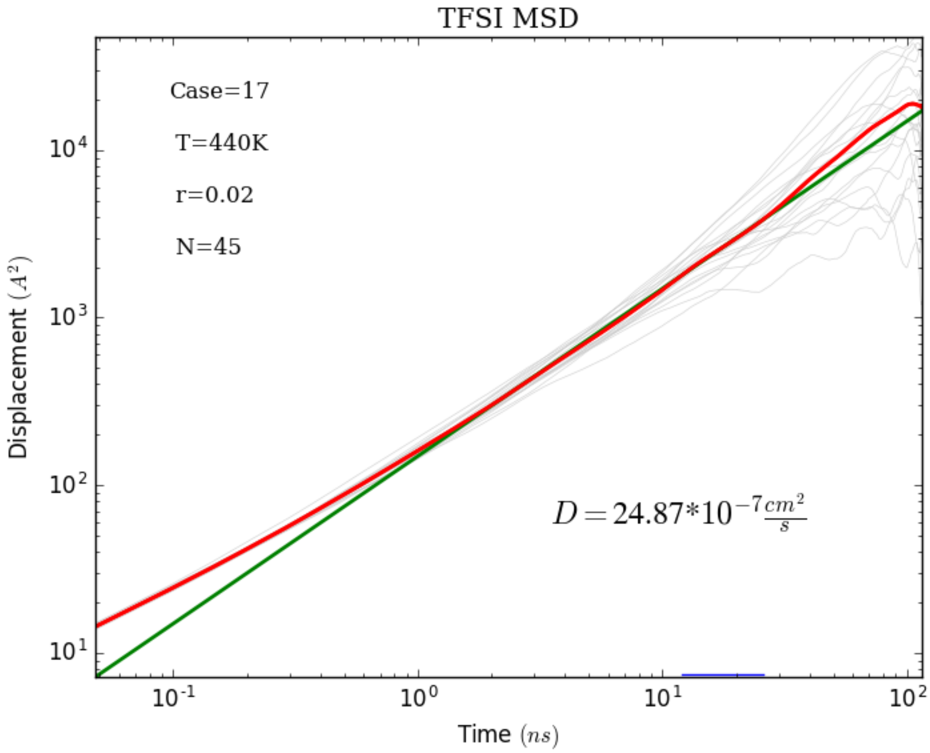
Li MSD
Case=15
T=360K
r=0.02
N=100
$D = 0.46*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

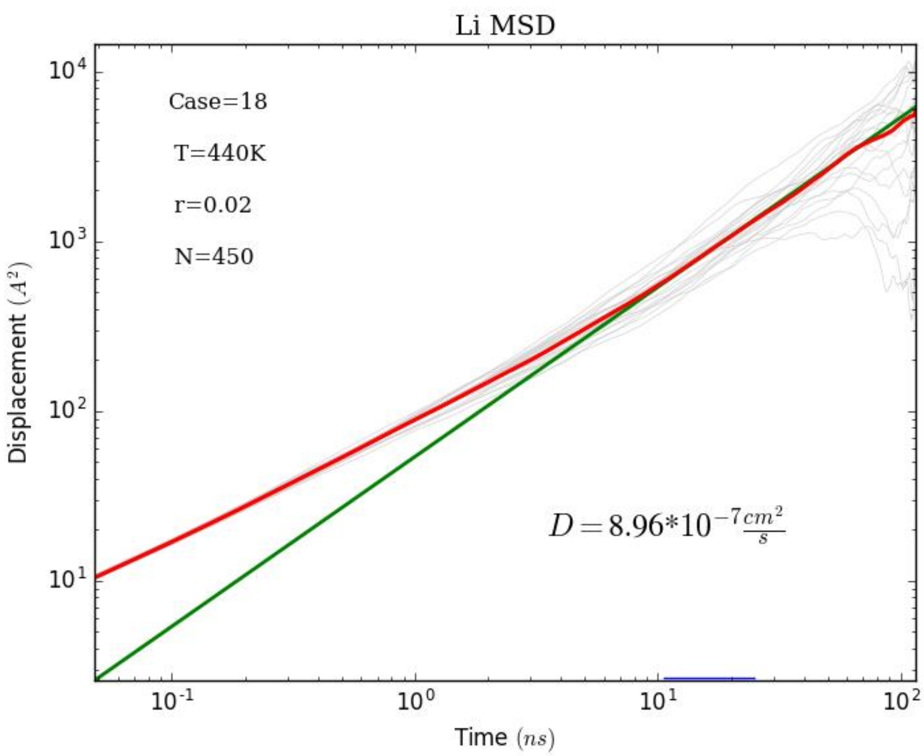

TFSI MSD
Case=15
T=360K
r=0.02
N=100
$D = 1.81*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

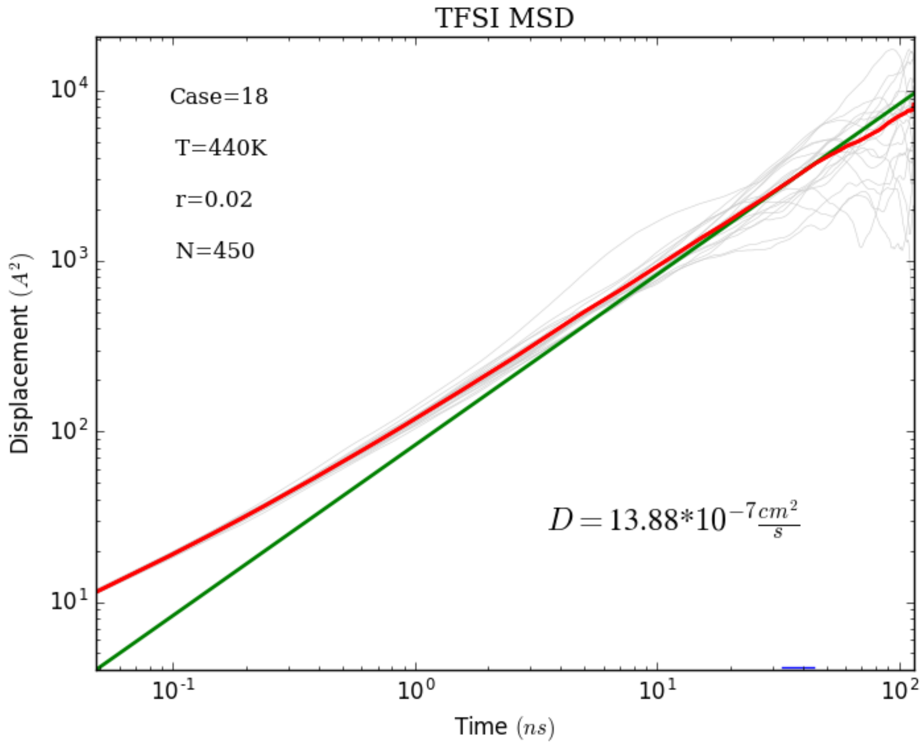

Li MSD
Case=16
T=440K
r=0.02
N=23
$D = 13.88*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

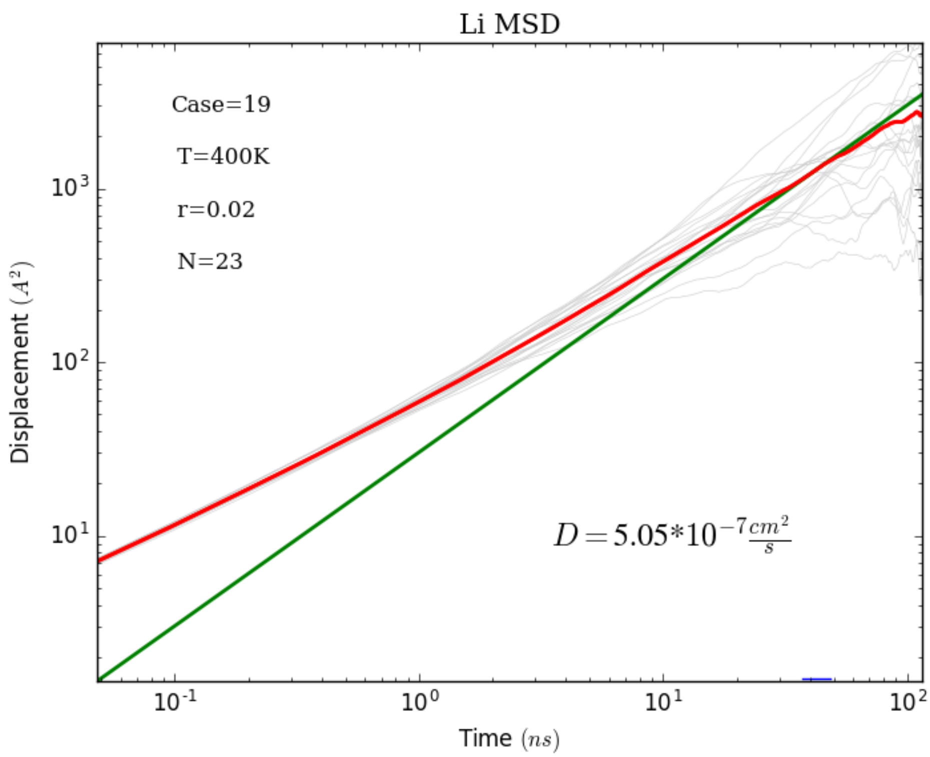

TFSI MSD
Case=16
T=440K
r=0.02
N=23
$D = 31.77 * 10^{-7} \frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^1
10^2
10^3
10^4
10^{-1}
10^0
10^1
10^2

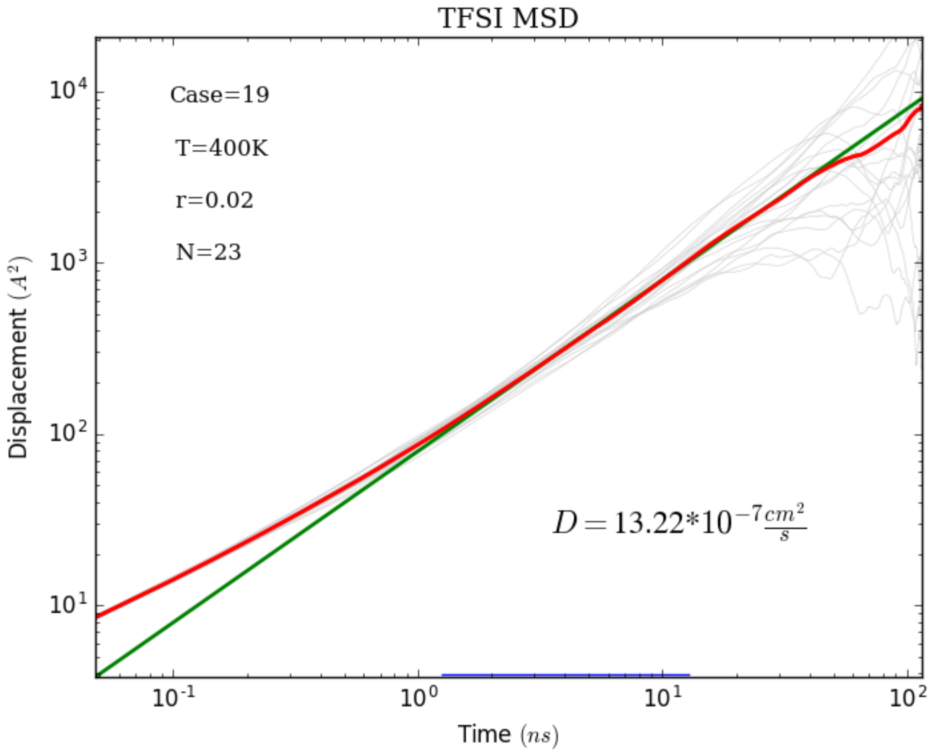

Li MSD
Case=17
T=440K
r=0.02
N=45
$D = 11.43 * 10^{-7} \frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^1
10^2
10^3
10^4
10^{-1}
10^0
10^1
10^2

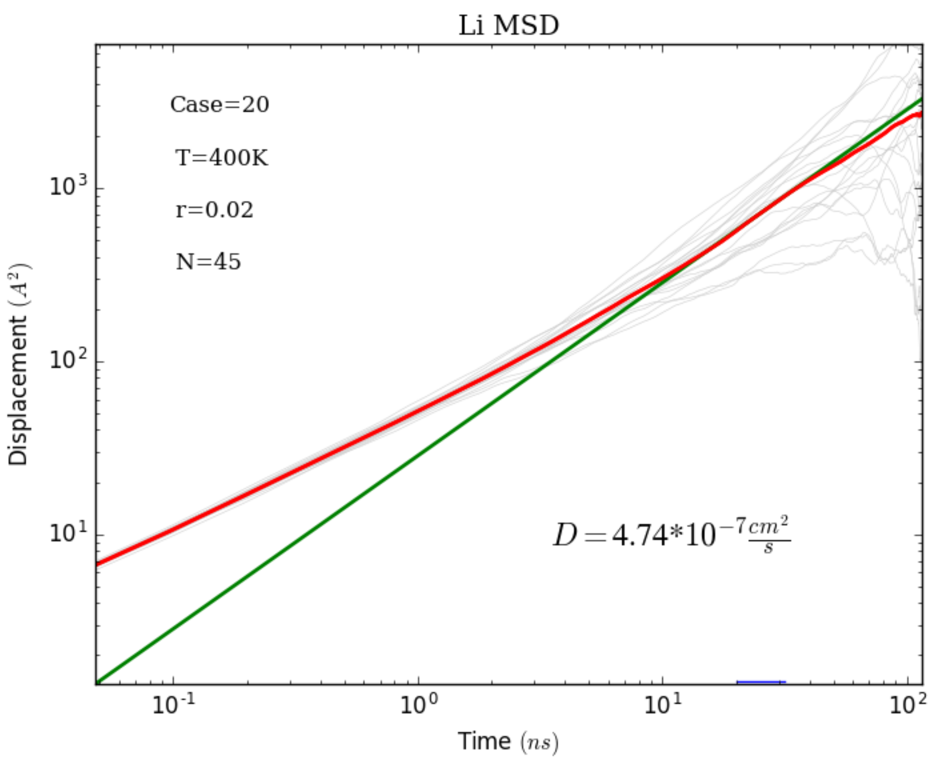

TFSI MSD
Case=17
T=440K
r=0.02
N=45
$D = 24.87*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

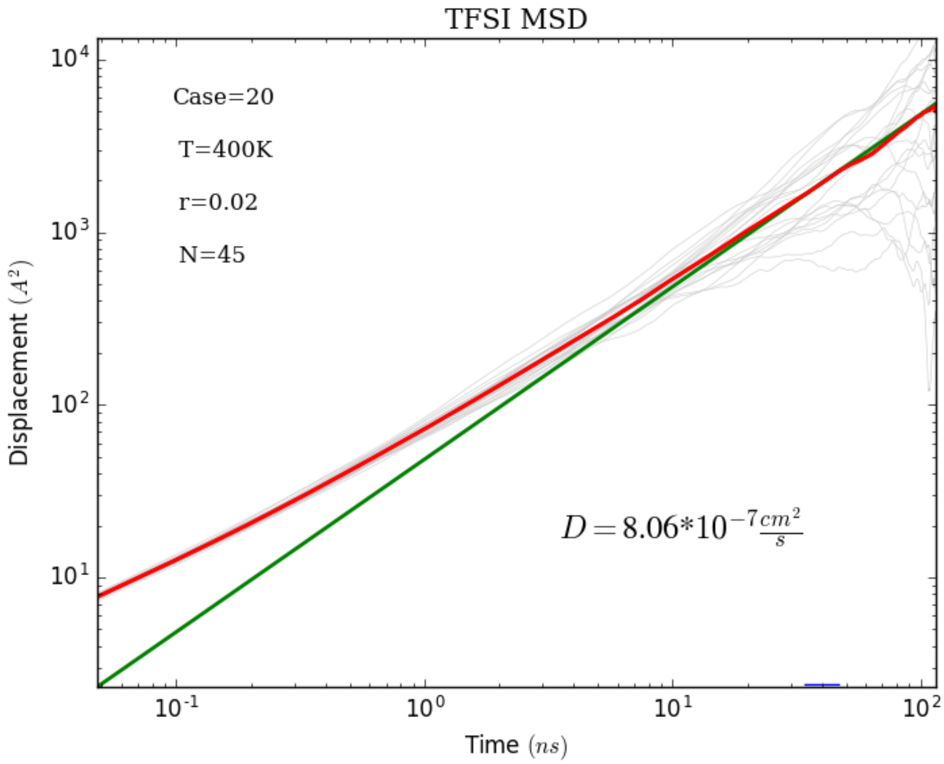

Li MSD
Case=18
T=440K
r=0.02
N=450
$D = 8.96*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

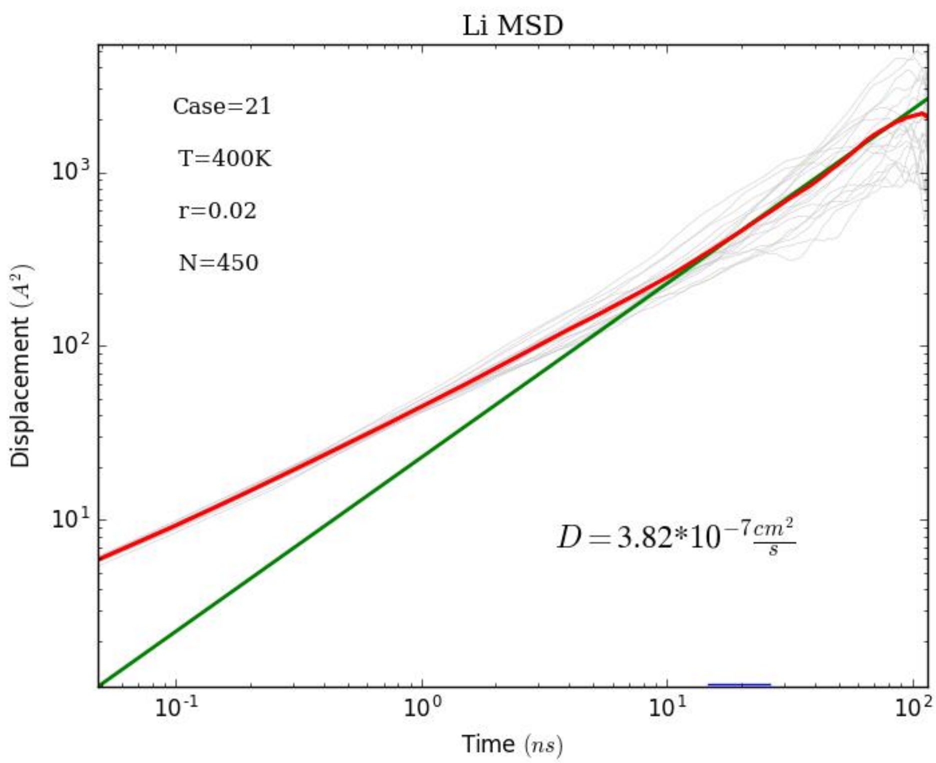

TFSI MSD
Case=18
T=440K
r=0.02
N=450
$D = 13.88*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

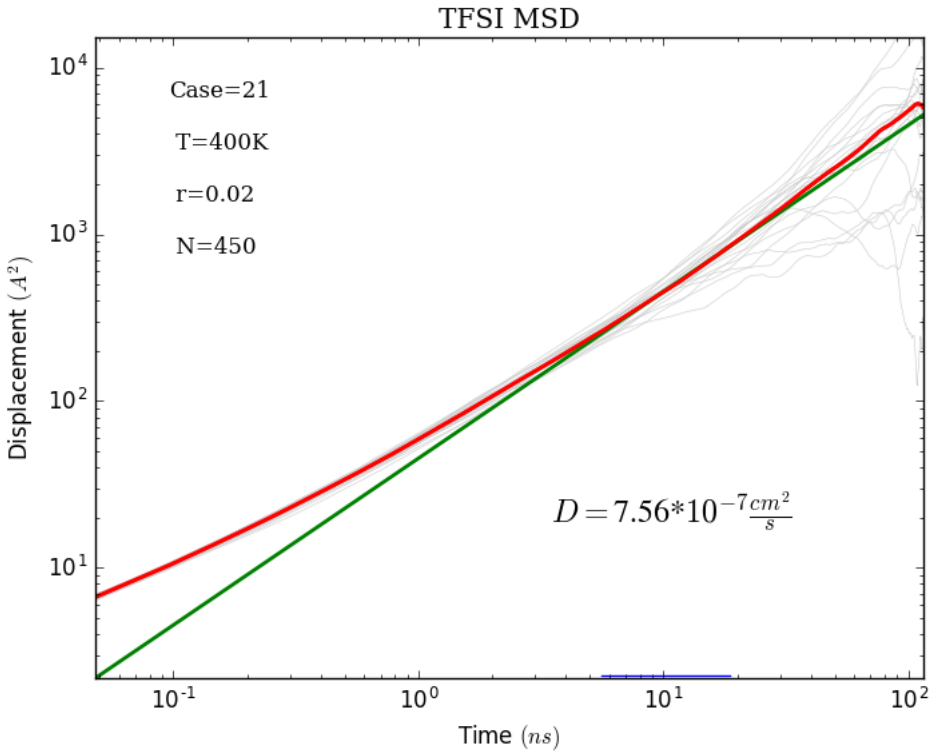

Li MSD
Case=19
T=400K
r=0.02
N=23
$D = 5.05*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

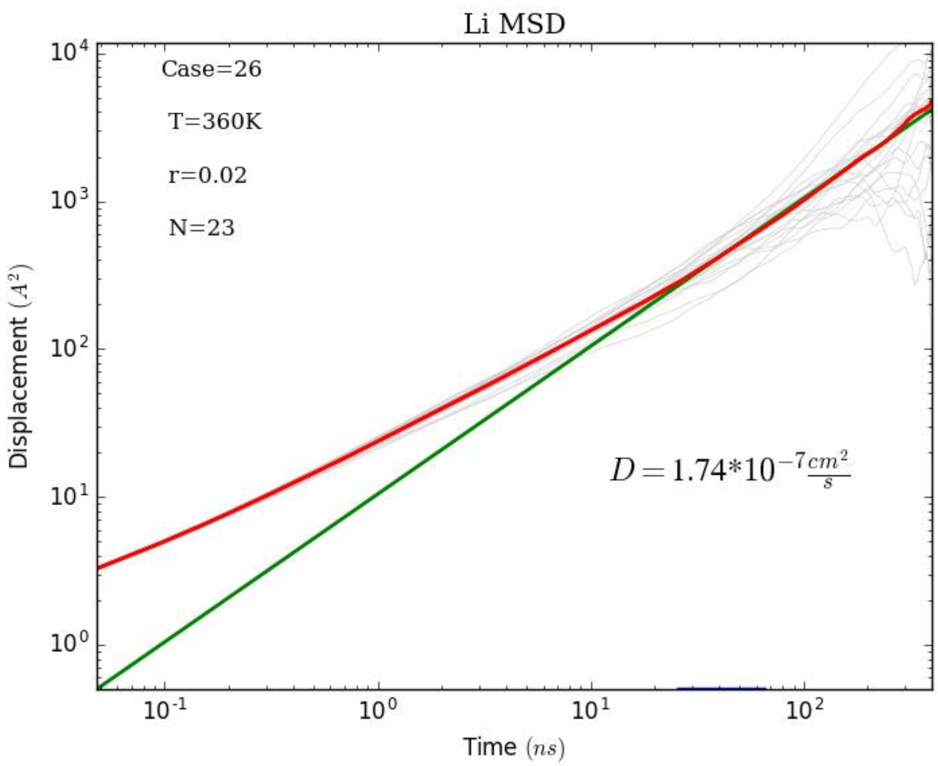

TFSI MSD
Case=19
T=400K
r=0.02
N=23
$D = 13.22*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

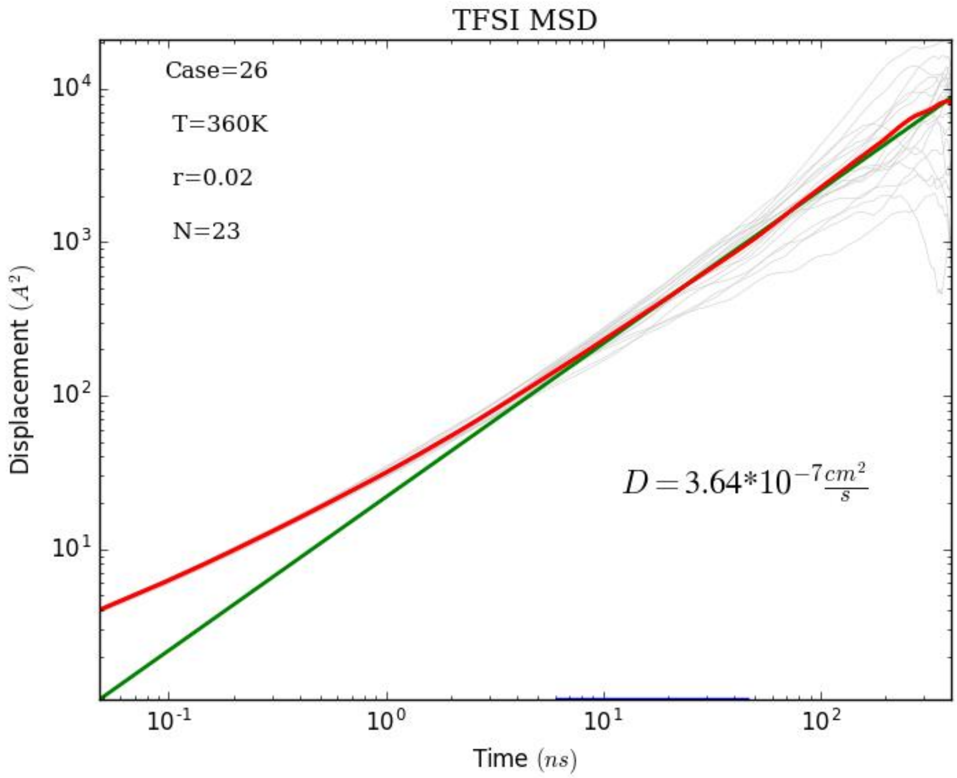

Li MSD
Case=20
T=400K
r=0.02
N=45
$D = 4.74*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)


TFSI MSD
Case=20
T=400K
r=0.02
N=45
$D = 8.06*10^{-7} \frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

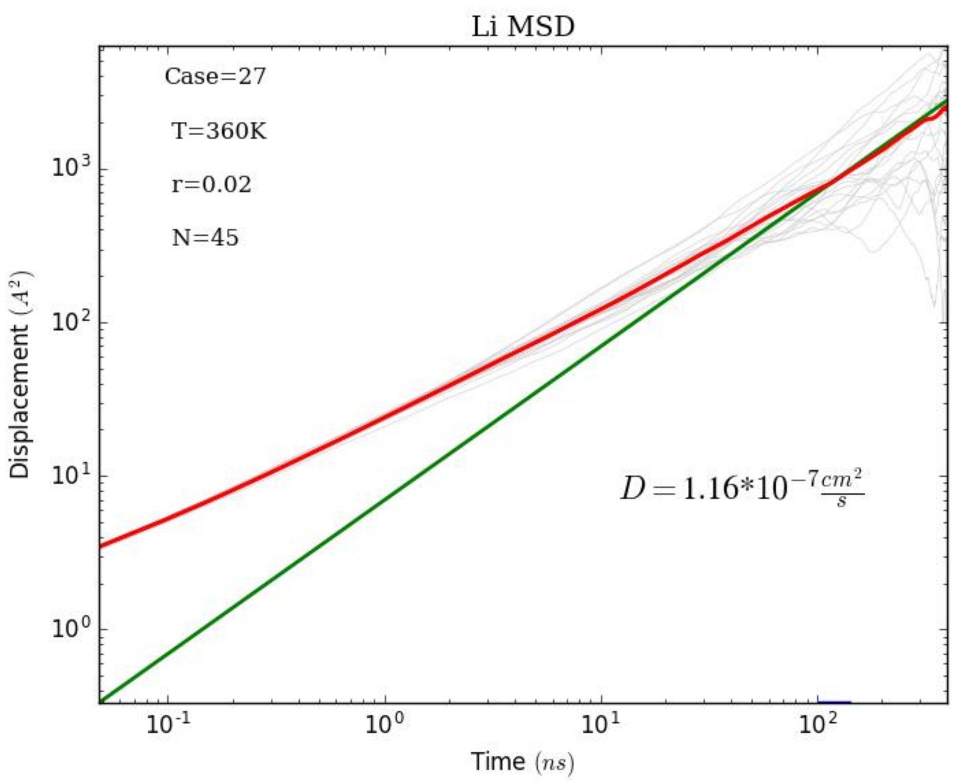

Li MSD
Case=21
T=400K
r=0.02
N=450
$D = 3.82*10^{-7} \frac{cm^2}{s}$
Displacement (A^2)
Time (ns)


TFSI MSD
Case=21
T=400K
r=0.02
N=450
$D = 7.56*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^4
10^3
10^2
10^1
10^{-1}
10^0
10^1
10^2

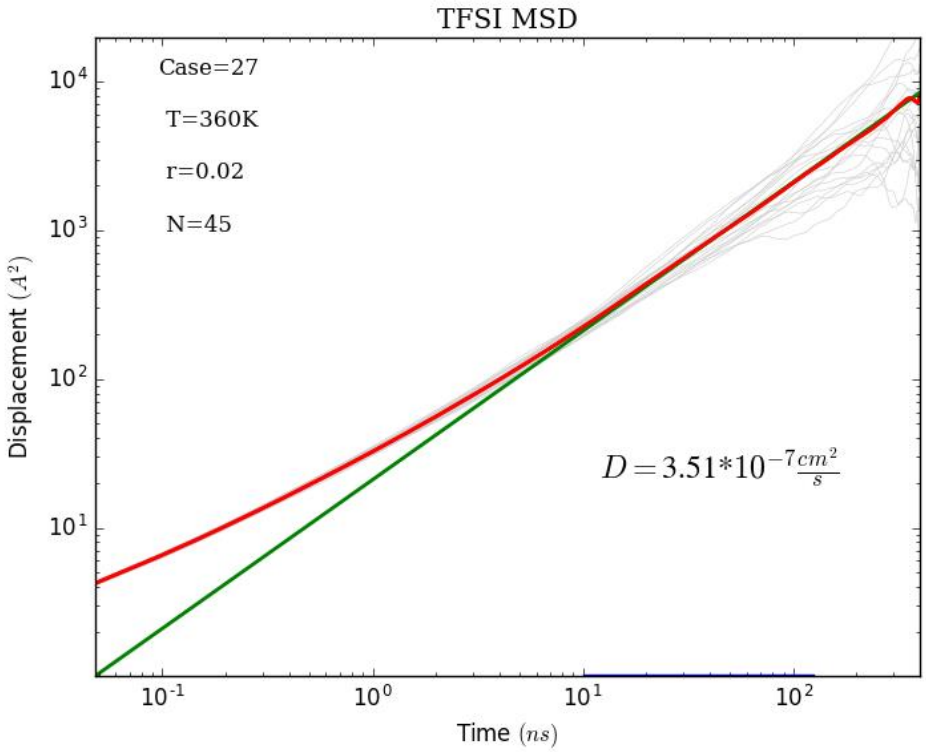

Li MSD
Case=26
T=360K
r=0.02
N=23
$D = 1.74*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^0
10^1
10^2

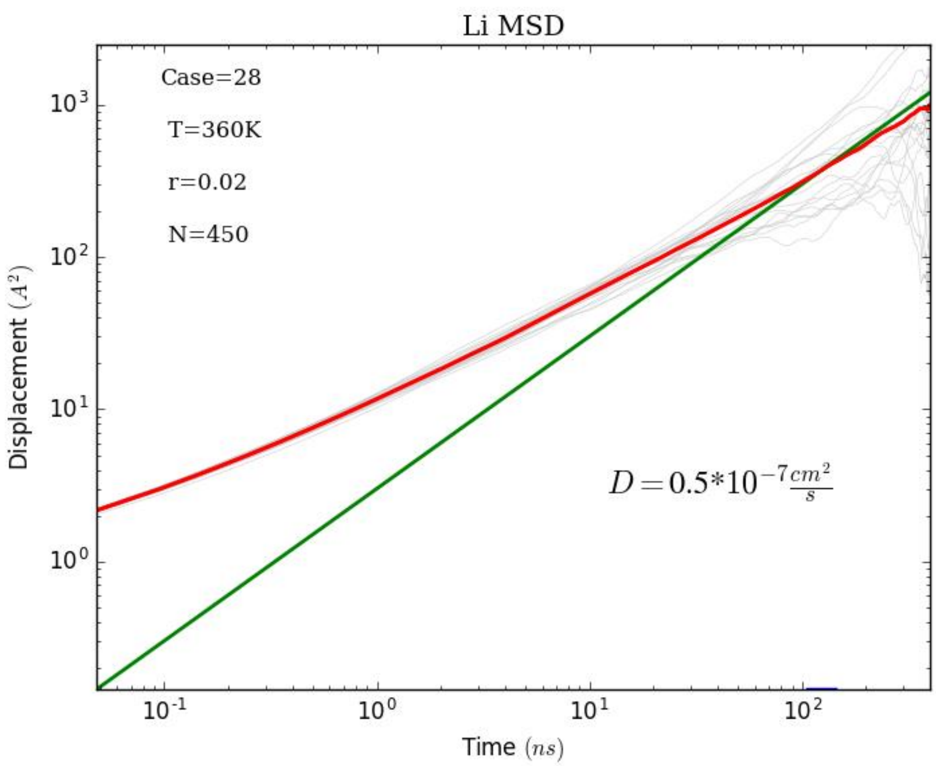


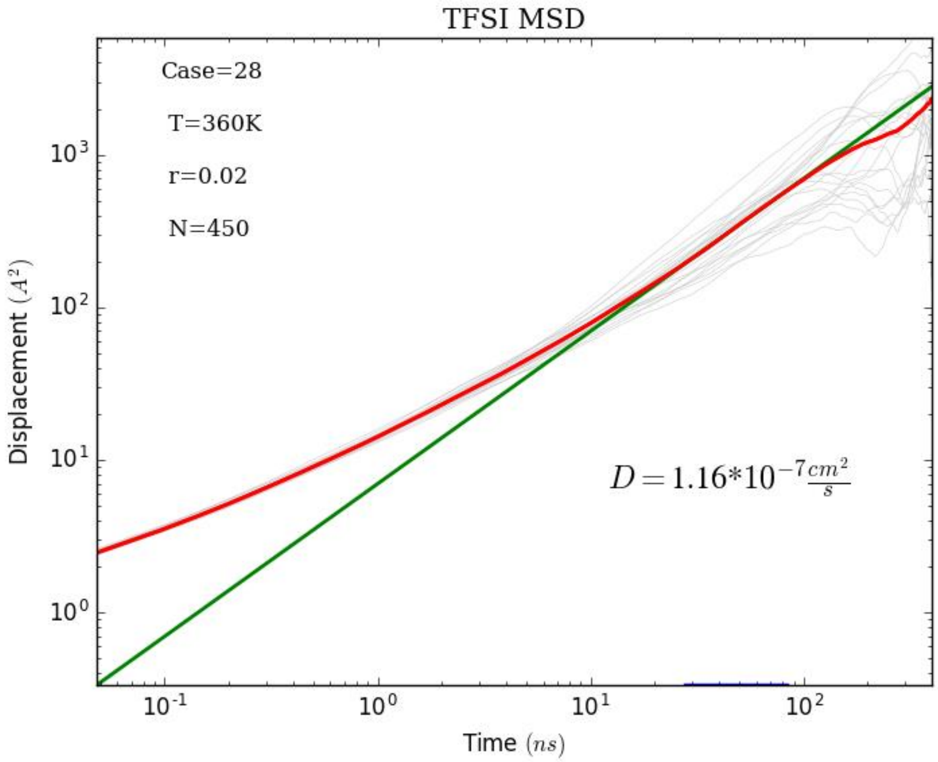
TFSI MSD
Case=26
T=360K
r=0.02
N=23
$D = 3.64*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

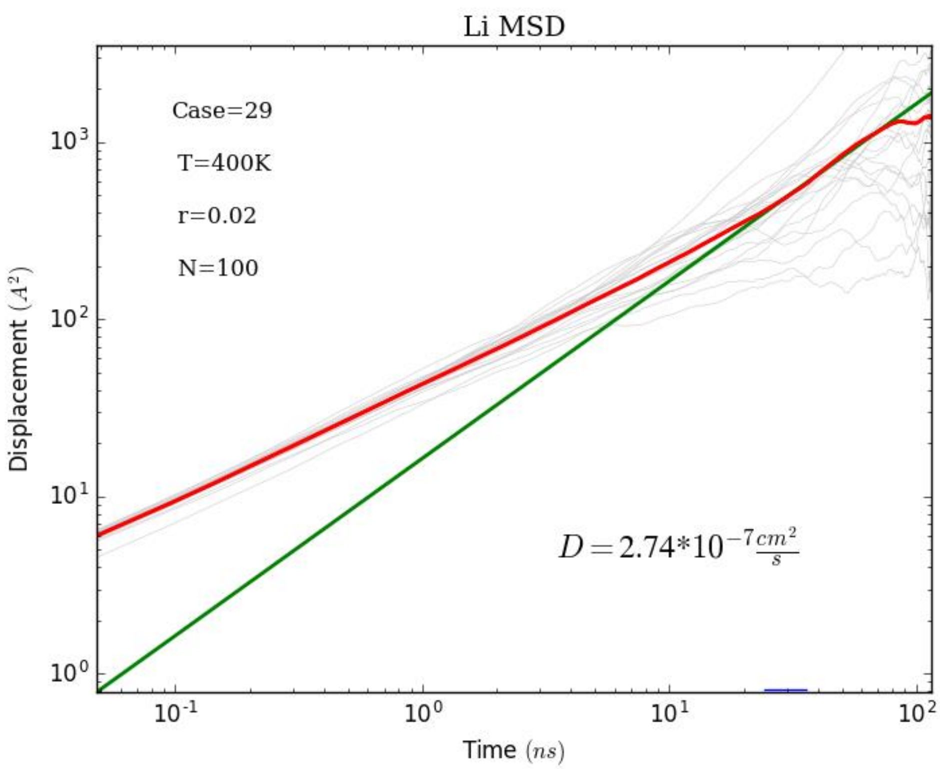


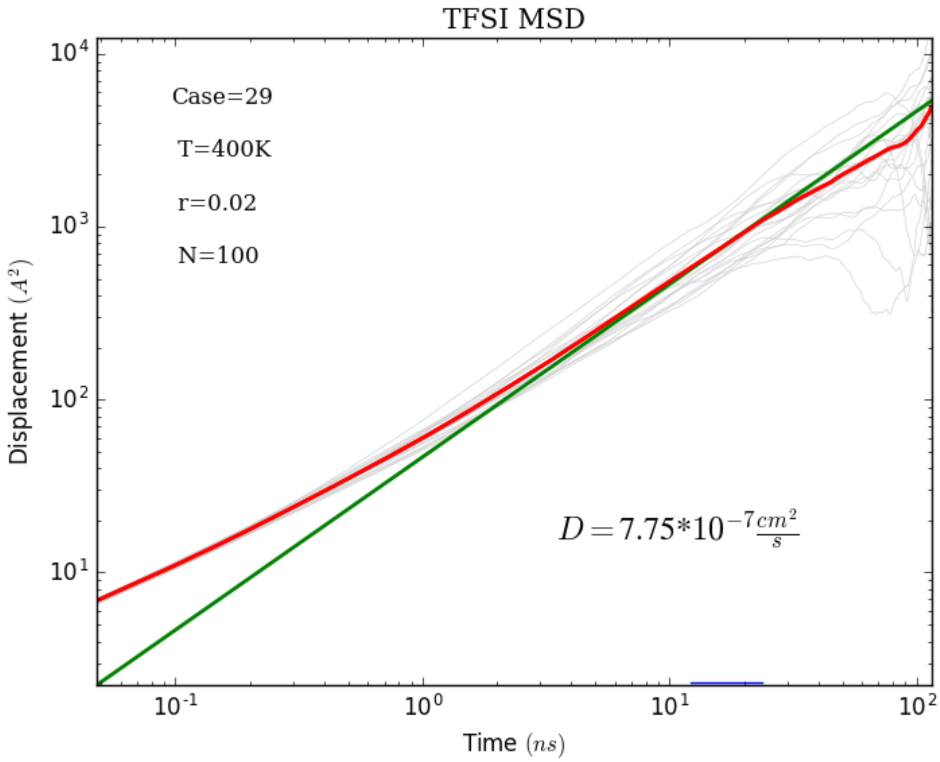
Li MSD
Case=27
T=360K
r=0.02
N=45
$D = 1.16*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

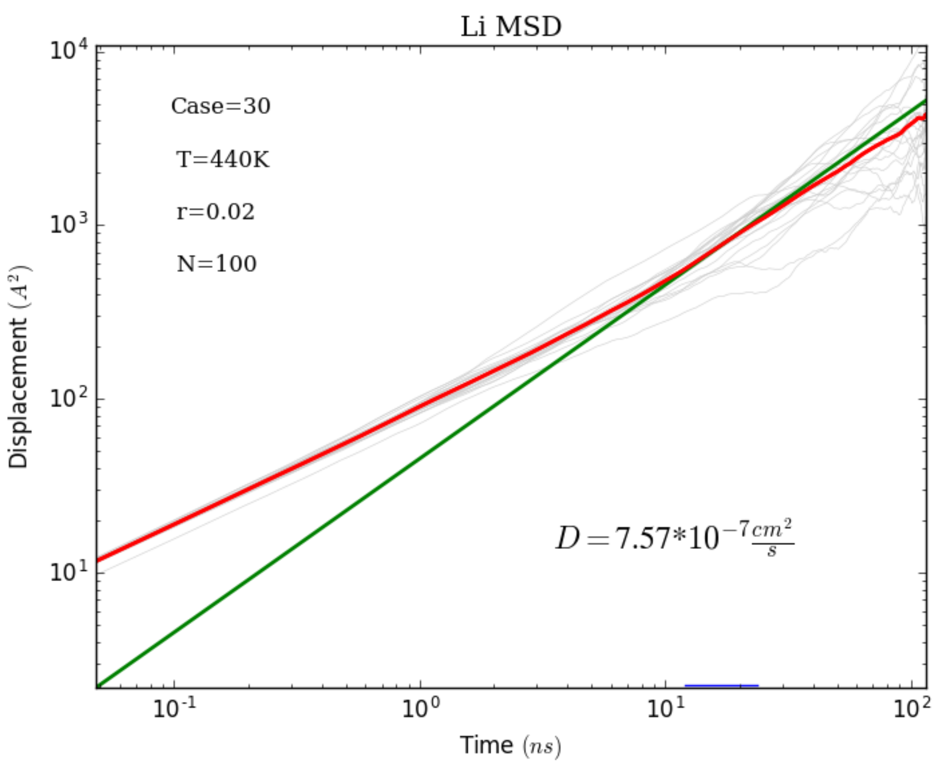

TFSI MSD
Case=27
T=360K
r=0.02
N=45
$D = 3.51*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

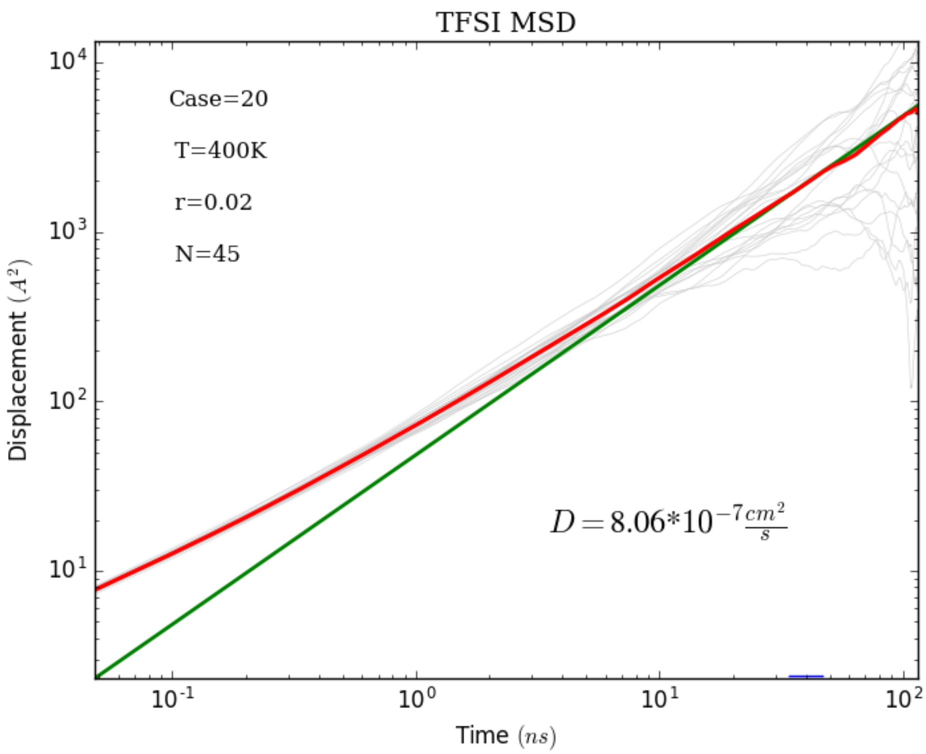

Li MSD
Case=28
T=360K
r=0.02
N=450
$D = 0.5*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

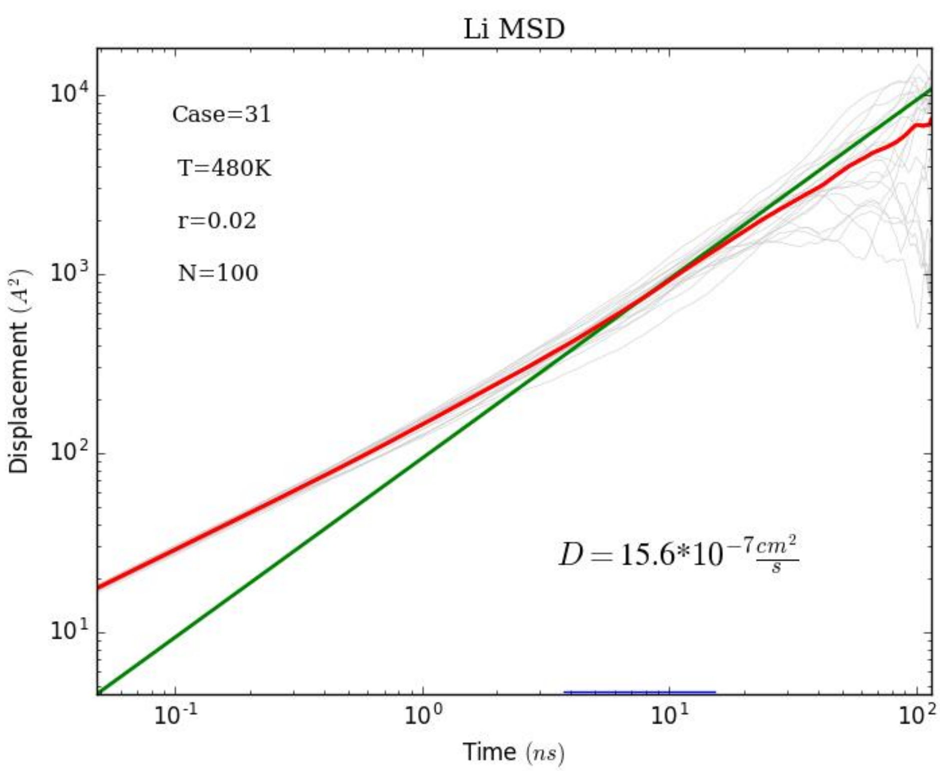

TFSI MSD
Case=28
T=360K
r=0.02
N=450
$D = 1.16*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}


Li MSD
Case=29
T=400K
r=0.02
N=100
$D = 2.74*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}


TFSI MSD
Case=29
T=400K
r=0.02
N=100
$D=7.75*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)


Li MSD
Case=30
T=440K
r=0.02
N=100
$D=7.57*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)


TFSI MSD
Case=20
T=400K
r=0.02
N=45
$D = 8.06*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)


Li MSD
Case=31
T=480K
r=0.02
N=100
$D = 15.6*10^{-7}\frac{cm^2}{s}$
Displacement (A^2)
Time (ns)

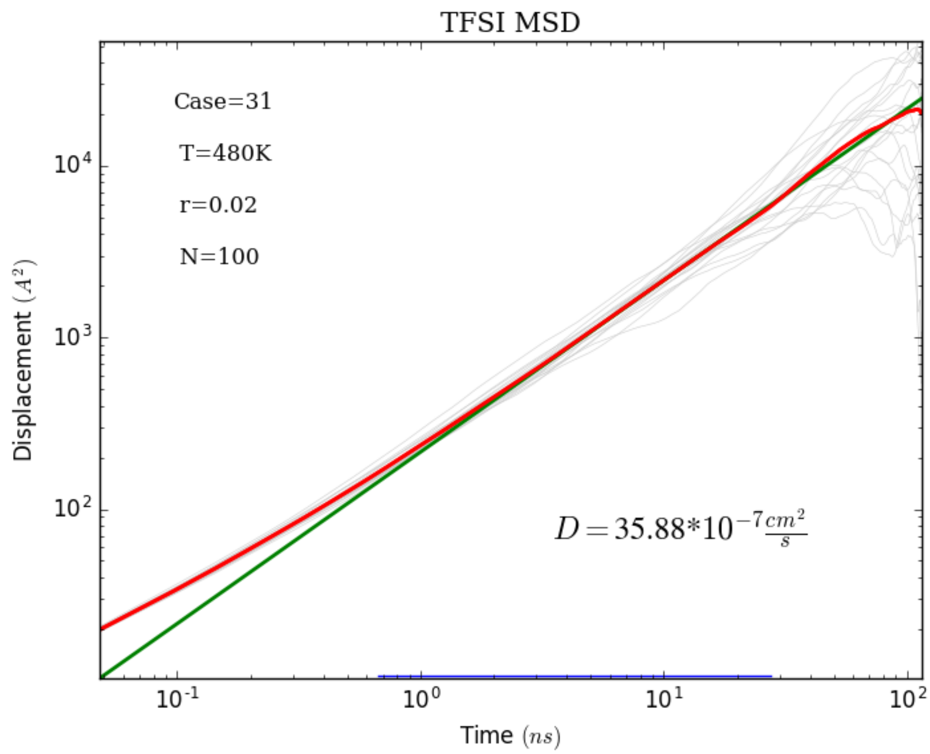


Figure S2. MSD plots and predicted ionic diffusion coefficients for PEO-LiTFSI.

4. Computationally Predicted Li Diffusion Coefficients, compared to Impedance Spectroscopy (IS) and Nuclear Magnetic Resonance (NMR) Experiments

Although the absolute diffusion coefficient obtained from polymer simulations depends greatly on parameters such as ionic charges,[6] the relative diffusion coefficients are useful for predicting physical trends.[7] The Li diffusion coefficients (Figure S3) obtained from these simulations are in excellent agreement with the IS measurements.[9] However both the theory and the IS experiments are a factor of ~5 slower than experimental NMR.[8]

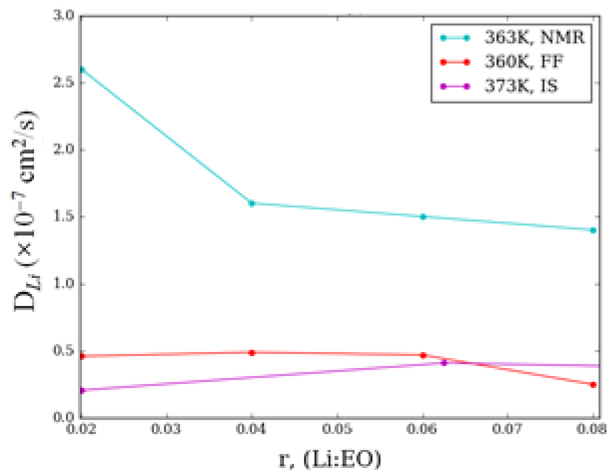
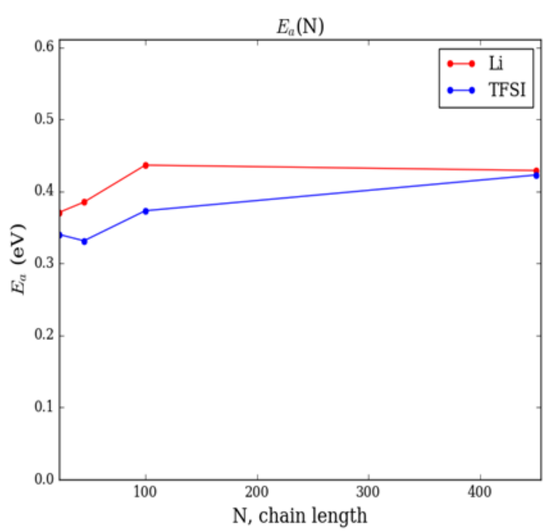
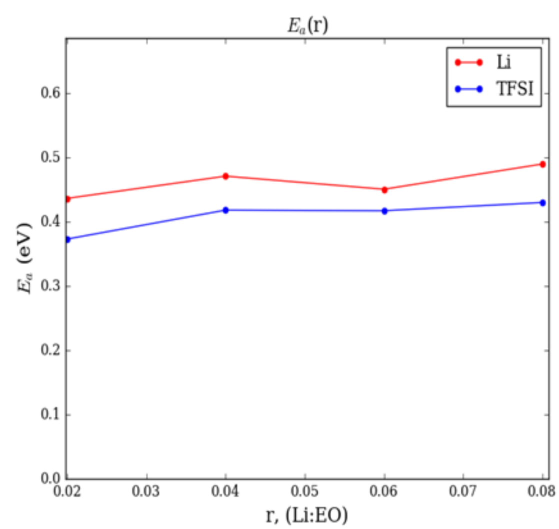


Figure S3. Diffusion coefficients obtained from simulation (red), NMR (green), and IS (purple) measurements.

4. Plots of Activation Energies for Li and TFSI Ionic Diffusion



a



b

Figure S4. Li and TFSI activation energies over a range of chain lengths, N=23, 45, 100, 450 (a) and concentrations r=0.02, 0.04, 0.06 and 0.08 Li:EO (b). The computed activation energy depends weakly on chain length and concentration within this regime, in agreement with experimental measurements.[10]

The predicted activation energies for Li and TFSI ionic diffusion are shown in Figure S4 as a function of chain length and ionic concentration. These values are in the range reported by Gorecki et al.,[10] (Table S2) and suggest that the computed diffusion coefficients are transferable across a range of temperatures.

Table S2. Experimental lithium and TFSI activation energies (E_a) at high molecular weight (N≈ 20,000) obtained by Gorecki et al.[10] with pulsed magnetic field gradient measurements for r=0.05, 0.10, 0.13, and 0.17 Li:EO.

	r=0.05	r=0.10	r=0.13	r=0.17
E_{Li} (eV)	0.38	0.39	0.40	0.43
E_{TFSI} (eV)	0.43	0.45	0.40	0.49

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