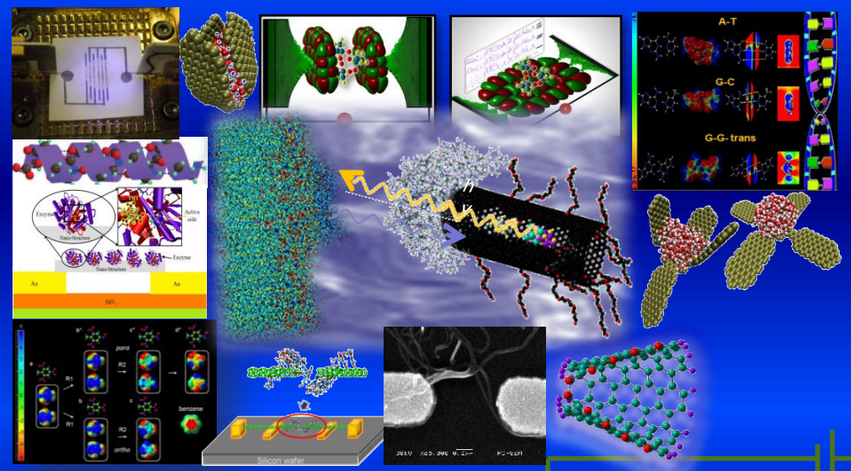
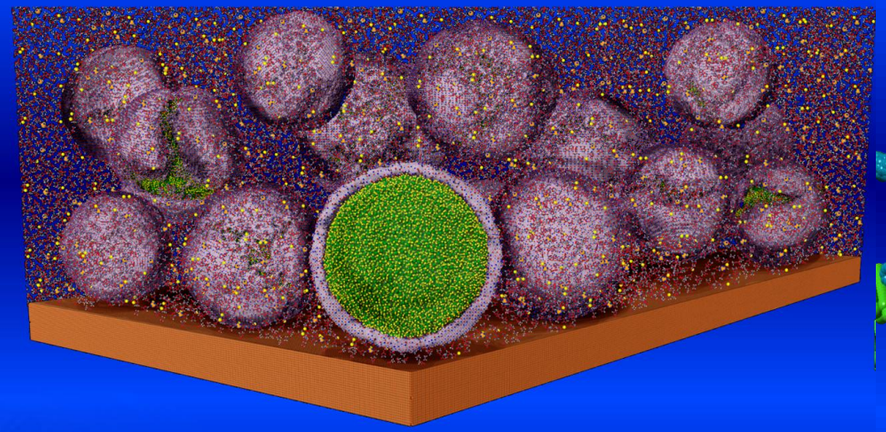
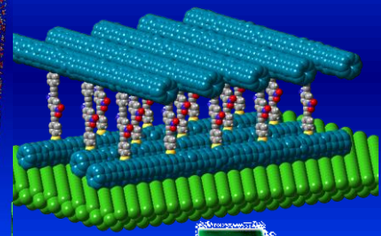
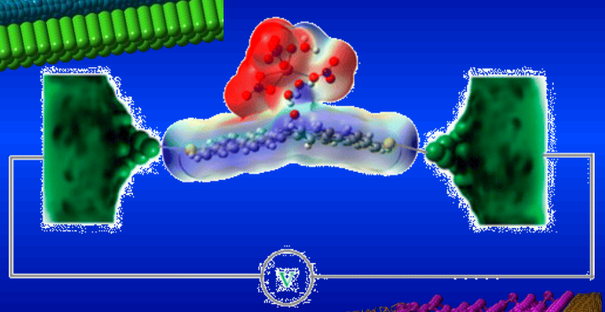
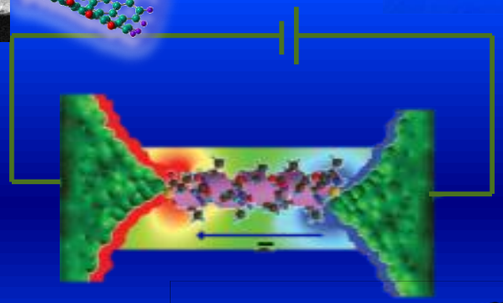
# Atomistic Classical and Quantum Simulations of Nanobatteries – Part 2

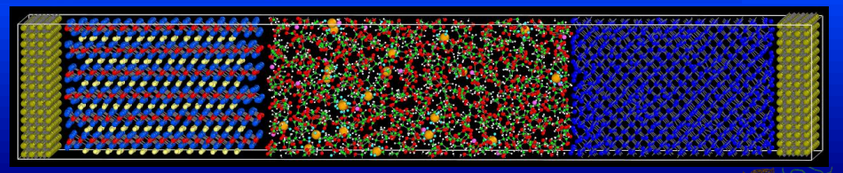


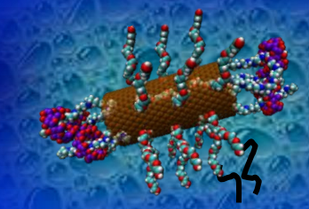



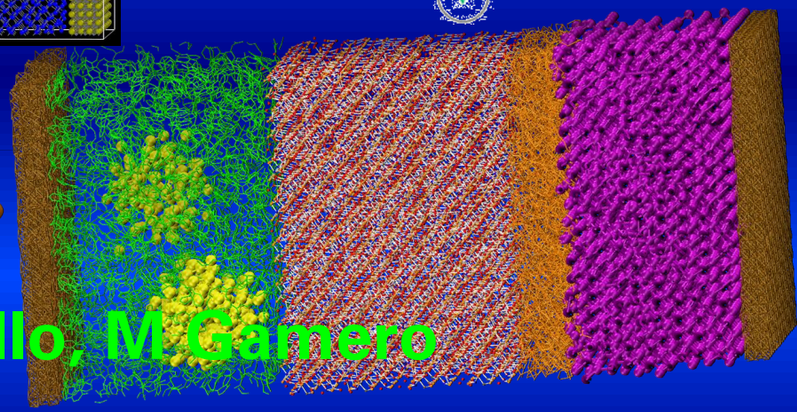










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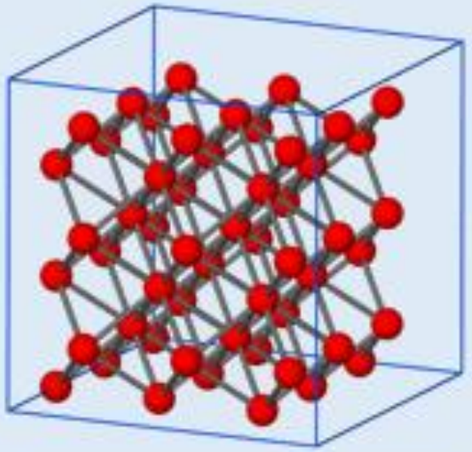
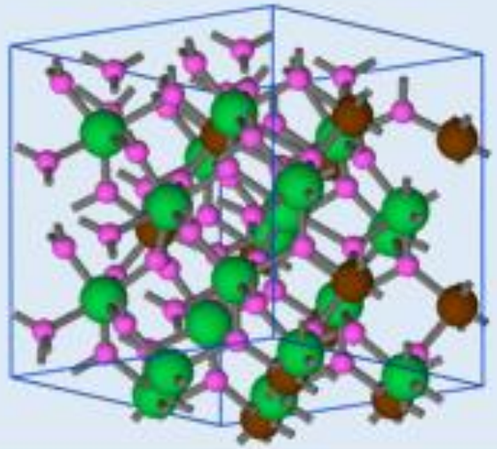
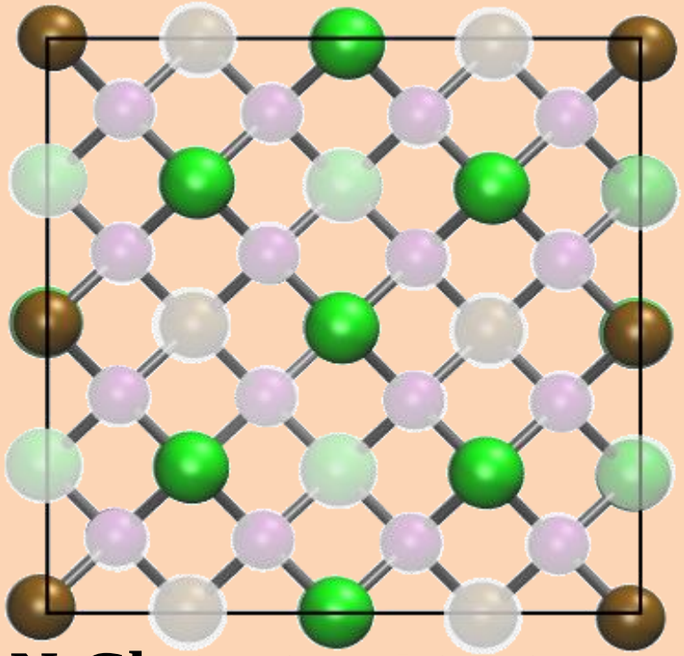


**Pristine boxes: Li-metal & $Li_9N_2Cl_3$ solid-state electrolyte**



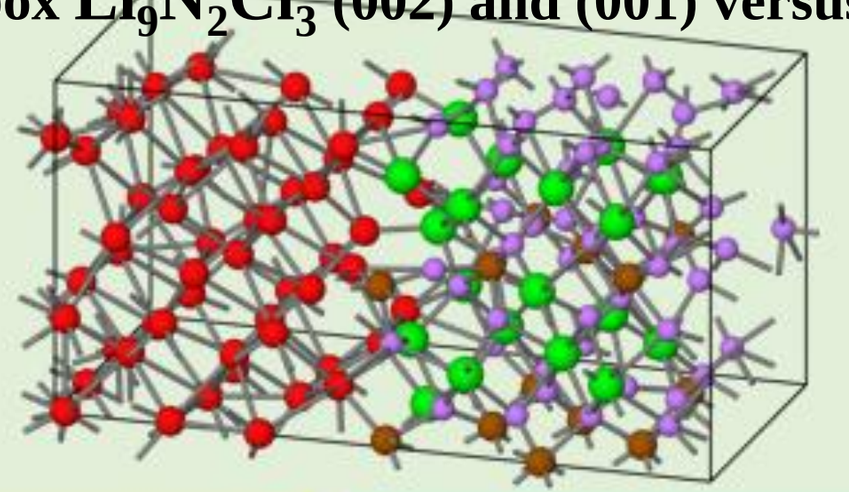
Li Metal

Solid Electrolyte



**$Li_9N_2Cl_3$ (002) and (001) planes atoms on top highlighted.**

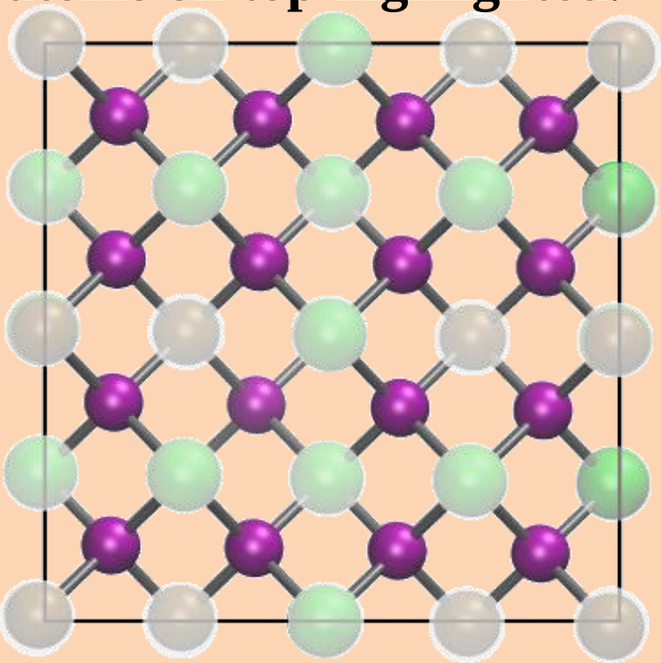
**Interfacial box $Li_9N_2Cl_3$ (002) and (001) versus (001) Li-metal**



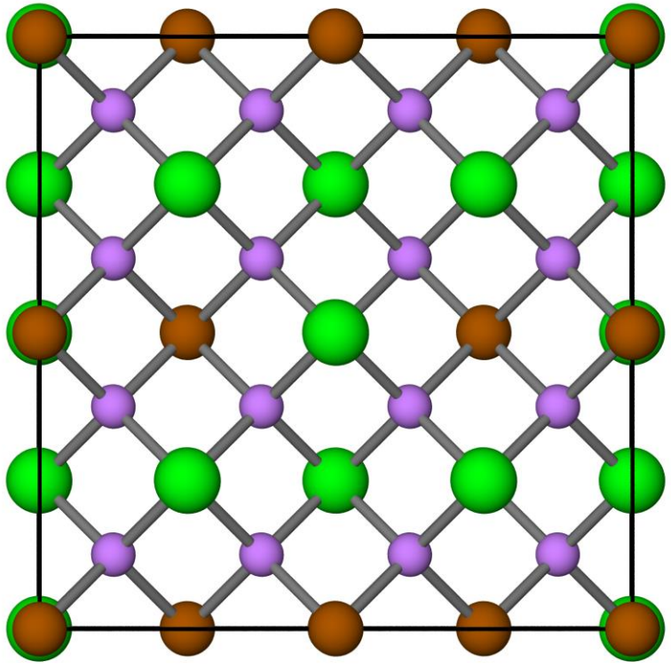
**$Li_m$ (red)**
**Li (purple)**
**N (brown)**
**Cl (green)**

Li Metal

Solid Electrolyte

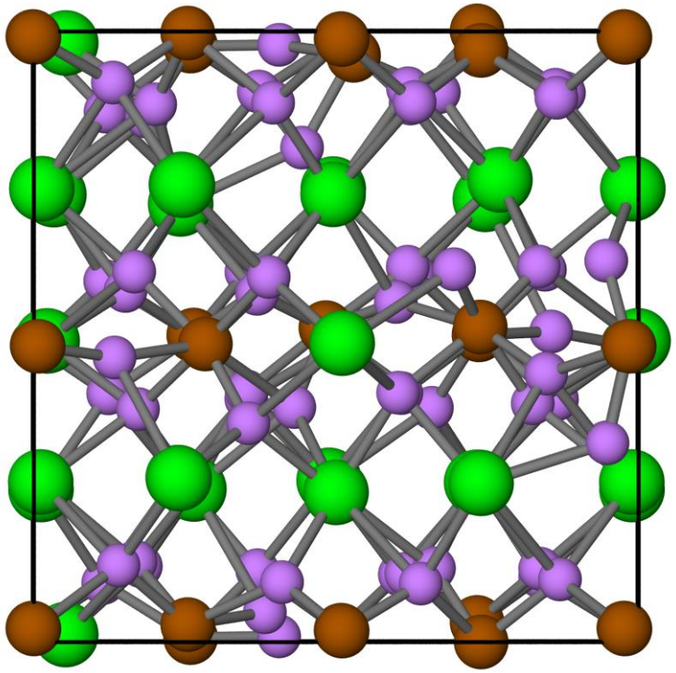


Experimental (space group 225) cubic crystal structure of $Li_9N_2Cl_3$.

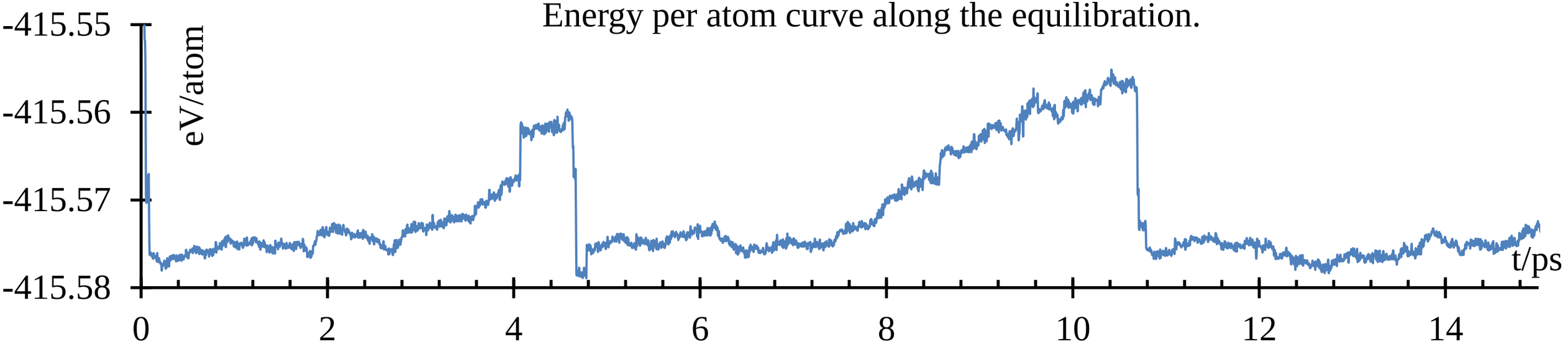


Li (purple),
N (brown)
Cl (light green)

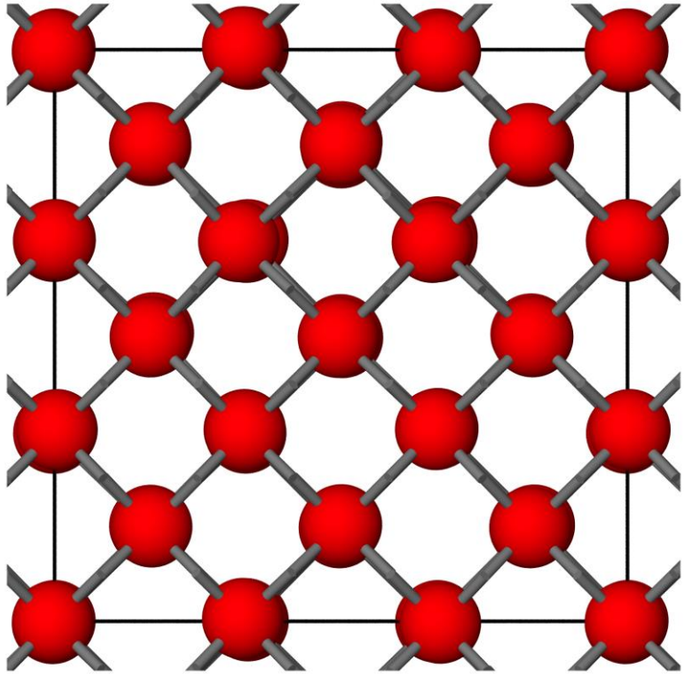
Crystal Structure after 15 ps of equilibration.



Energy per atom curve along the equilibration.

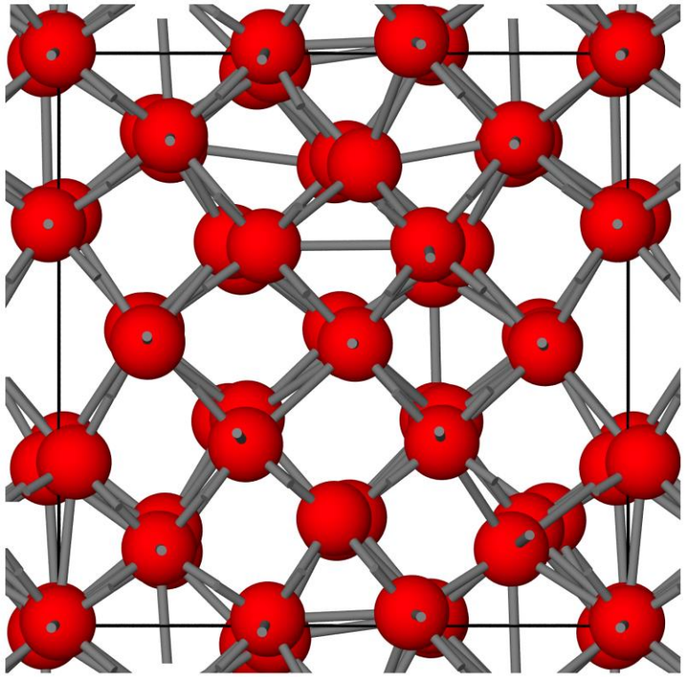


Experimental BCC (space group 225) crystal structure of Li-metal

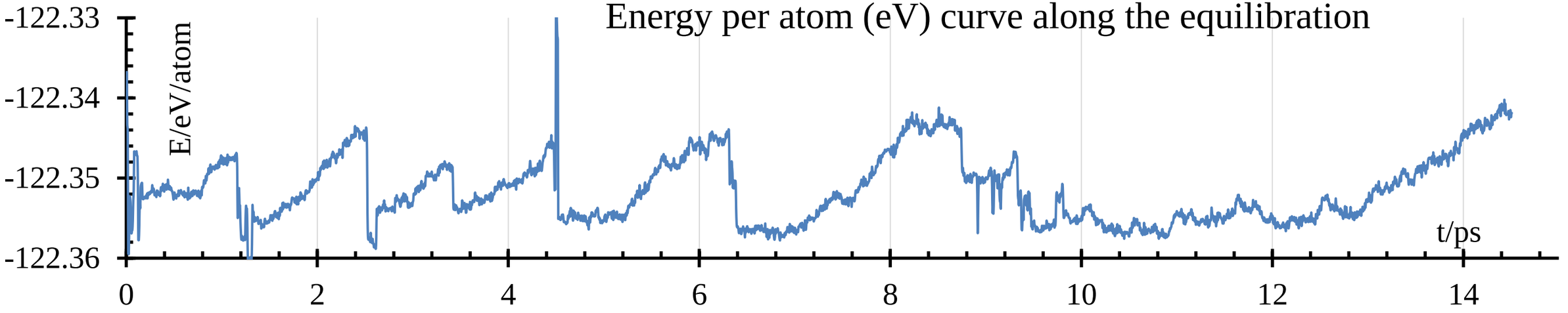


$Li_{(s)}$ (red)

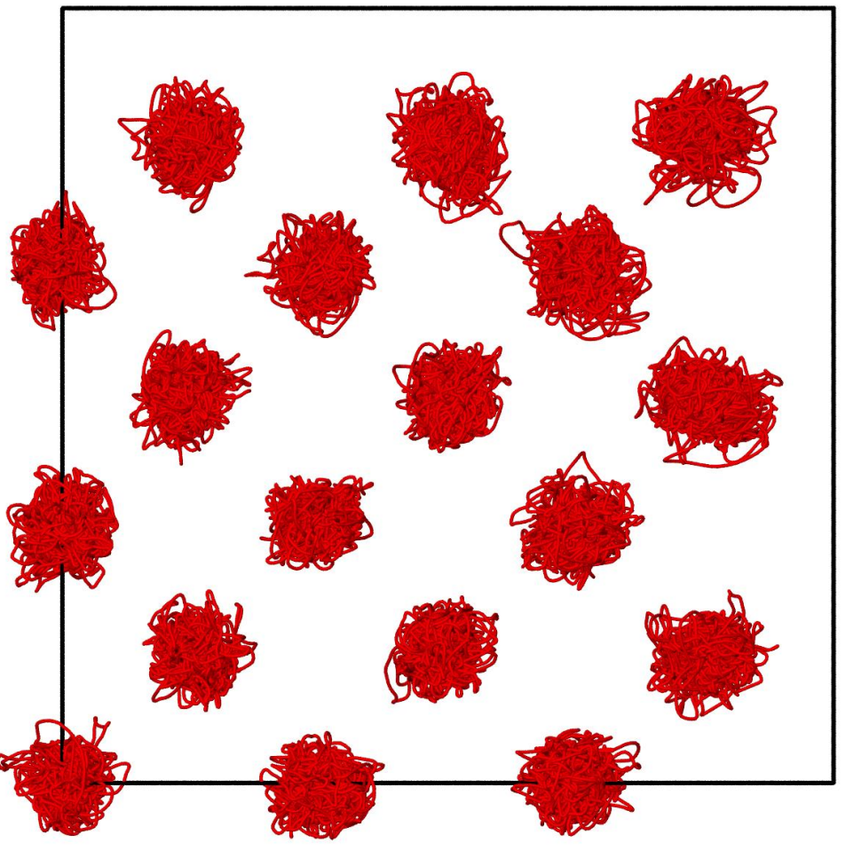
after 15 ps of AIMD equilibration

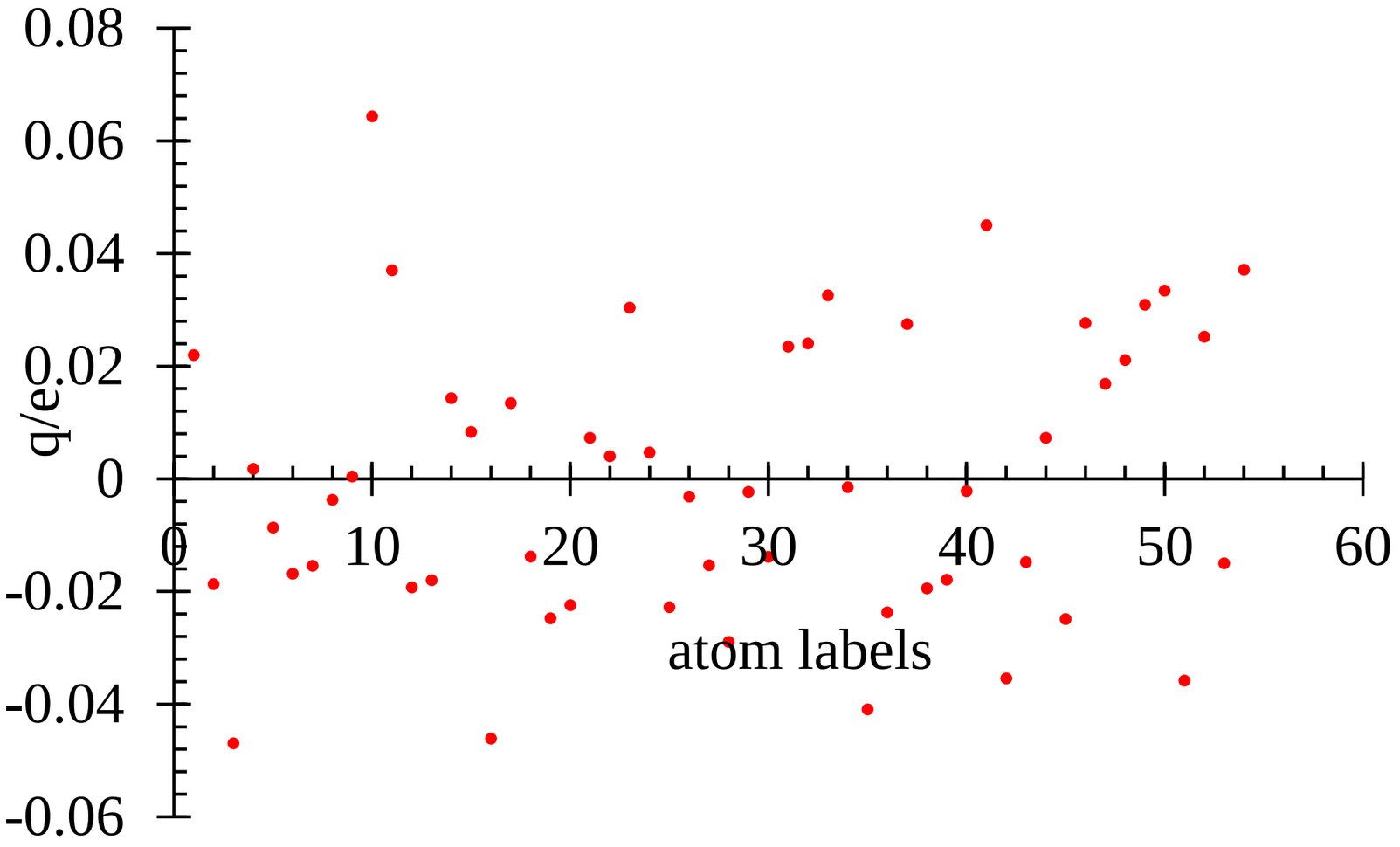


Energy per atom (eV) curve along the equilibration



# Li-metal trajectories & final Bader charges

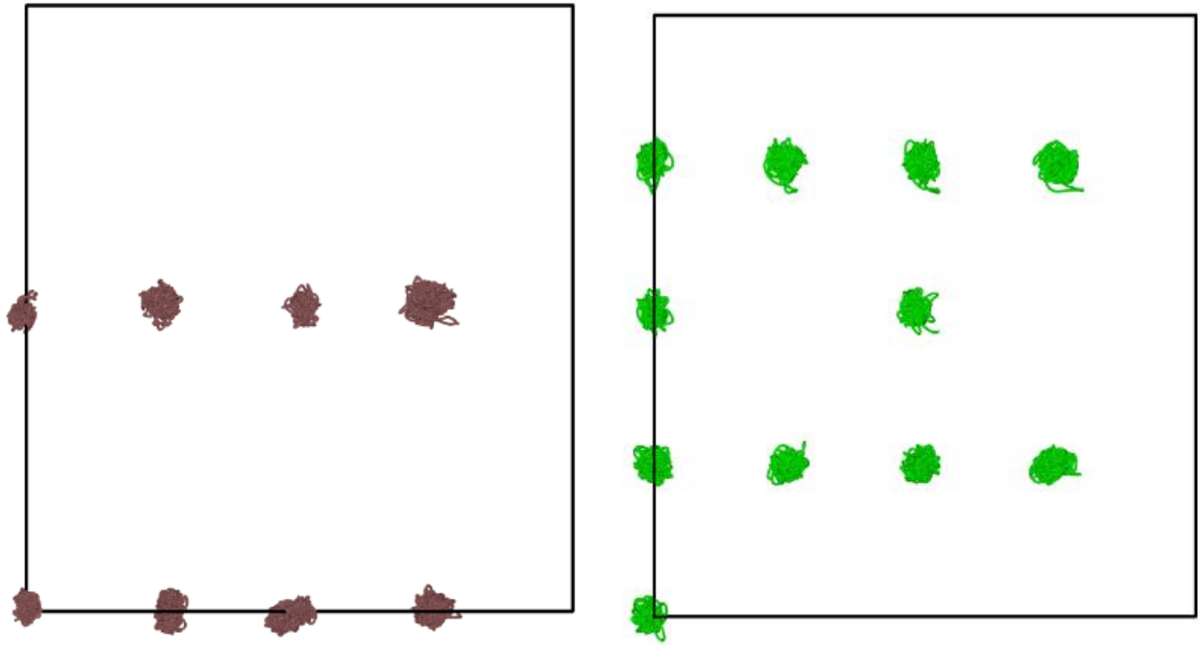




Experimental and AIMD lattice parameters (Å), and density (g/cm$^3$) for the Li metal crystal structure. Experimental ($\tau$ = 0.5 fs, NPT ensemble) for $Li_9N_2Cl_3$ AIMD shows parameters averages

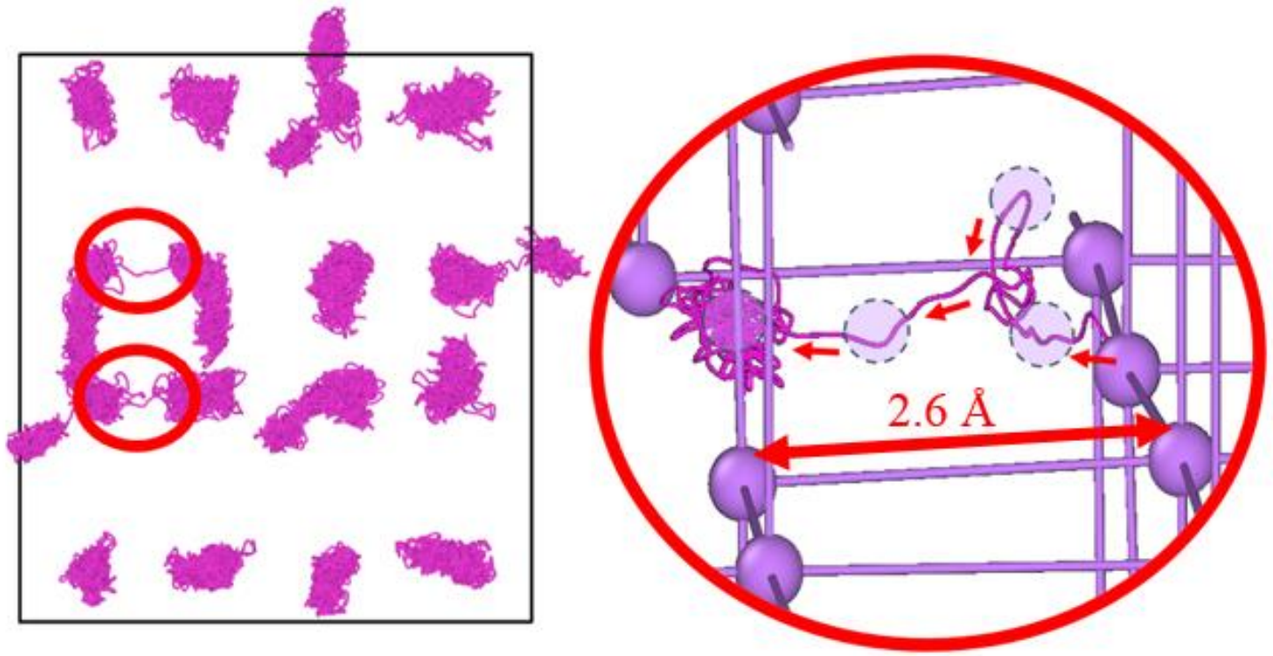
| Method | a | b | c | volume | Density |
|---|---|---|---|---|---|
| Experimental | 10.53 | 10.53 | 10.53 | 1167 | 0.53 |
| AIMD | 9.96 | 11.38 | 10.91 | 1237 | 0.50 |
| Difference [%] | 5.41 | 8.07 | 3.61 | 5.99 | 5.66 |

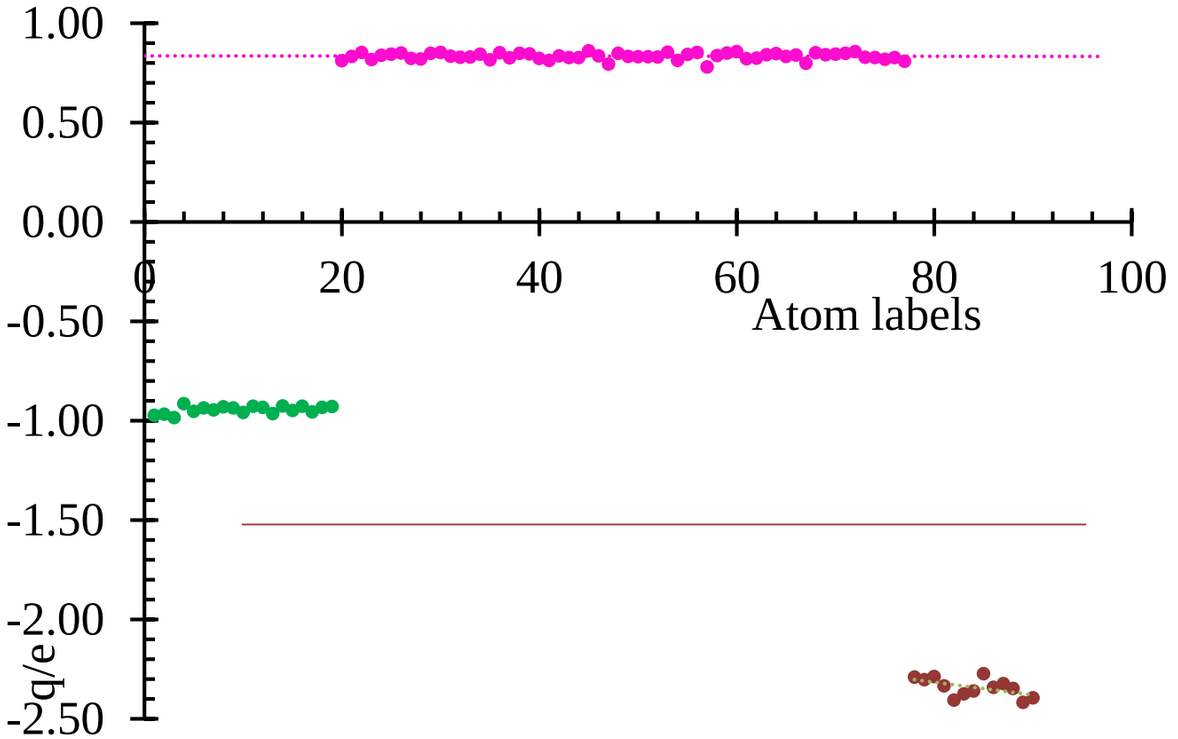
| Method | a | b | c | volume | Density |
|---|---|---|---|---|---|
| Experimental[49] | 10.814 | 10.814 | 10.814 | 1264 | 1.65 |
| AIMD | 10.205 | 11.406 | 10.296 | 1198 | 1.74 |
| Difference [%] | 5.60 | 5.47 | 4.79 | 5.22 | 5.45 |

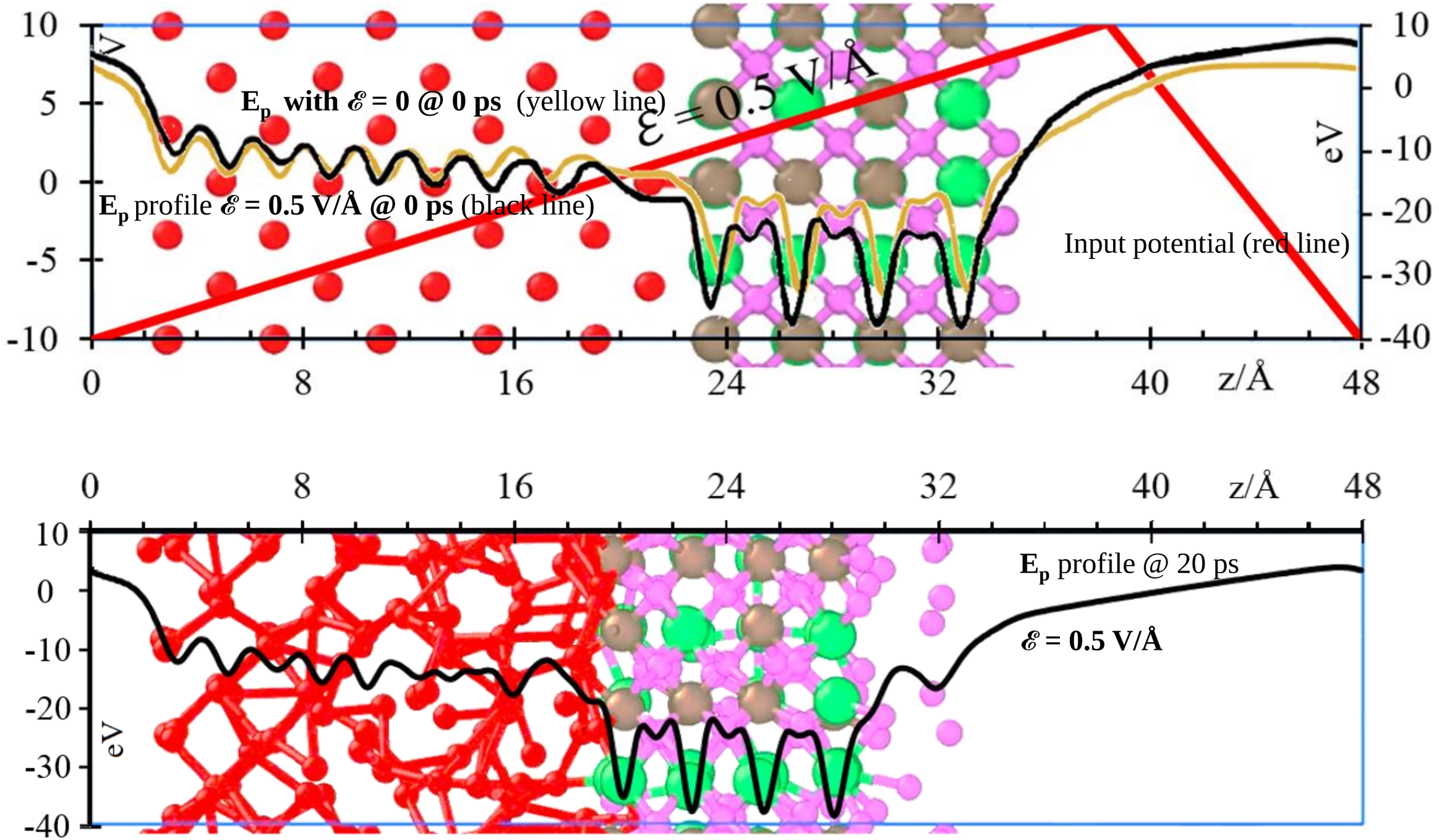


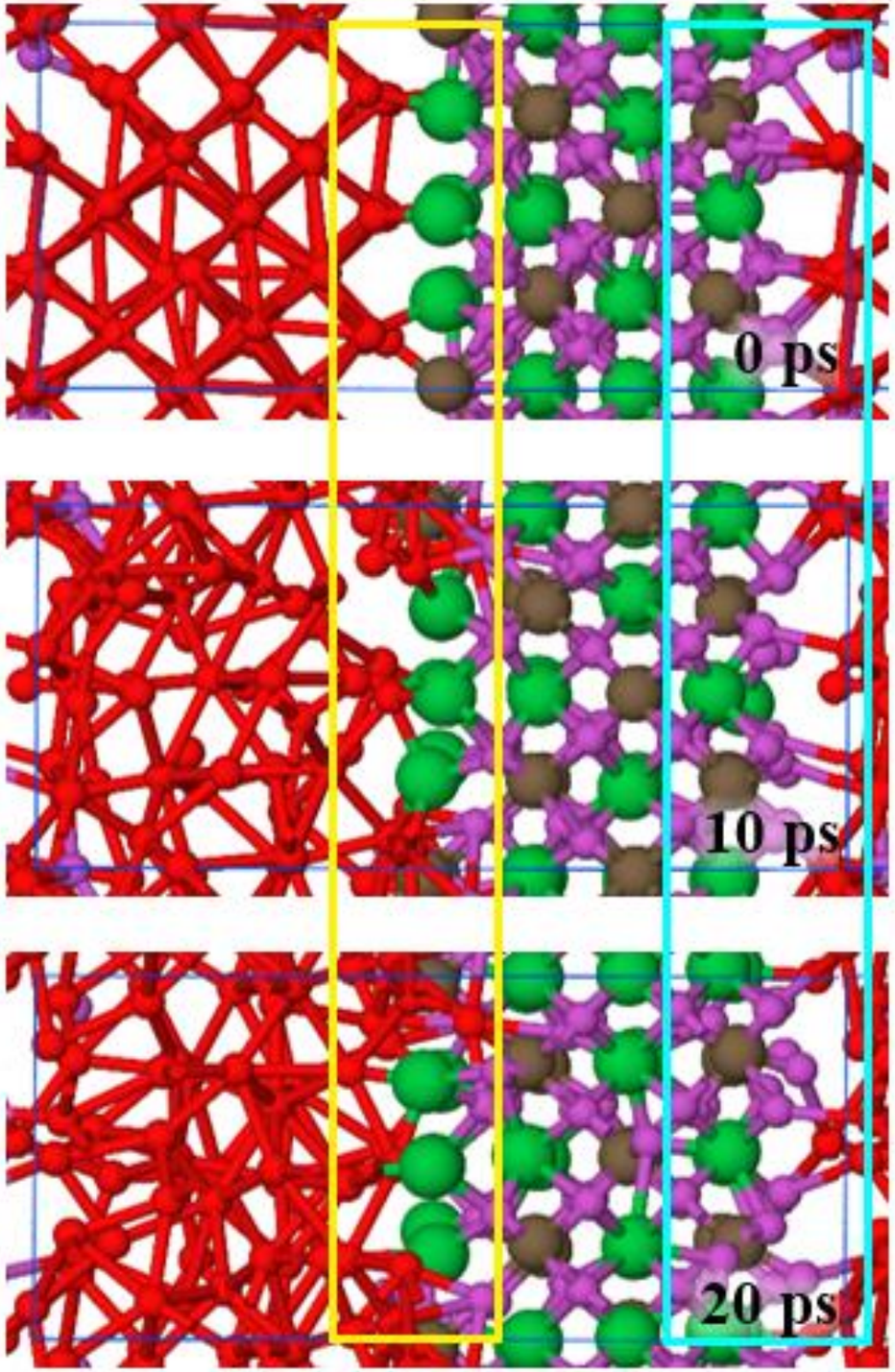
$Li_9N_2Cl_3$ diffusion trajectories during 15 ps of AIMD with a $\tau$ = 0.5 fs under NPT ensemble. (d) Atomic Bader charges after equilibration.

N (brown)
Cl (green)
Li (purple).

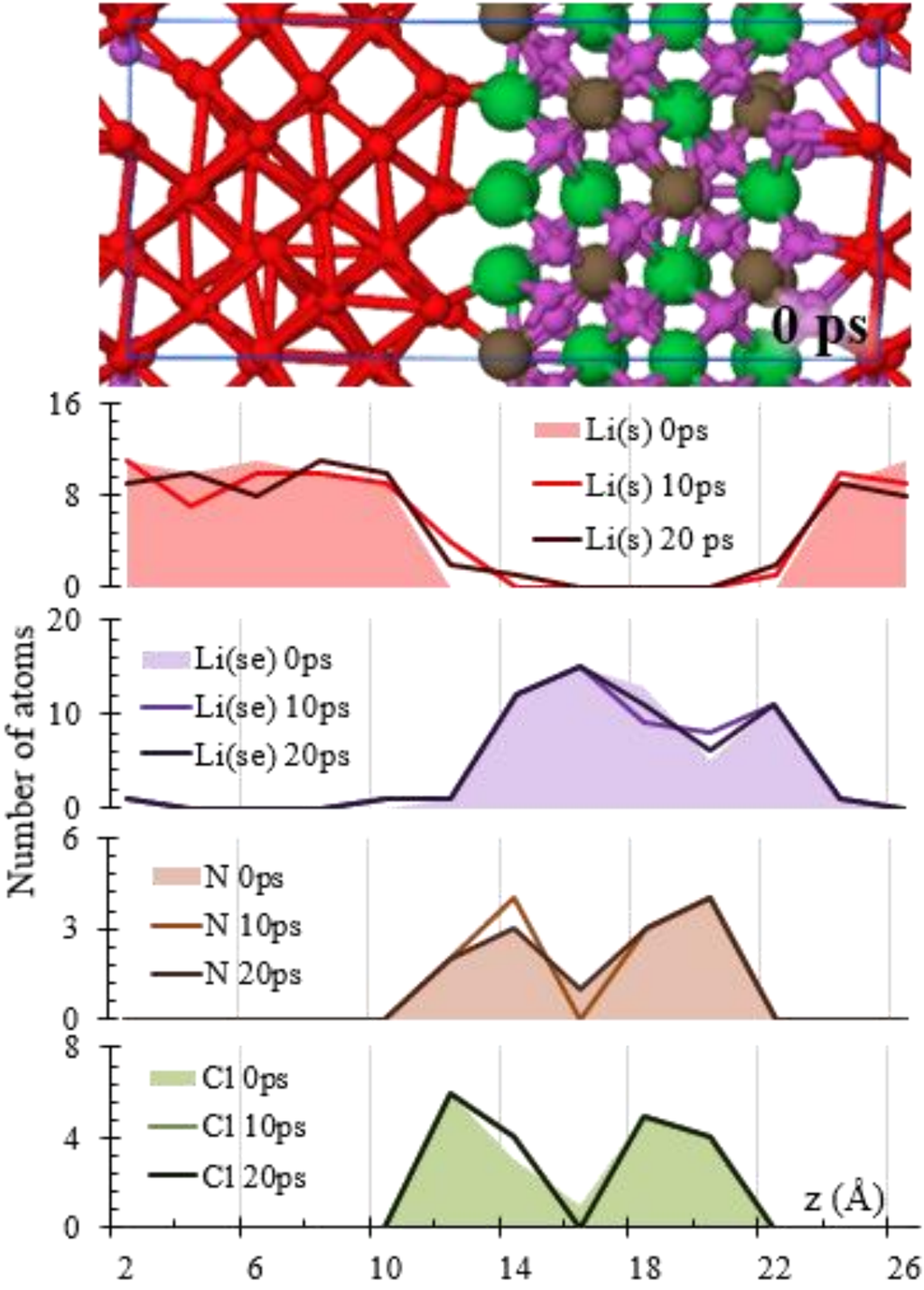


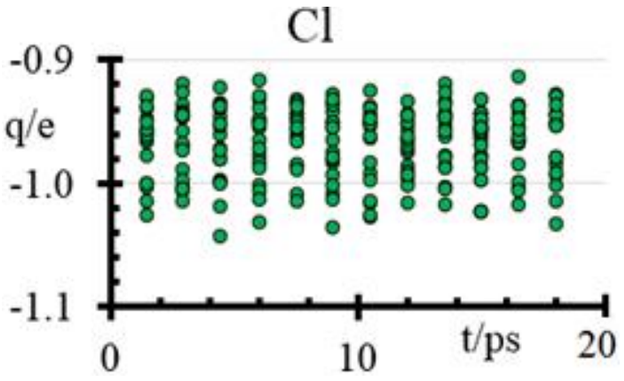

10
5
0
-5
-10
eV
$E_p$ with $\mathscr{E}$ = 0 @ 0 ps (yellow line)
$\mathscr{E} = 0.5$ V/Å
$E_p$ profile $\mathscr{E}$ = 0.5 V/Å @ 0 ps (black line)
Input potential (red line)
10
0
-10
-20
-30
-40
eV
0
8
16
24
32
40
z/Å
48
0
8
16
24
32
40
z/Å
48
10
0
-10
-20
-30
-40
eV
$E_p$ profile @ 20 ps
$\mathscr{E}$ = 0.5 V/Å

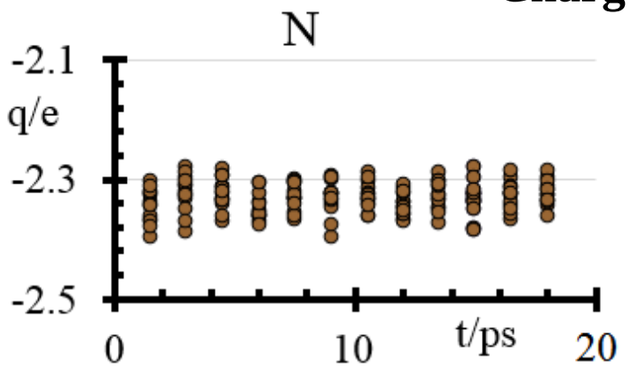


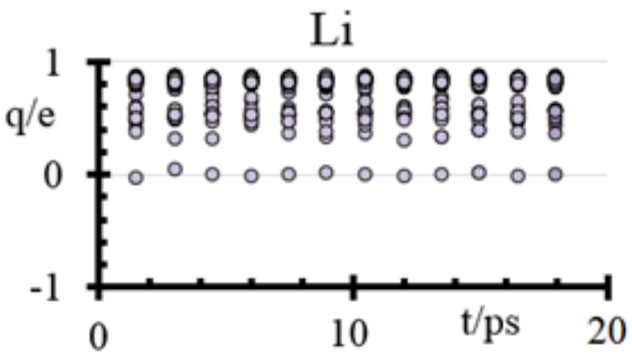

AIMD Atomic density distributions at 0, 10, 20 ps

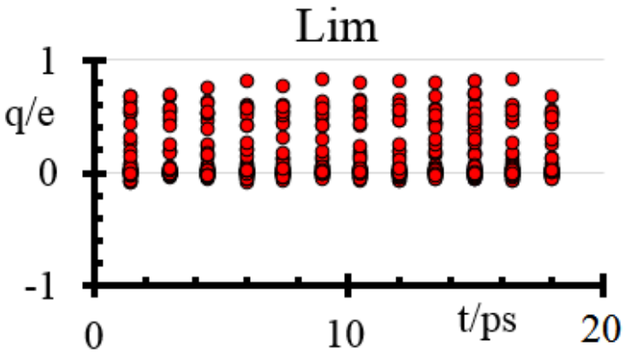


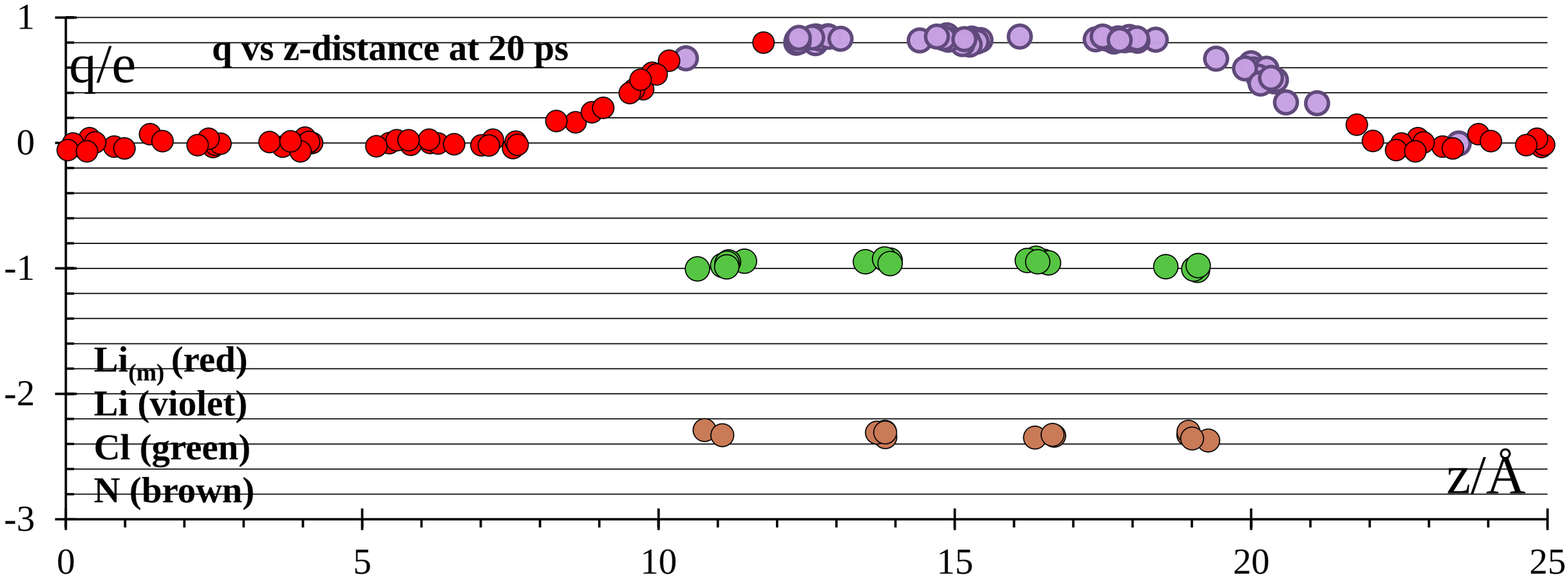
## Charge evolution



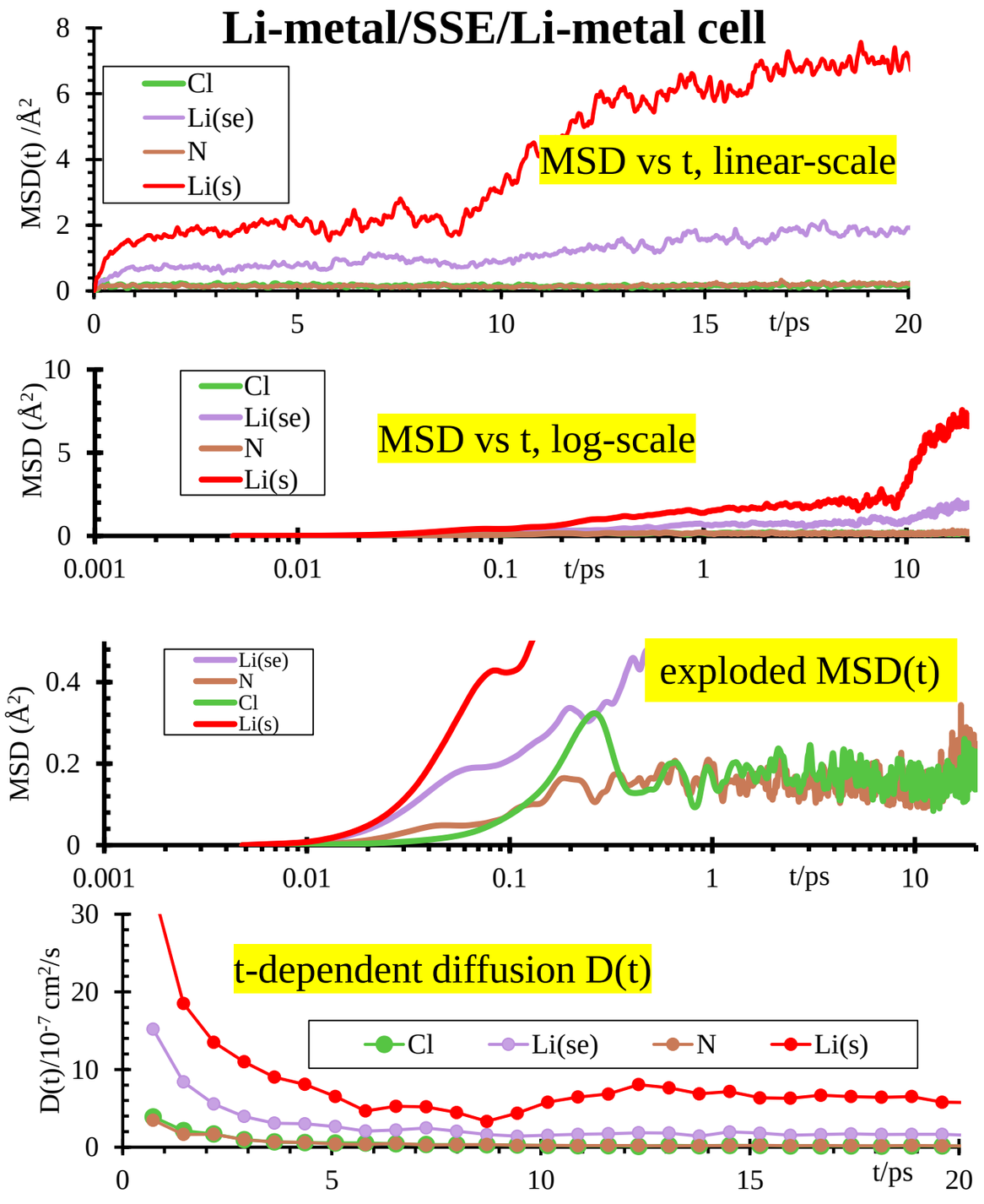



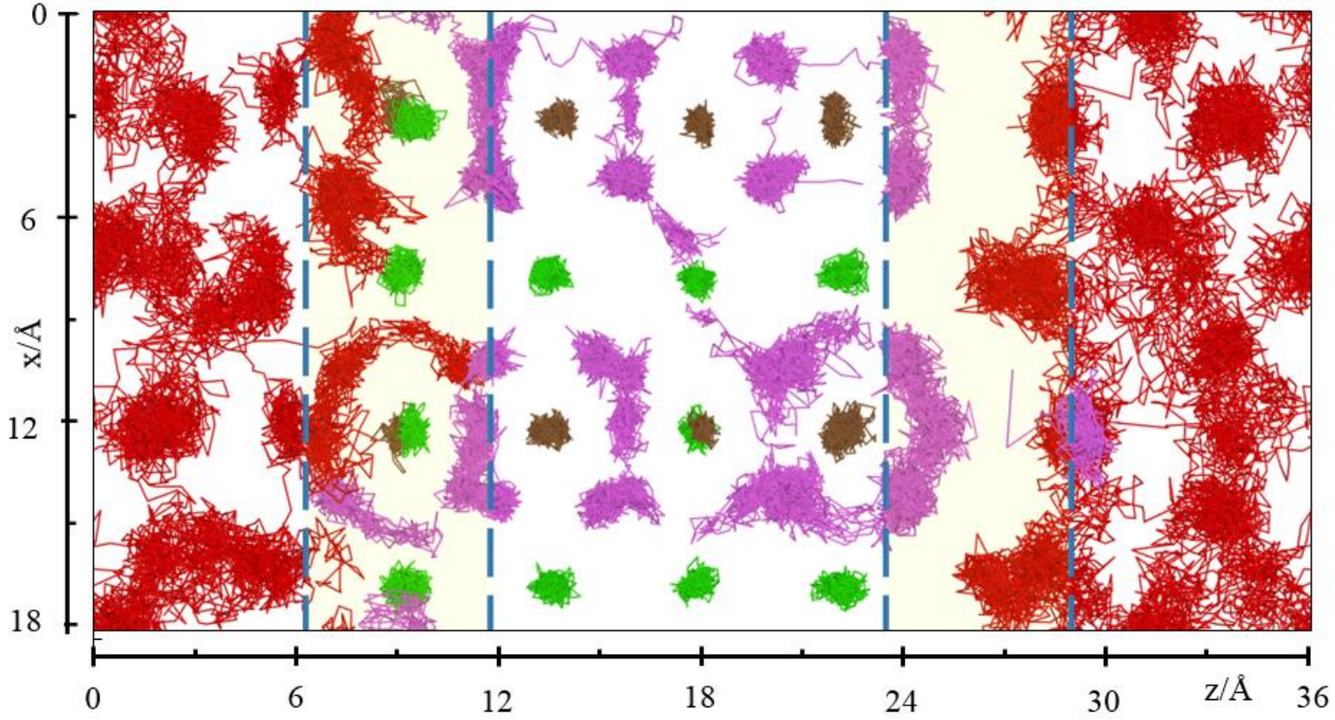
$$d^2(t) \equiv \text{MSD}$$

$$d^2(t) = \frac{1}{MN}\sum_{\tau=1}^{M}\sum_{n=1}^{N}\left(x_n(\tau+t) - x_n(\tau)\right)^2$$

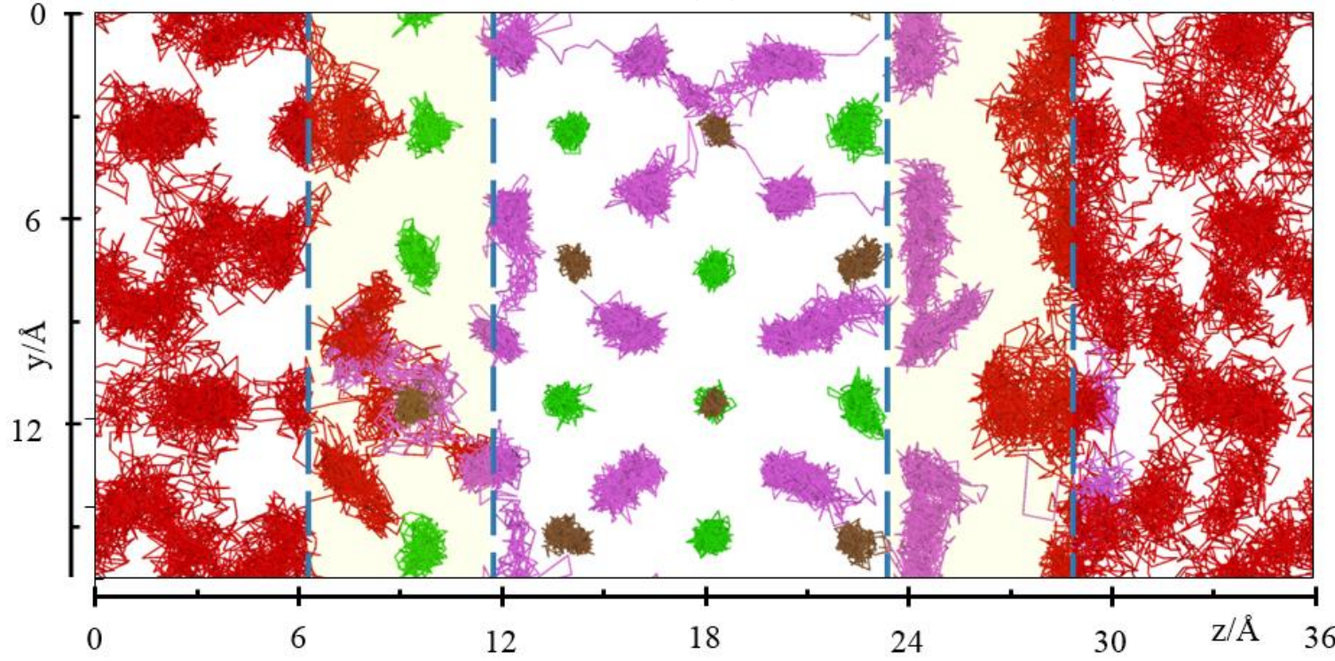
$$D(t) = \frac{1}{6}\frac{d^2(t)}{t}$$

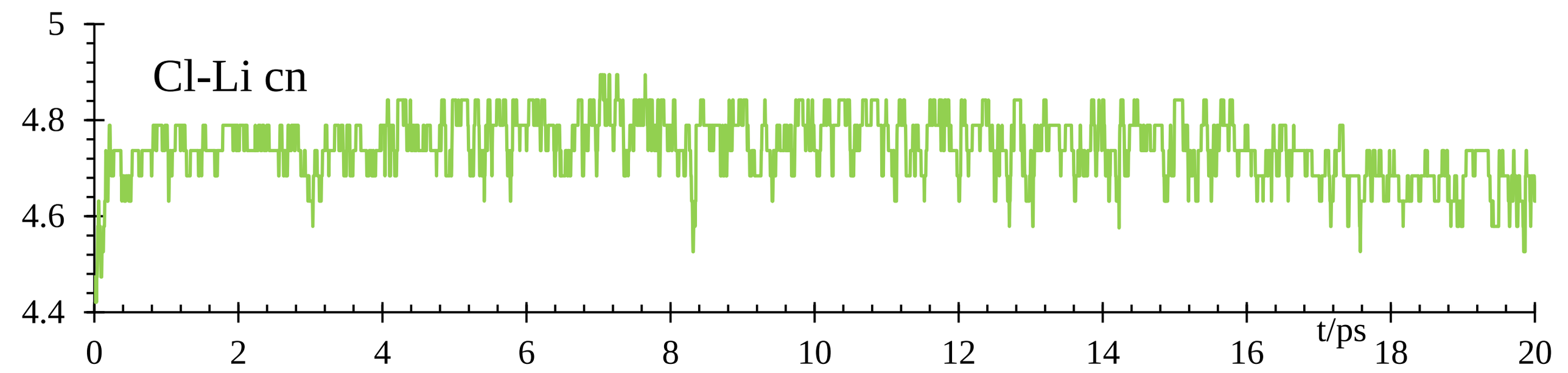
$$D(t) = \frac{1}{6MNt}\sum_{\tau=1}^{M}\sum_{n=1}^{N}\left(x_n(\tau+t) - x_n(\tau)\right)^2$$

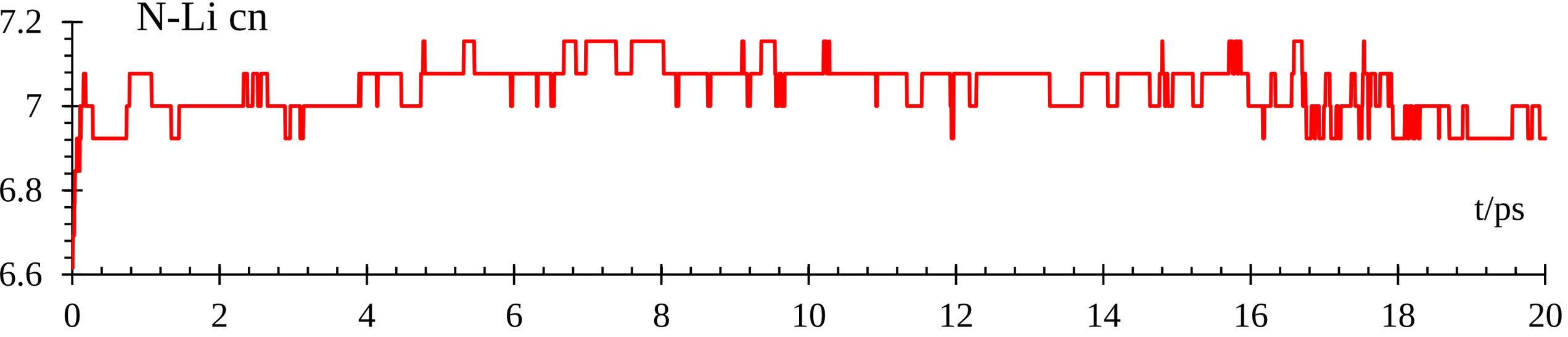


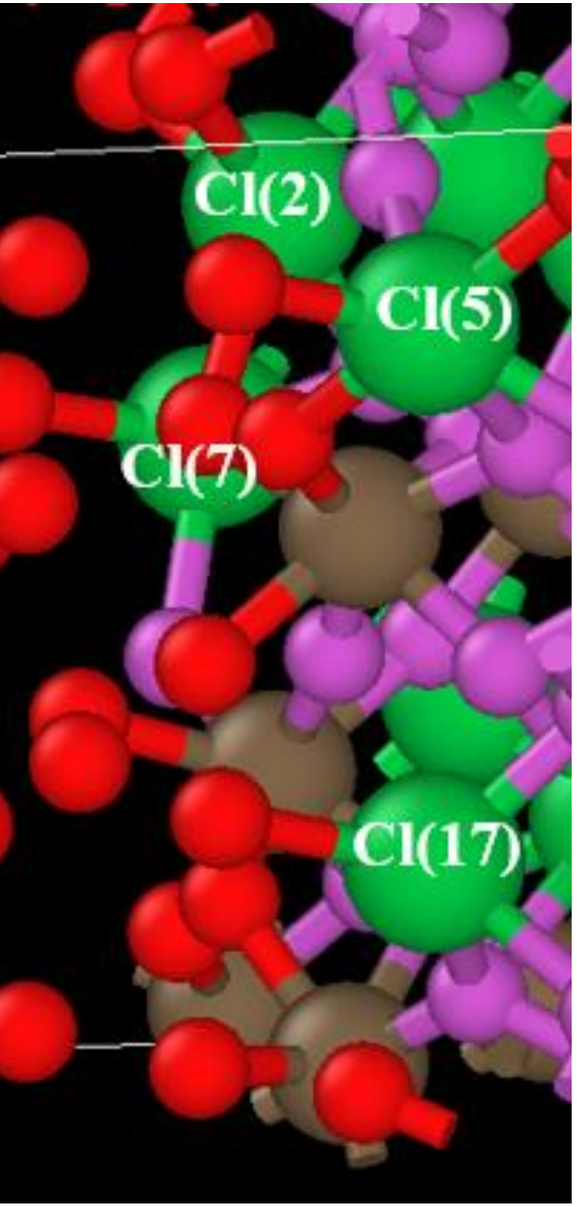

N (brown), Cl (green), $Li_{(se)}$ (purple) and $Li_{(s)}$ (red)

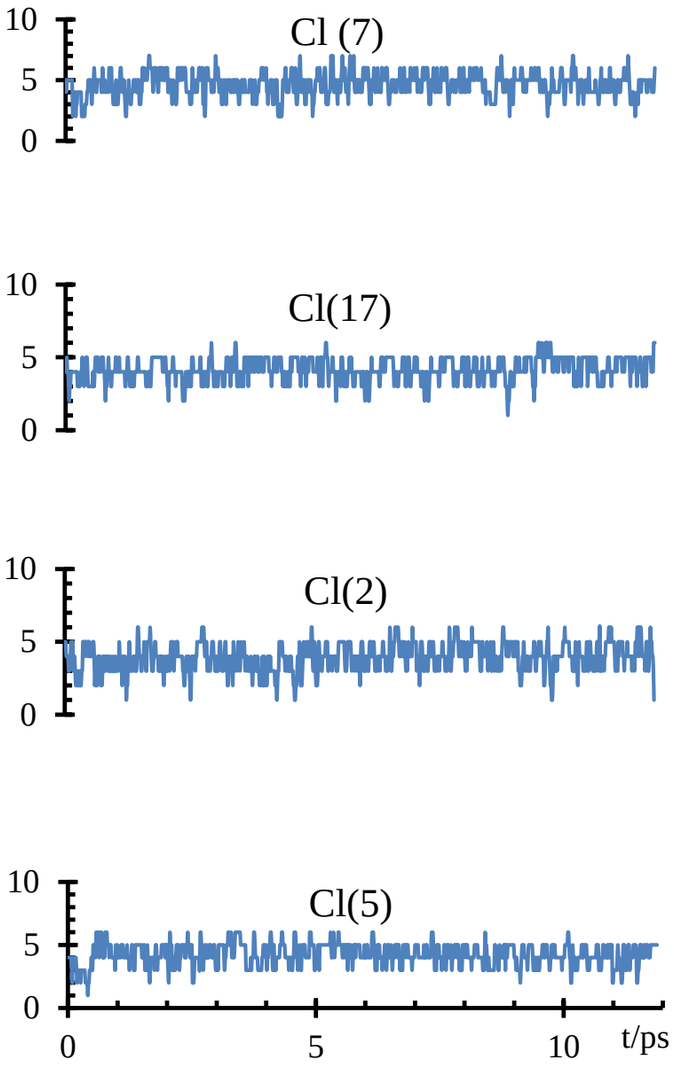


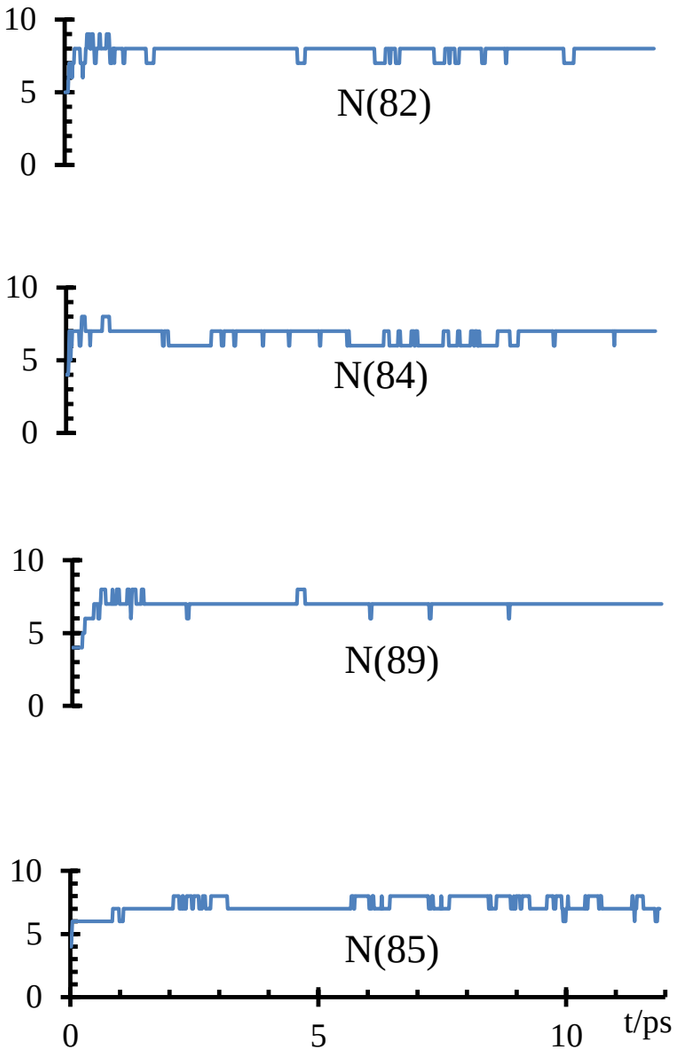

Cl-Li cn
5
4.8
4.6
4.4
0
2
4
6
8
10
12
14
16
18
20
t/ps

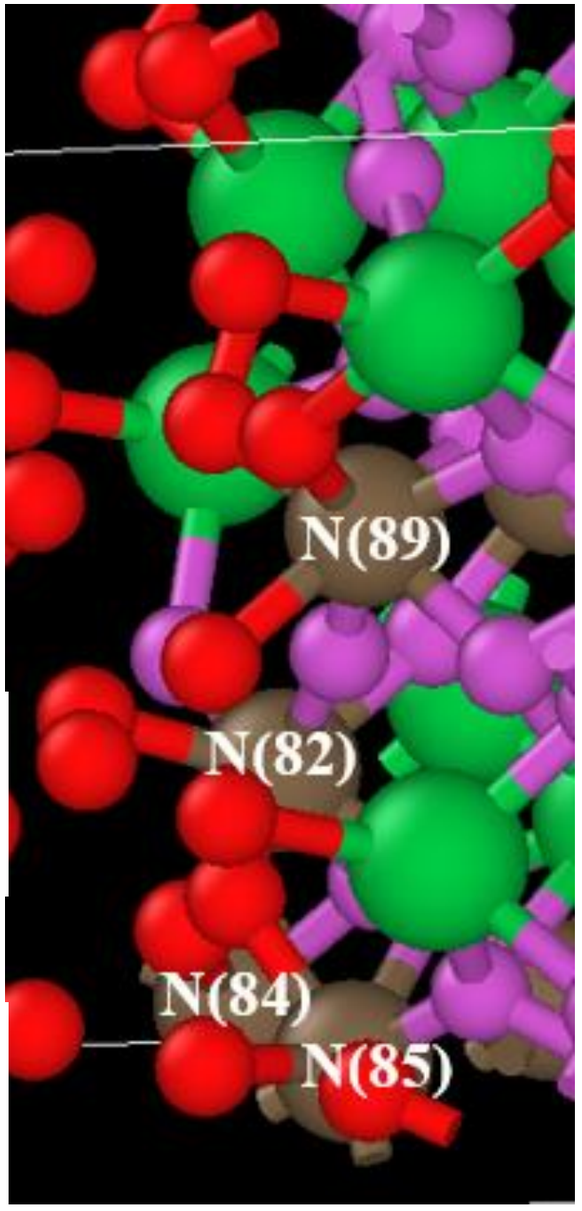

N-Li cn
7.2
7
6.8
6.6
0
2
4
6
8
10
12
14
16
18
20
t/ps

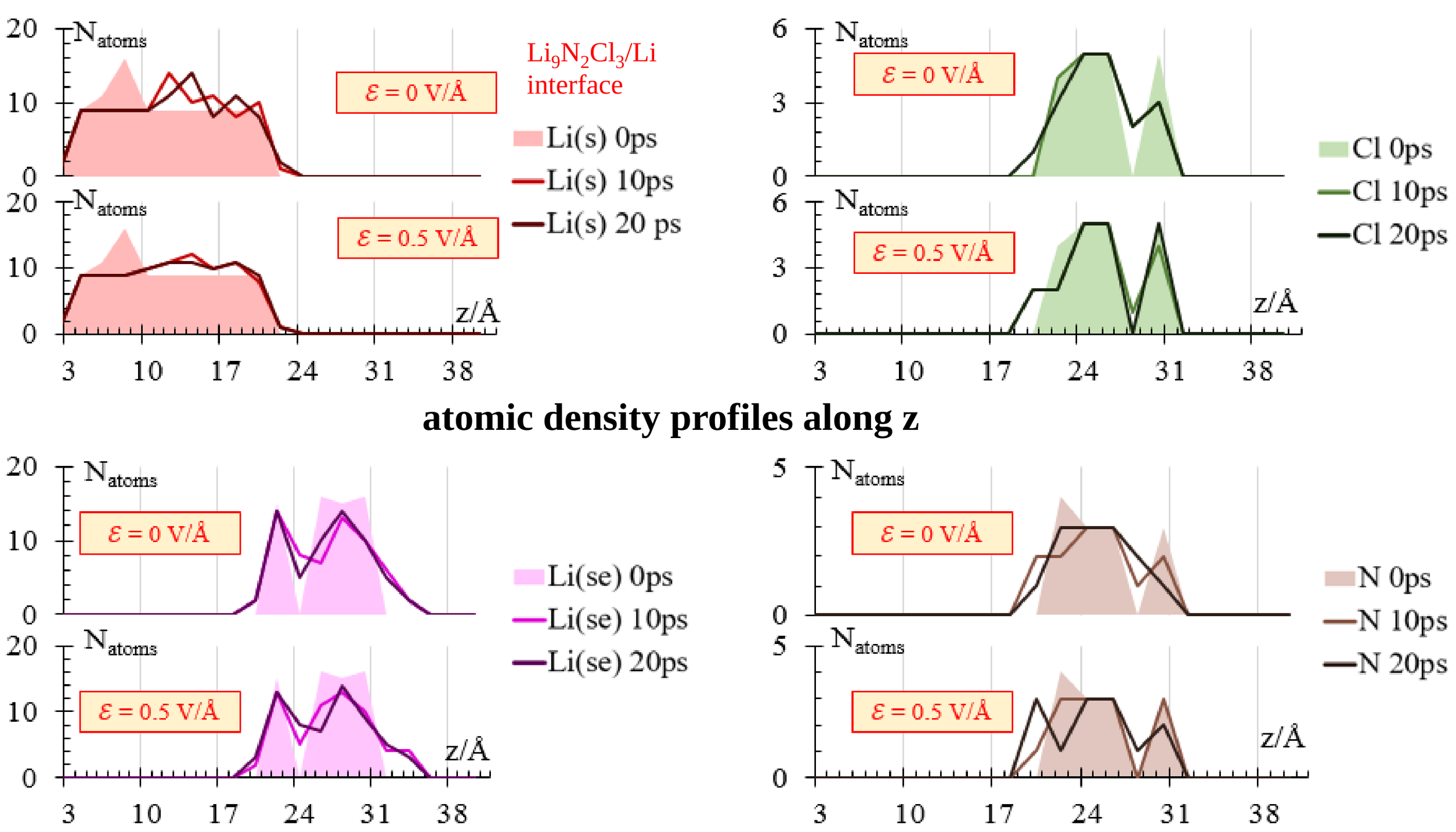
# Coordination number of Cl and N at the interphase during AIMD simulation



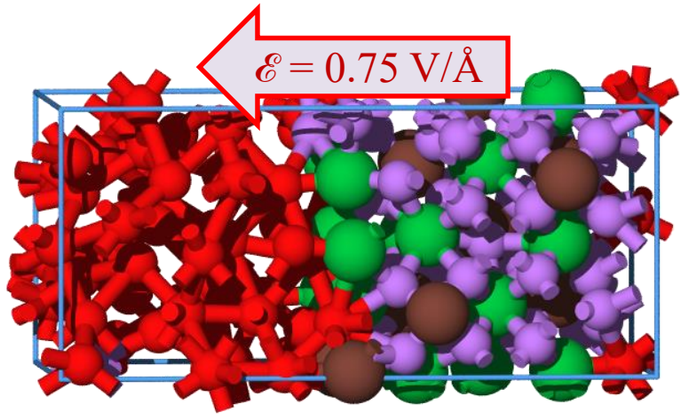



**atomic density profiles along z**

# Nano-battery model: Li-metal/$Li_9N_2Cl_3$/NMC

1 Ab-Initio MD model to study an take parameters of interfacial behavior Anode/Electrolyte

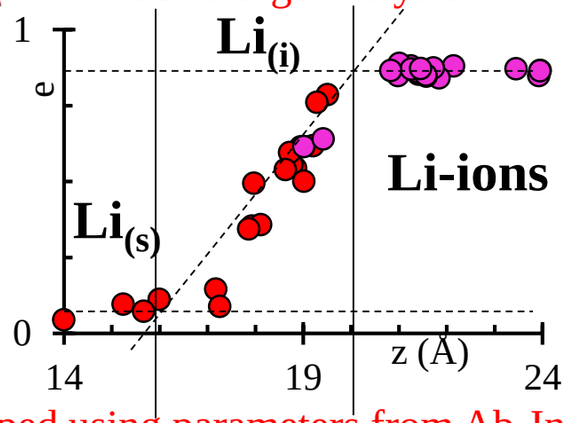
AIMD DFT PBE, $\tau$ = 0.5 fs, $t_{AIMD}$ = 50 ps, $E_{cutoff}$ = 40 Ry ($\lambda_{cutoff}$ = 0.5 Å), $\mathscr{E}$ = 0.75 V/Å



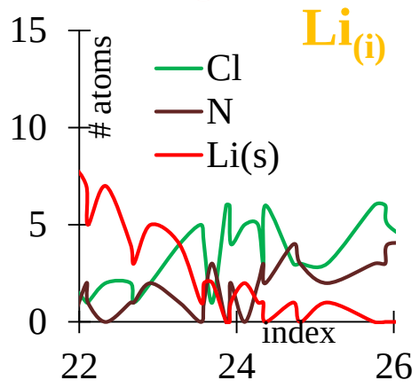

10.14 × 11.41 × 22.41 Å

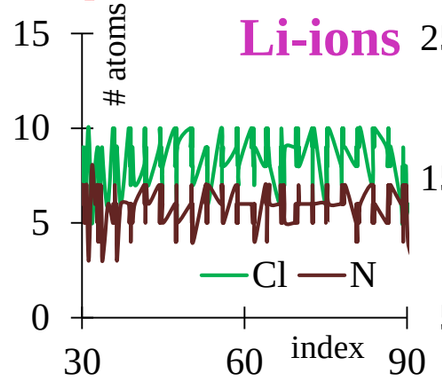
ML classifier is trained with data obtained from AIMD to develop a full Nano-battery model considering:

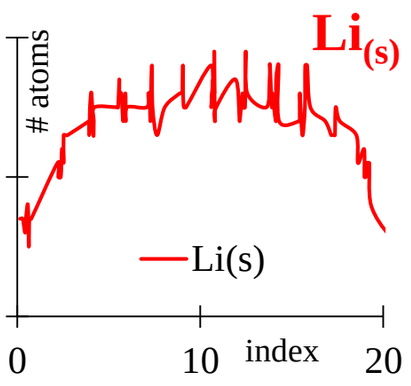
Bader charge analysis




Atoms neighborhood in an sphere with r = 5 Å / 3 Li types are recognized




2 Nanobattery MD model is developed using parameters from Ab-Initio MD simulation

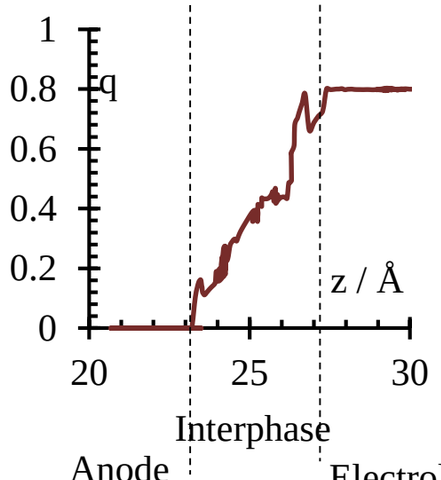
LAMMPS: MD, NVT, $\tau$ = 0.01 fs, $t_{MD}$ = 1.2 ns, $\mathscr{E}$ = 0.75 V/Å, ML algorithm every 1 fs

21.62 × 21.62 × 106 Å

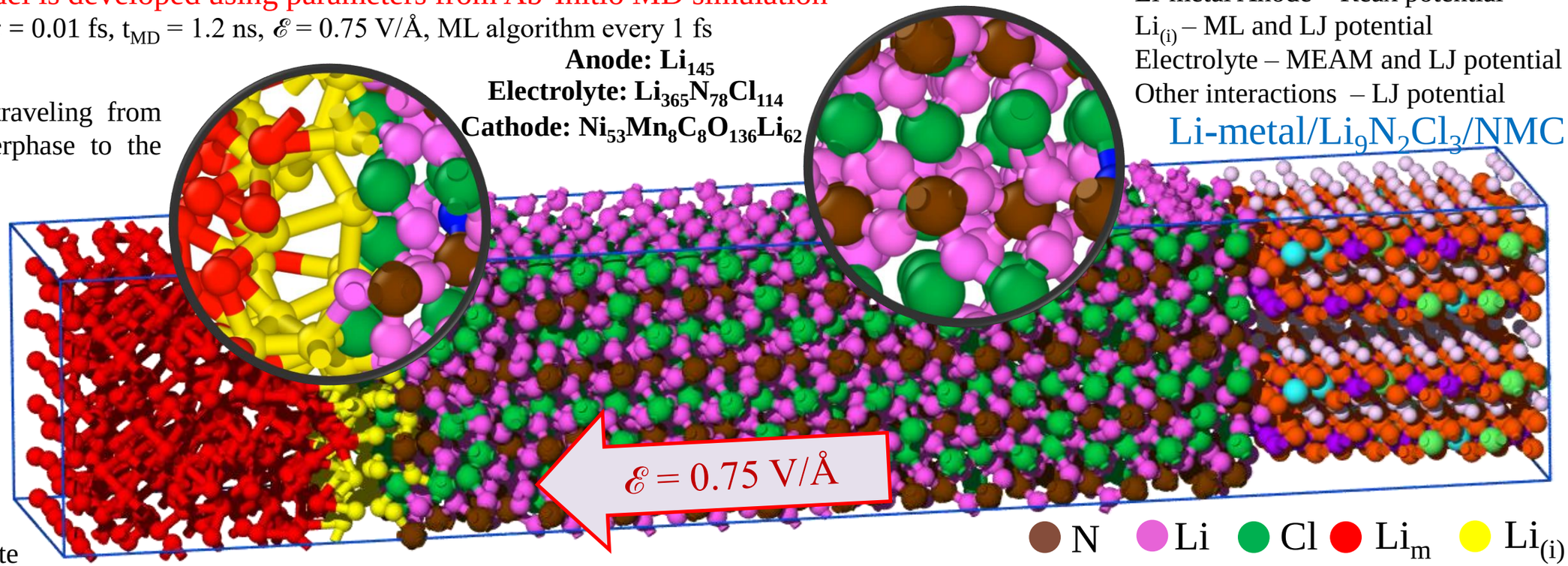
**Anode: $Li_{145}$**
**Electrolyte: $Li_{365}N_{78}Cl_{114}$**
**Cathode: $Ni_{53}Mn_8C_8O_{136}Li_{62}$**

Li-metal Anode – Reax potential
$Li_{(i)}$ – ML and LJ potential
Electrolyte – MEAM and LJ potential
Other interactions – LJ potential

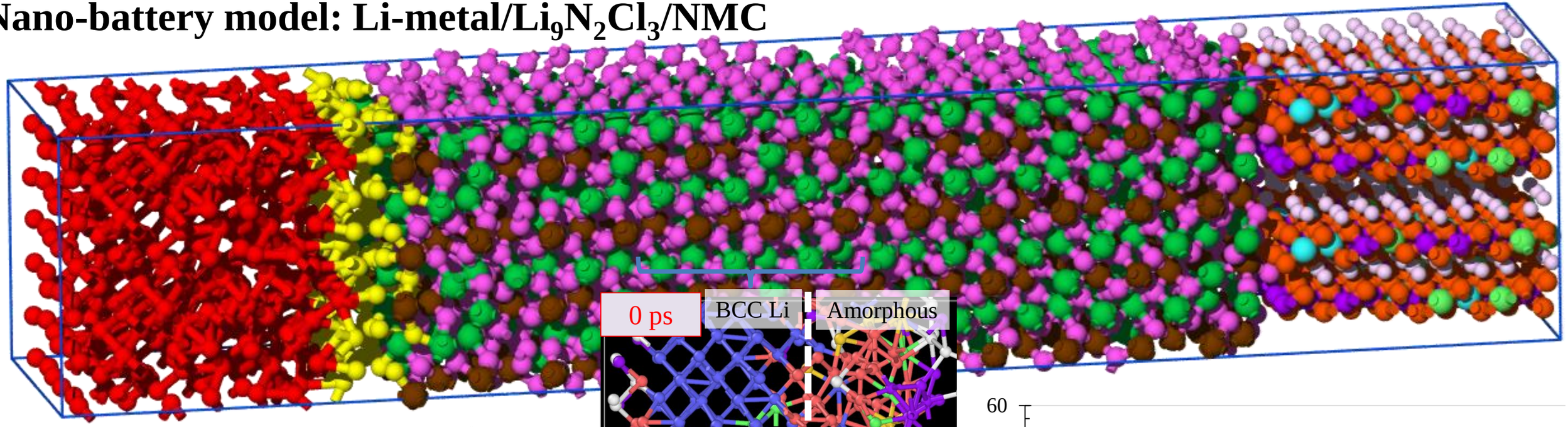
Charge evolution of a Li traveling from electrolyte through the interphase to the anode.




Li-metal/$Li_9N_2Cl_3$/NMC

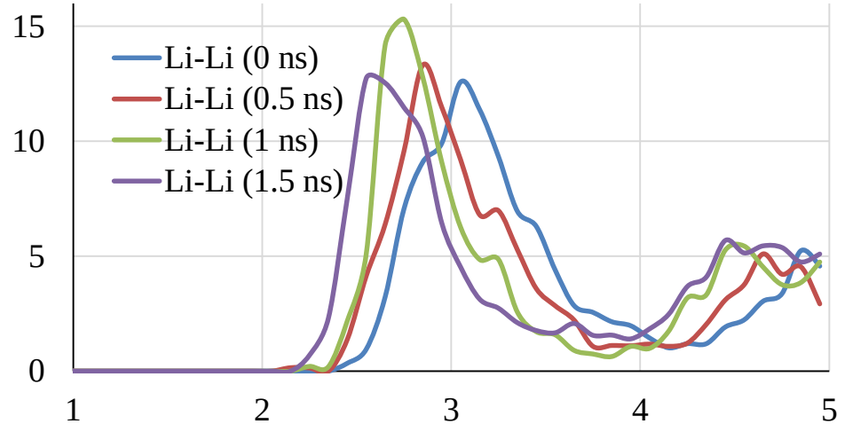


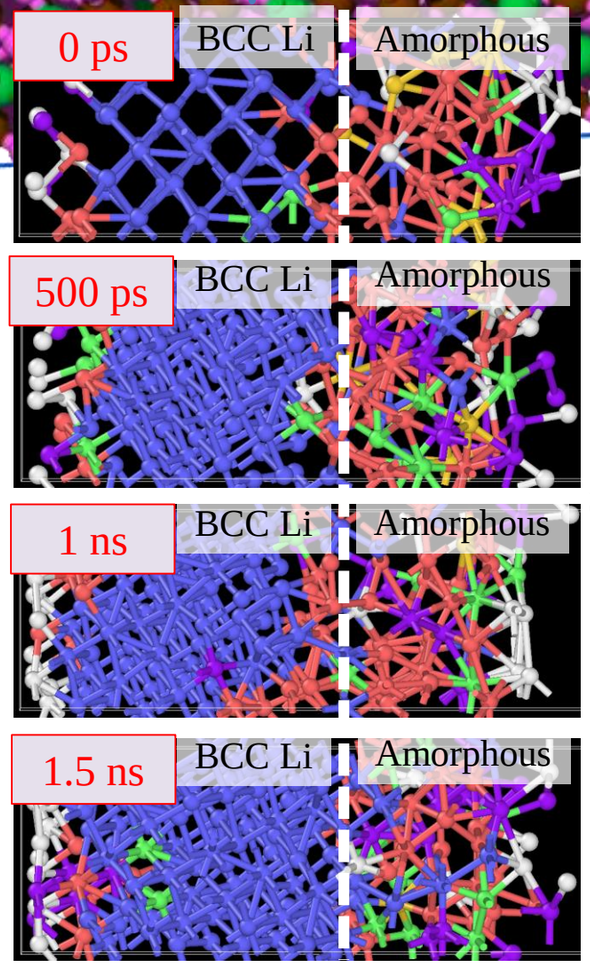
# Nano-battery model: Li-metal/$Li_9N_2Cl_3$/NMC

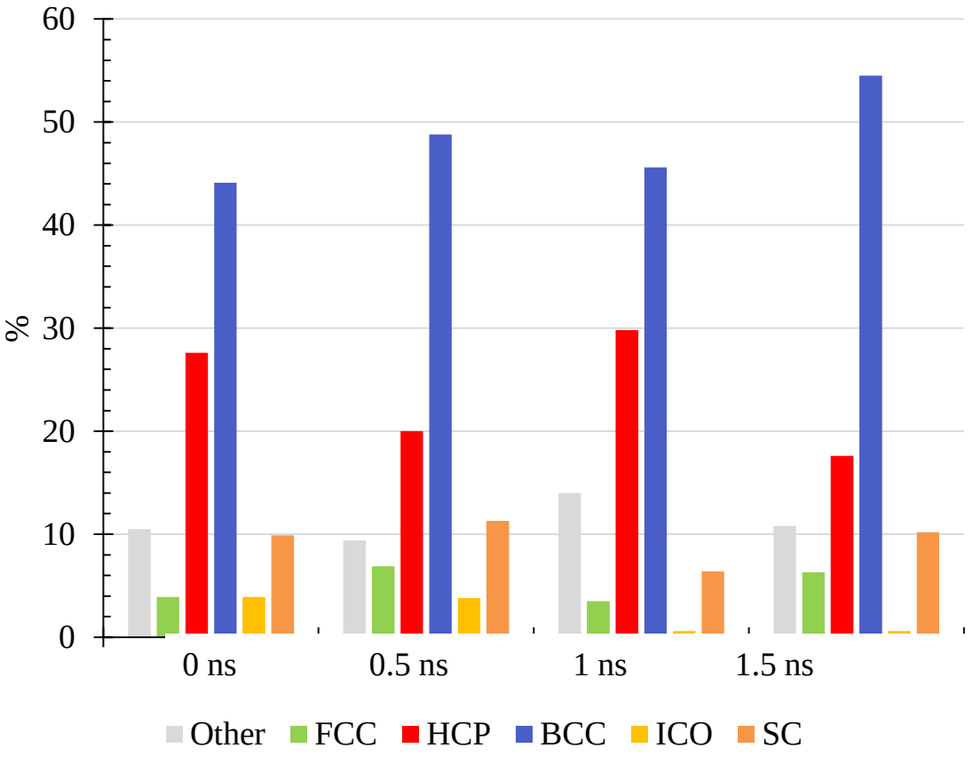


## Lithiation due to an $\mathscr{E} = 0.75$ V/Å

Polyhedral template matching algorithm is used to identify crystallographic structures.
Li-metal anode shows two clear phases during lithiation: BCC/Amorphous

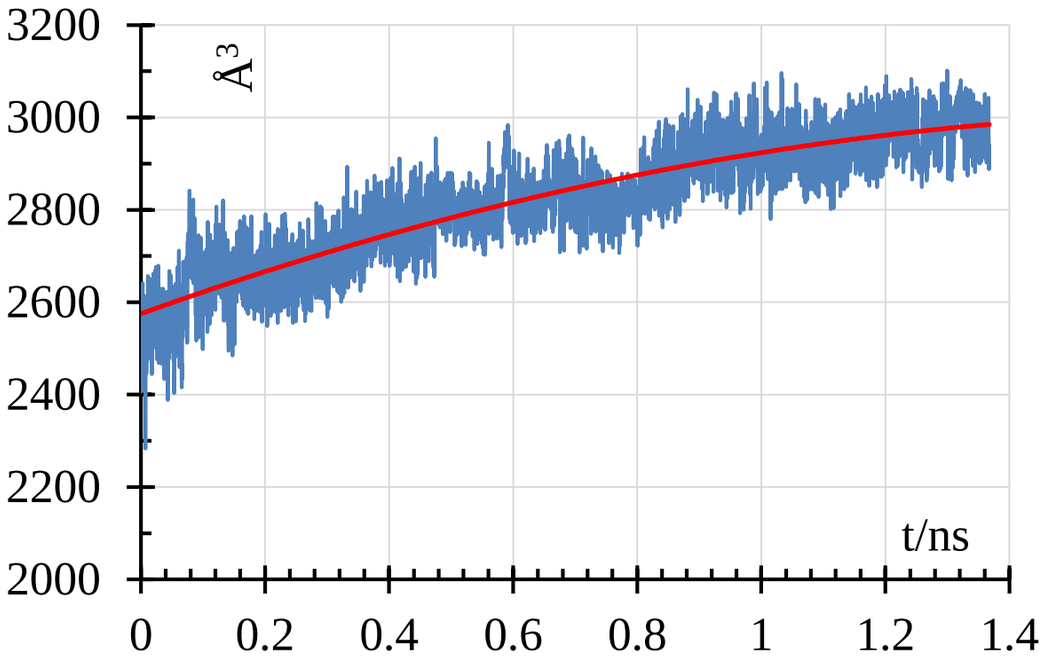


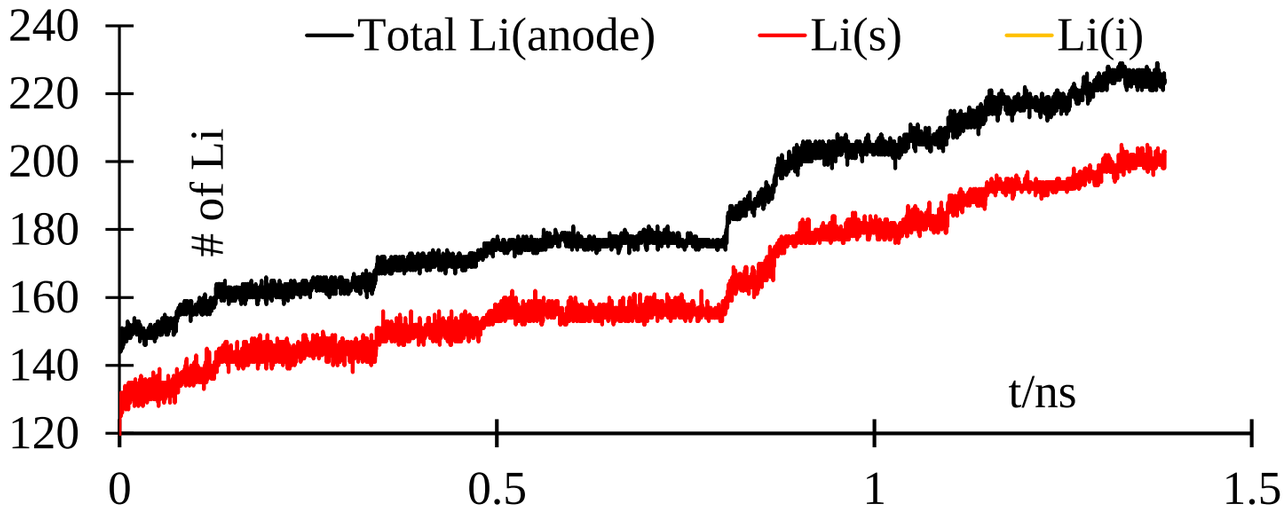



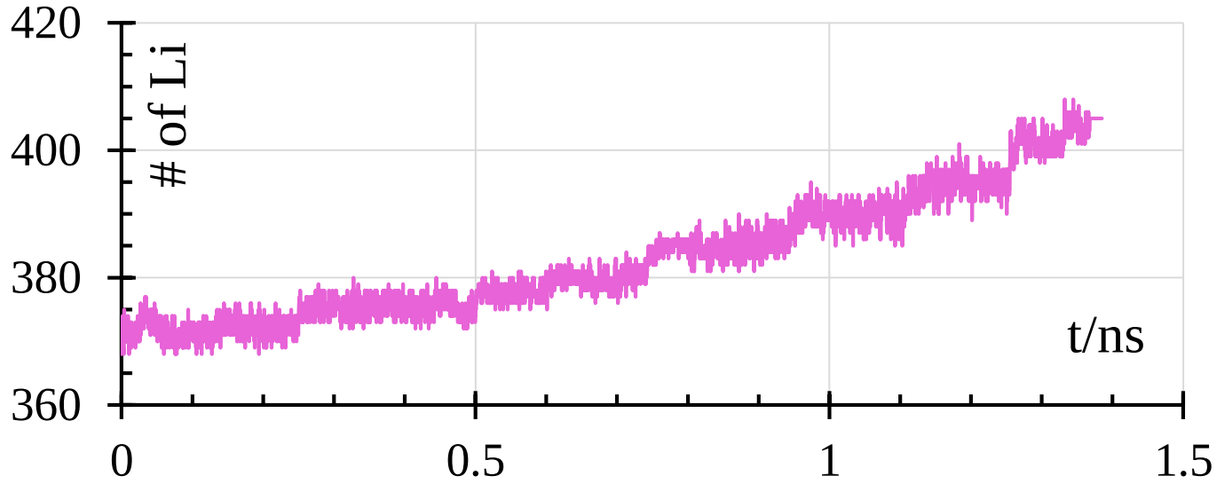



# Nano-battery model: Li-metal/$Li_9N_2Cl_3$/NMC

Lithiation due to an $\mathscr{E} = 0.75$ V/Å

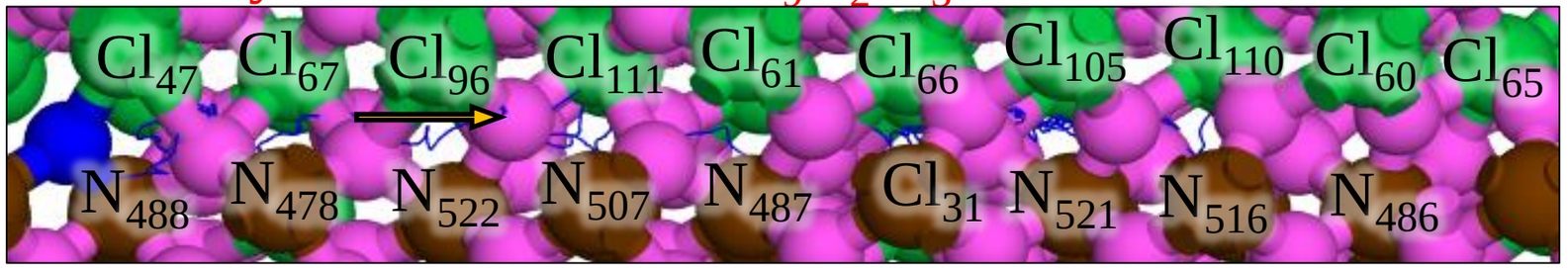


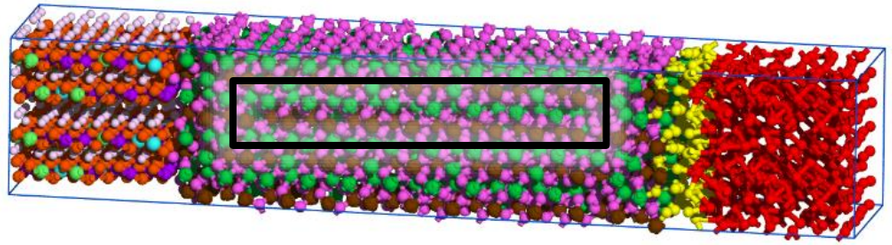



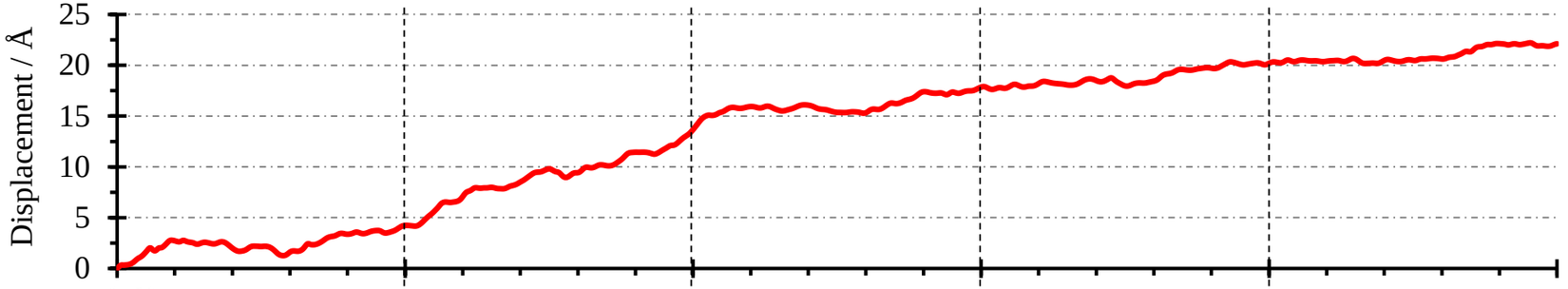



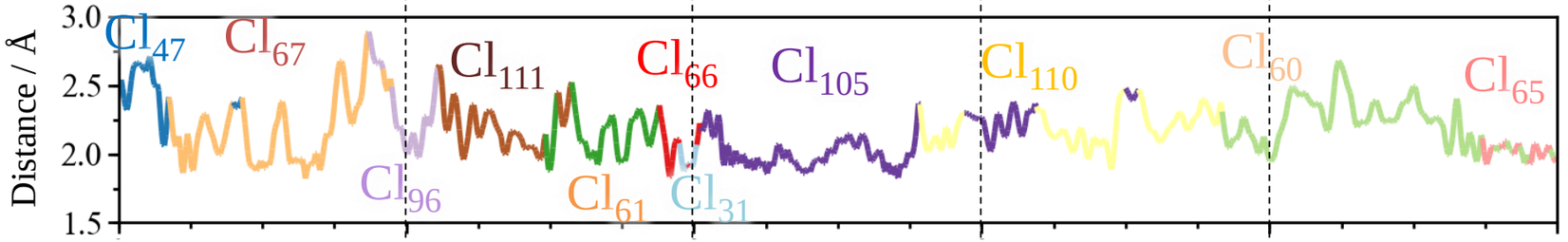
# Nano-battery model: Li-metal/$Li_9N_2Cl_3$/NMC

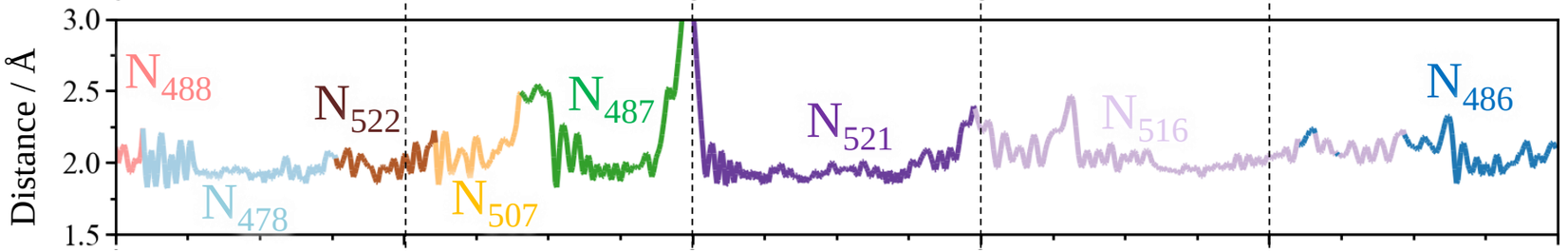
Trajectory of a Li-ion through the electrolyte (5 ps)

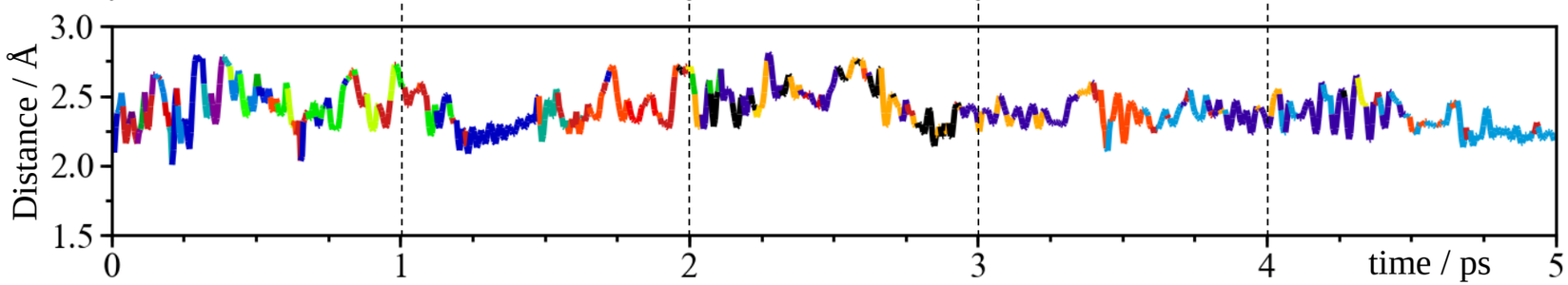


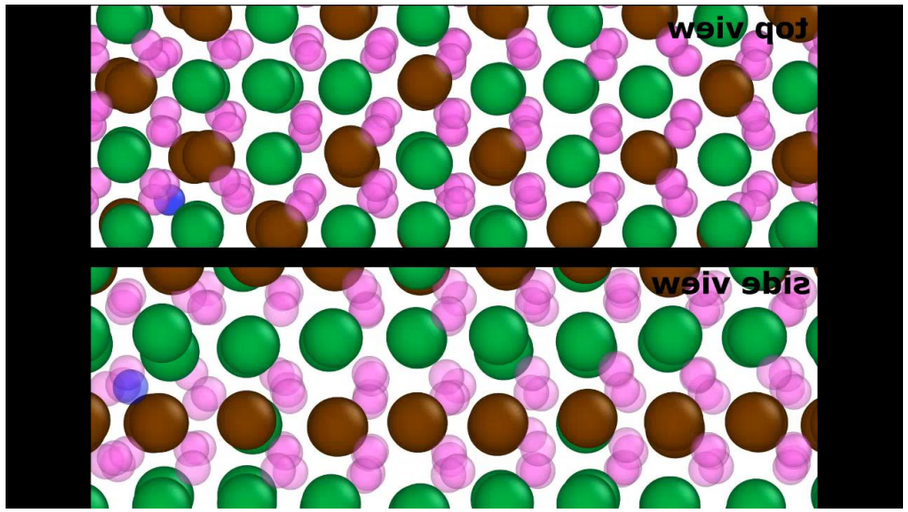



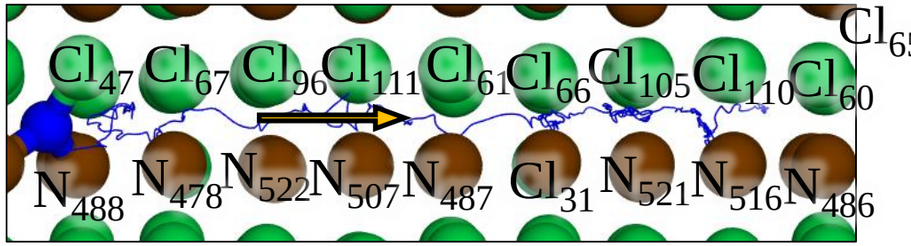



NN Li-ion

top view


side view

# Conclusions

- Li closest to interface shows major diffusion (B)
- new bonds with N and Cl of the SSE (B)
- SSE shows stability at the interface with Li-metal (B)
- Initial reactions on the SSE(002) plane (of $Li_9N_2Cl_3$) (NE)
- Reactions don't modify crystallographic structure of electrolyte (B)
- $Li_{(s)}$ density increases at both interfaces, (001) and (002) (NE)
- Major density change at (002) interface due to negative N and Cl (NE)
- N and Cl have 3-4 Li NNs at the beginning of the simulation (NE)
- To complete 7-8 Li NNs of $Li_9N_2Cl_3$, N and Cl take $Li_{(s)}$ from anode
- $Li_{(s)}$ diffusion anode to electrolyte at (001) lower than at (002) (NE)
- Because Cl and N already have at least 7 Li at the $Li_9N_2Cl_3$(001) no need to take $Li_{(s)}$ from the anode. (NE)

# Conclusions

- Li-BCC structure changes into HCP (E)
- But BCC and HCP energies difference ≤ 10 meV
- Thus, @ 300 K (26 meV), transitions are highly possible (E)
- but not necessarily due to the electric field.
- (001) better than (002) of SSE to reduce deformation of anode (NE)
- No new phase formed due to interfacial interactions (B)
- no expected, if we extend the simulation times based on MSD trends and charge stability. (B)
- $Li_9N_2Cl_3$ remains very stable in contact with Li-metal (B)
- Theory correctly model metallic-insulator interface (B)

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TACC

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