Ionic Liquids simulations : obtention of structural and transport properties from molecular dynamics

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Ionic Liquids simulations : obtention of structural and transport properties from molecular dynamics

OUTLINE

1. **INTRODUCTION : MOLECULAR DYNAMICS (MD)**
   - ➢ ENSEMBLE AVERAGE
   - ➢ ERGODIC HYPOTHESIS
   - ➢ AB-INITIO MD vs CLASSICAL MD
2. **METHODOLOGY**
   - ➢ FORCE FIELD
   - ➢ IONIC LIQUID MIXTURES
   - ➢ COMPUTATIONAL TOOLS
   - ➢ SIMULATION SCHEME
3. **RESULTS**
   - ➢ LIQUID DENSISTY
   - ➢ HAMILTONIAN CONSERVATION FUNCTION
   - ➢ STRUCTURAL PROPERTIES
   - ➢ TRANSPORT PROPERTIES
   - ➢ MECHANISM OF THE Li^+ CATION TRANSPORT

I. INTRODUCTION : MOLECULAR DYNAMICS (MD)

- **MD is a specialized discipline of Computer Simulation (CS) based on Statistical Mechanics (SM)**

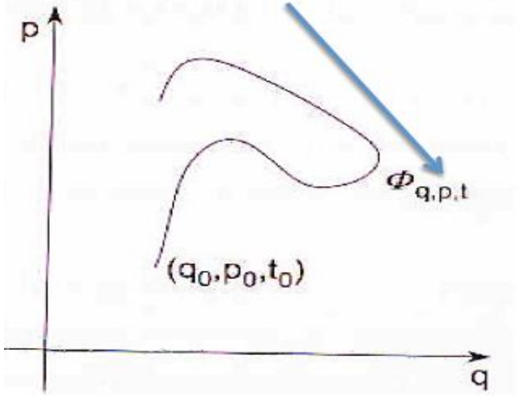
  - CS is a mathematical prediction of physical process on modern computer systems.

    ✓ *Particle models* ➔physical systems consists of discrete particles and their interactions

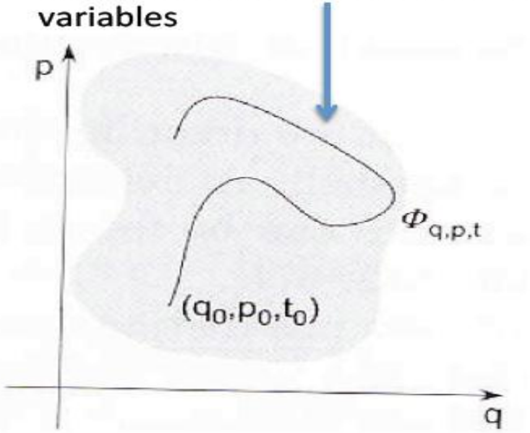
  - SM studies how systems in an ensemble behave on average

    ✓ **Phase space** Γ ➔space spanned by 6N (being N number of particles) generalized positions $\mathbf{q}(t) = (\mathbf{q}_1(t), \ldots, \mathbf{q}_N(t))$ and momenta $\mathbf{p}(t) = (\mathbf{p}_1(t), \ldots, \mathbf{p}_N(t))$

Trajectory=evolution of system over the time



Ensemble=set of physically similar systems which led to the same values for the macroscopic state variables



I. INTRODUCTION : MOLECULAR DYNAMICS (MD)

- **ENSEMBLE AVERAGE**

Physical quantity

$$\langle A \rangle = \frac{\int_\Gamma A(\mathbf{p},\mathbf{q},t) f_N(\mathbf{p},\mathbf{q},t) d\mathbf{p} d\mathbf{q}}{\int_\Gamma f_N(\mathbf{p},\mathbf{q},t) d\mathbf{p} d\mathbf{q}}$$

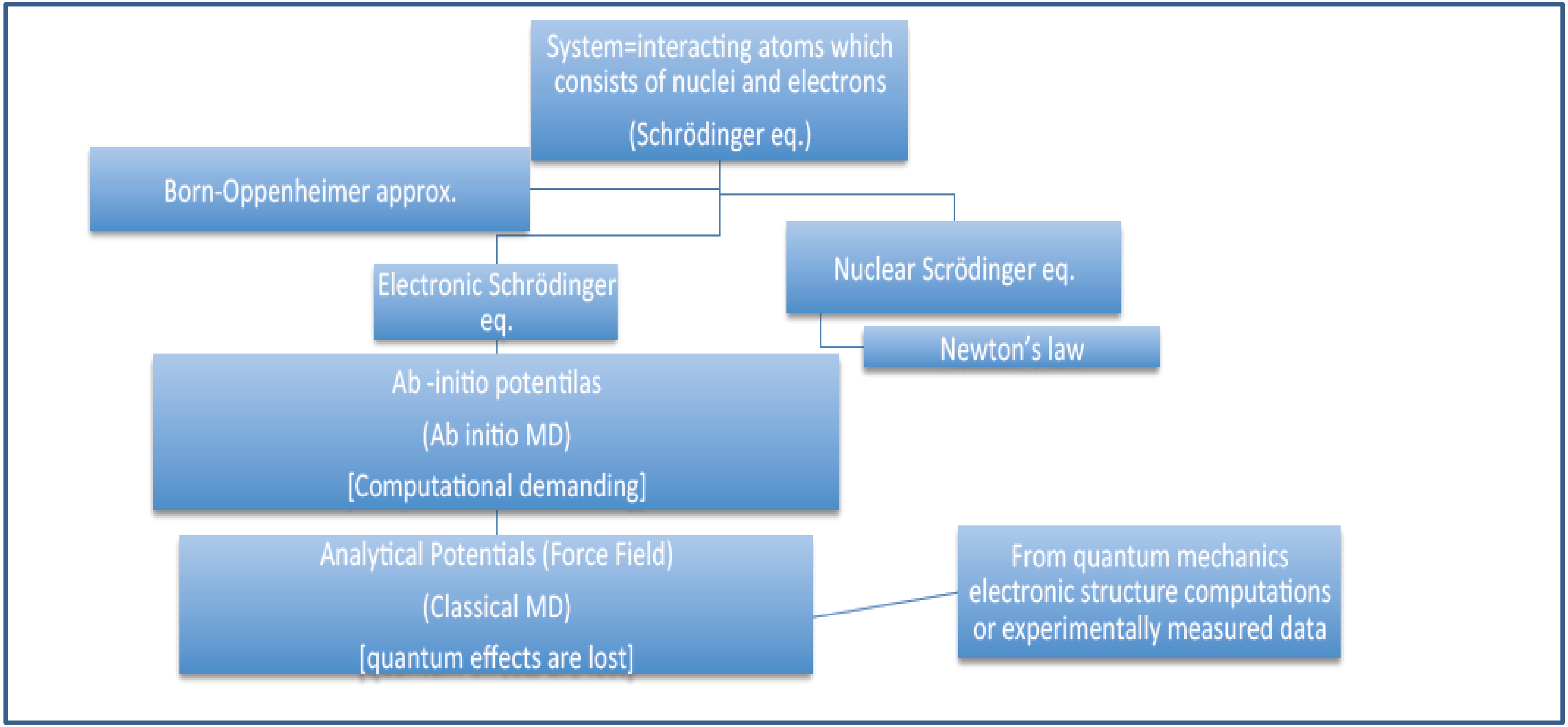
Phase density $f_N(\mathbf{p},\mathbf{q},t)$= probability density of the system to be found in subdomain $[\mathbf{q},\mathbf{q}+d\mathbf{q}] \times [\mathbf{p},\mathbf{p}+d\mathbf{p}]$

- **ERGODIC HYPOTHESIS**

$\langle A \rangle = \bar{A}$ where $\bar{A} = \frac{1}{\tau}\int_{t_0}^{t_0+\tau} A\left(\Phi_{\mathbf{q},\mathbf{p},t}(t)\right) dt$ is the **time average**

I. INTRODUCTION : MOLECULAR DYNAMICS (MD)

- **AB-INITIO MD vs CLASSICAL MD**



System=interacting atoms which consists of nuclei and electrons

(Schrödinger eq.)

Born-Oppenheimer approx.

Electronic Schrödinger eq.

Nuclear Scrödinger eq.

Newton's law

Ab -initio potentilas

(Ab initio MD)

[Computational demanding]

Analytical Potentials (Force Field)

(Classical MD)

[quantum effects are lost]

From quantum mechanics electronic structure computations or experimentally measured data

II. METHODOLOGY

- **APPLE&P**[1,2] → Transferable, quantum-chemistry-based, Atomistic many-body Polarizable Potential for Liquids, Electrolytes, & Polymers force field.

$$U^{\mathrm{tot}}(\mathbf{r}) = U^{\mathrm{NB}}(\mathbf{r}) + \sum_{\mathrm{bends}} U^{\mathrm{BEND}}(\theta_{ijk}) + \sum_{\mathrm{dihedrals}} U^{\mathrm{DIHEDRAL}}(\phi_{ijkl}) + \sum_{\substack{\mathrm{improper} \\ \mathrm{dihedrals}}} U^{\mathrm{IMP}}(\phi_{ijkl}^{\mathrm{imp}})$$

Bonded interactions

$$U^{\mathrm{BEND}}(\theta_{ijk}) = \frac{1}{2}k_{\alpha\beta\gamma}^{\mathrm{BEND}}(\theta_{ijk} - \theta_{ijk}^{0})^{2}$$

$$U^{\mathrm{DIHEDRAL}}(\phi_{ijkl}) = \sum_{n} \frac{1}{2}k_{\alpha\beta\gamma\delta,n}^{\mathrm{DIHEDRAL}}[1 - \cos(n\phi_{ijkl})]$$

$$U^{\mathrm{IMP}}(\phi_{ijkl}^{imp}) = \frac{1}{2}k_{\alpha\beta\gamma\delta}^{\mathrm{IMP}}(\phi_{ijkl}^{\mathrm{imp}})^{2}$$

Non-Bonded interactions

$$U^{\mathrm{NB}}(\mathbf{r}) = U^{\mathrm{RD}}(\mathbf{r}) + U^{\mathrm{coul}}(\mathbf{r}) + U^{\mathrm{pol}}(\mathbf{r}) = \sum_{i>j}\left(A_{\alpha\beta}\exp(-B_{\alpha\beta}r_{ij}) - C_{\alpha\beta}r_{ij}^{-6} + D\left(\frac{12}{B_{\alpha\beta}r_{ij}}\right)^{12}\right) + \sum_{i>j}\left(\frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}\right) - \frac{1}{2}\sum_{i}\vec{\mu}_i \cdot \vec{\mathrm{E}}_i^{0}$$

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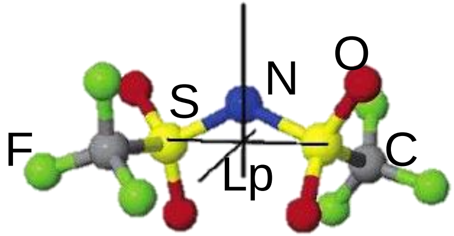
[1] O. Borodin and G. D. Smith, *J. Chem. Phys. B,* 6279-6292 (**2006**)

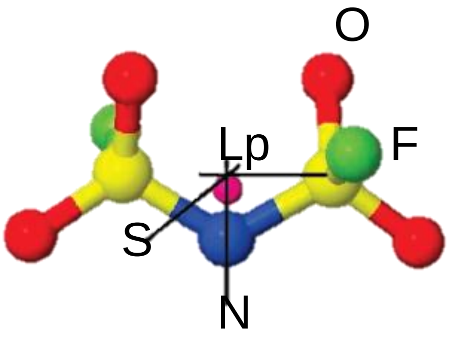
[2] O. Borodin, *J. Chem. Phys. B,* 11463-11478 (**2009**)

II. METHODOLOGY

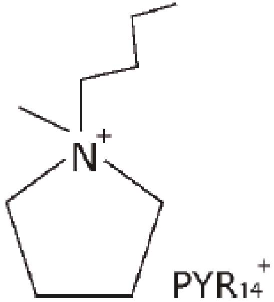
- **IONIC LIQUID** (**IL**) → $PYR_{14}TFSI$ ($PYR_{14}FSI$) doped with 0.10 mol fraction LiTFSI (LiFSI)



bis[(trifluoromethyl)sulfonyl]imide anion (TFSI)



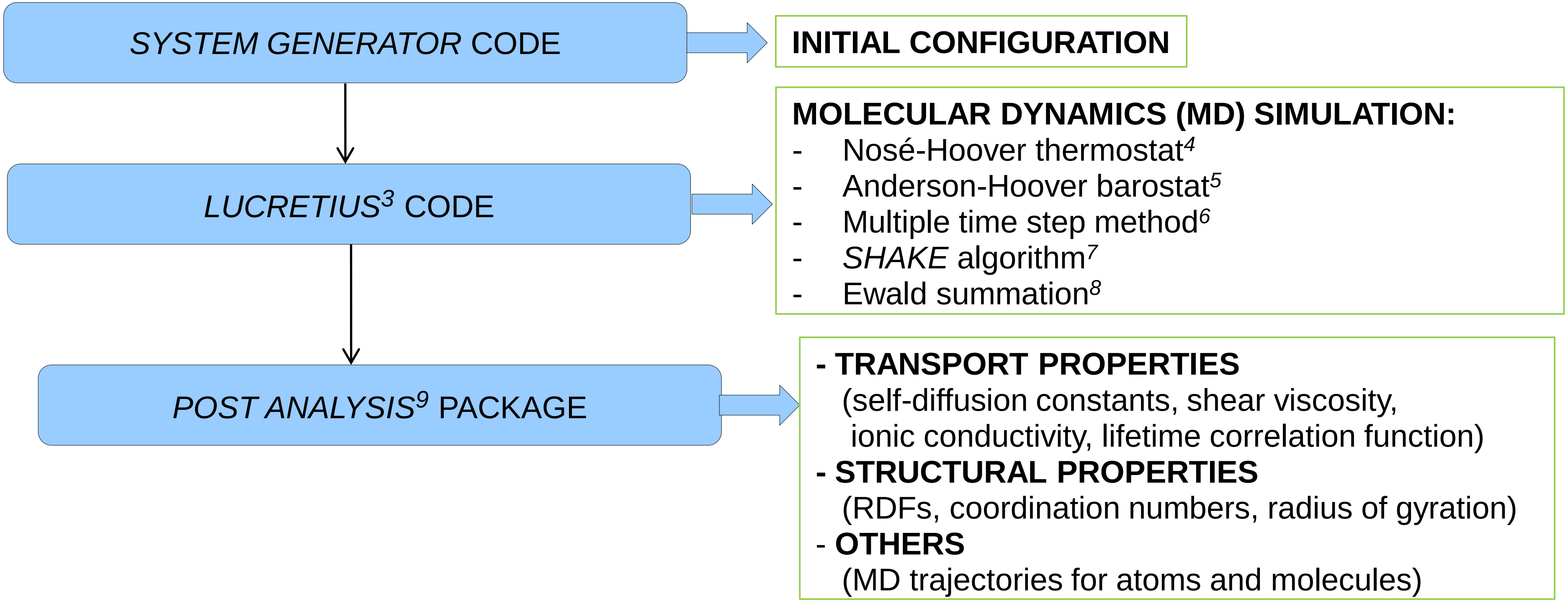
bis(fluorosulfonyl)imide anion (FSI)



***N*-butyl-*N*-methylpyrrolidinium cation (PYR_{14})**

II. METHODOLOGY

. COMPUTATIONAL TOOLS



SYSTEM GENERATOR CODE

INITIAL CONFIGURATION

LUCRETIUS[3] CODE

MOLECULAR DYNAMICS (MD) SIMULATION:

- Nosé-Hoover thermostat[4]
- Anderson-Hoover barostat[5]
- Multiple time step method[6]
- *SHAKE* algorithm[7]
- Ewald summation[8]

POST ANALYSIS[9] PACKAGE

- TRANSPORT PROPERTIES

(self-diffusion constants, shear viscosity, ionic conductivity, lifetime correlation function)

- STRUCTURAL PROPERTIES

(RDFs, coordination numbers, radius of gyration)

- **OTHERS**

(MD trajectories for atoms and molecules)

[3] Ayyagari, C.; Bedrov, D.; Borodin, O.; Smith, G. D. *Lucretius, MD simulation code* http://www.eng.utah.edu/gdhsmith/lucretius.html

[4] Martyna,G. J.; Klein, M. L.; Tuckerman, M. *J. Chem. Phys.* **97**, 2635-2643 (1992)

[5] Melchionna, S.; Ciccoq, G.; Holian, B. L. *Mol. Phys.* **78**, 533-544 (1993)

[6] Tuckerman, M. E.; Berne, B. J.; Martyna, G. J. *J. Chem. Phys.* **94**, 6811-6815 (1991)

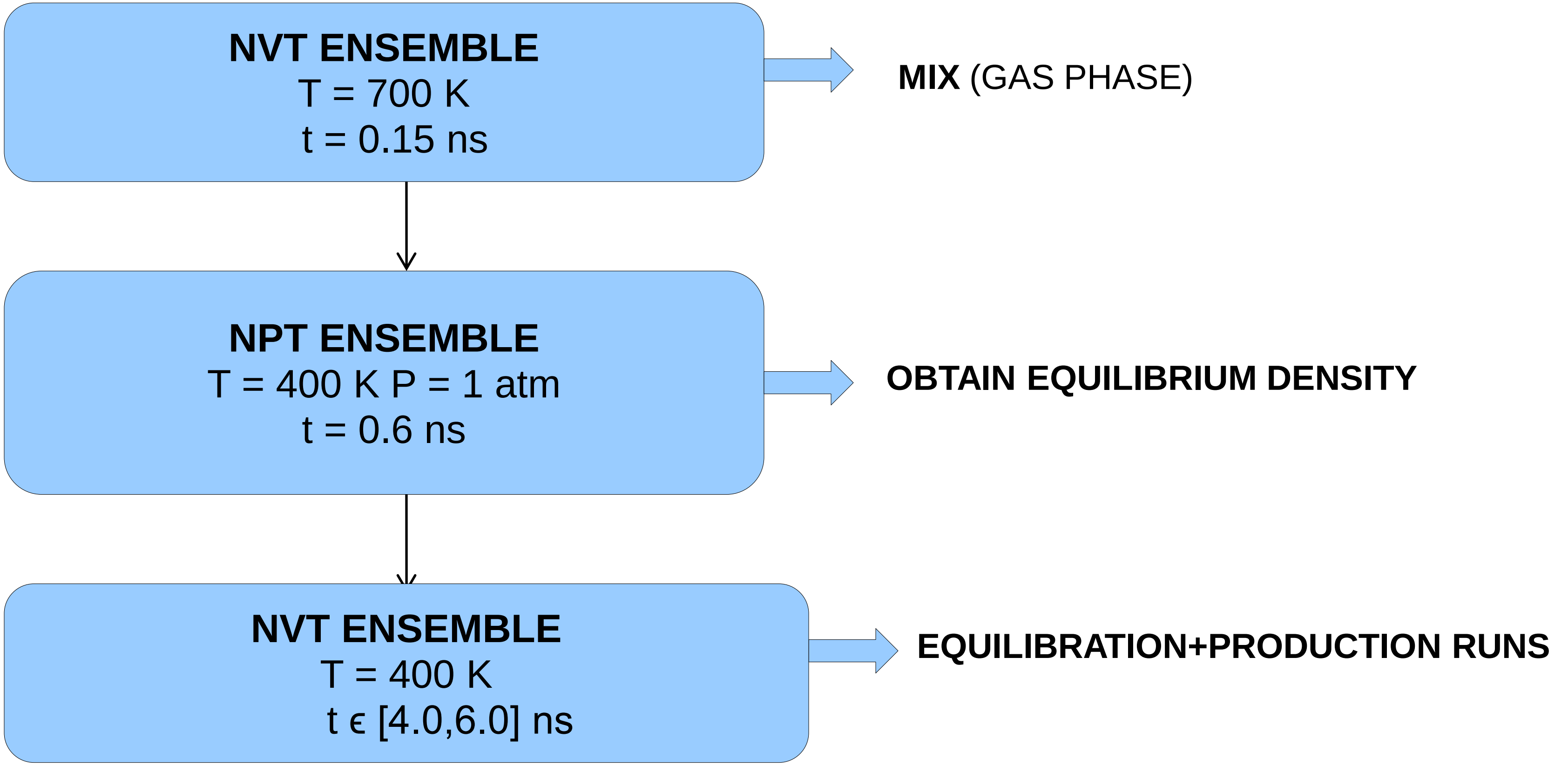
[7] Palmer, B. J. *J. Comp. Phys*. **104**, 470-472 (1993)

[8] Abdulnour Y. Toukmaji and John A. Board Jr. *Comp. Phys. Com.* **95**, 73-92 (1996)

[9] Solano, C. J. F. *MD Post analysis package* (UMons)

II. METHODOLOGY

. SIMULATION SCHEME



NVT ENSEMBLE
T = 700 K
t = 0.15 ns

MIX (GAS PHASE)

NPT ENSEMBLE
T = 400 K P = 1 atm
t = 0.6 ns

OBTAIN EQUILIBRIUM DENSITY

NVT ENSEMBLE
T = 400 K
t ϵ [4.0,6.0] ns

EQUILIBRATION+PRODUCTION RUNS

III. RESULTS

LIQUID DENSITY

- Excellent predictive capabilities of the force field in previous simulations.

- 0.10LiTFSI-PYR14TFSI > 0.10LiFSI-PYR14FSI

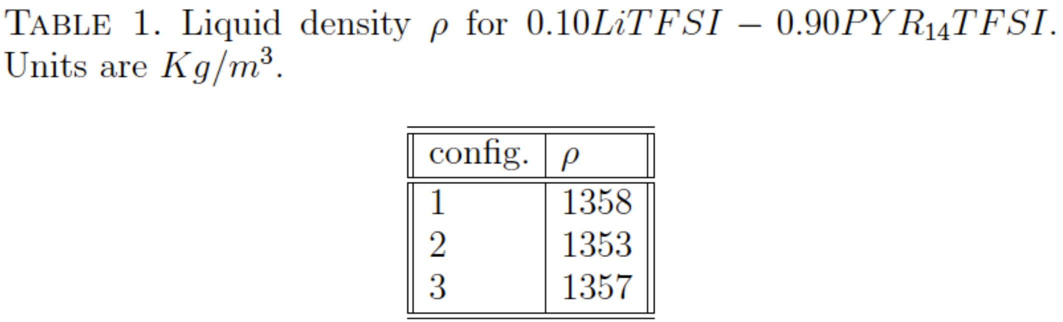


TABLE 1. Liquid density ρ for $0.10LiTFSI - 0.90PYR_{14}TFSI$. Units are Kg/m^3.

config.	ρ
1	1358
2	1353
3	1357

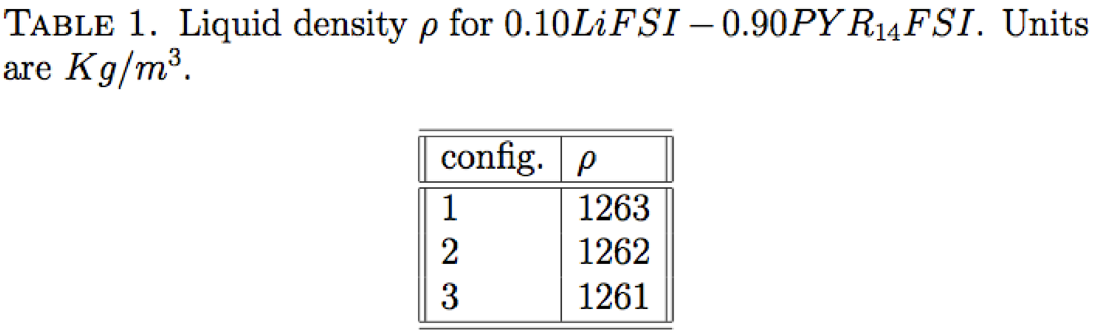


TABLE 1. Liquid density ρ for $0.10LiFSI - 0.90PYR_{14}FSI$. Units are Kg/m^3.

config.	ρ
1	1263
2	1262
3	1261

III. RESULTS

HAMILTONIAN CONSERVATION FUNCTION

- Hamiltonian is a conserved quantity for the equations of motion in NVT and NPT ensembles.

- In MD simulations, Hamiltonian conservation function allows to estimate if Hamiltonian conservation is acceptable.

$$\Delta\hat{H}(\Delta t) = \frac{1}{N}\sum_{k=1}^{N}\left|\frac{H(k\Delta t) - H(0)}{H(0)}\right|$$

$N\Delta t$ → Total simulation time

TABLE 2. Hamiltonian conservation function (ΔH) for $0.10LiTFSI - 0.90PYR_{14}TFSI$.

config.	method	$ln\Delta H$
1	one step	-3.76
2	one step	-3.62
3	one step	-3.97
1	two steps	-3.73
2	two steps	-3.78

TABLE 2. Hamiltonian conservation function (ΔH) for $0.10LiFSI - 0.90PYR_{14}FSI$.

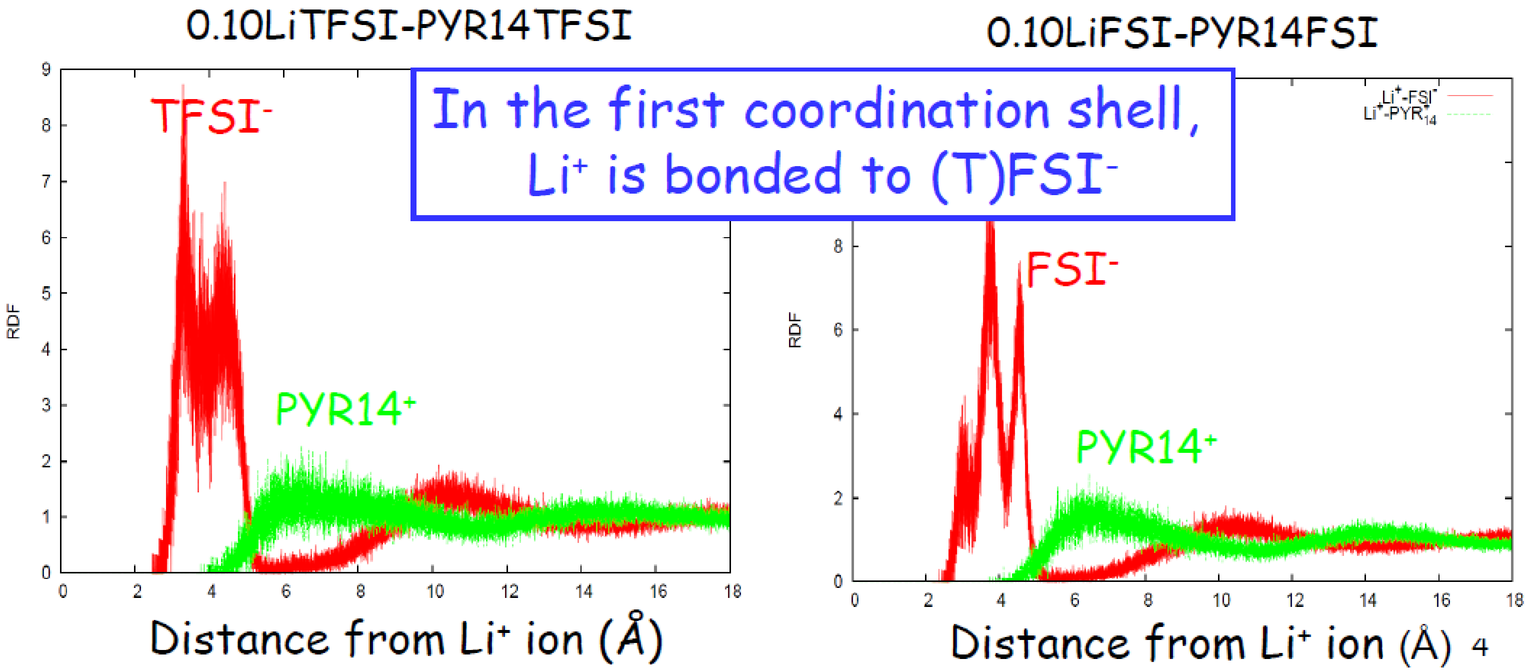
config.	method	$ln\Delta H$
1	one step	-5.11
2	one step	-4.62
3	one step	-5.20
1	two steps	-4.75
2	two steps	-4.68

III. RESULTS

• STRUCTURAL PROPERTIES : RADIAL DISTRIBUTION FUNCTIONS (RDF)

- RDF describes how the density of different type of atoms (molecules) varies as a function of the distance from a reference type of atom (molecule).

- CM RDF for Li+ cation :


0.10LiTFSI-PYR14TFSI

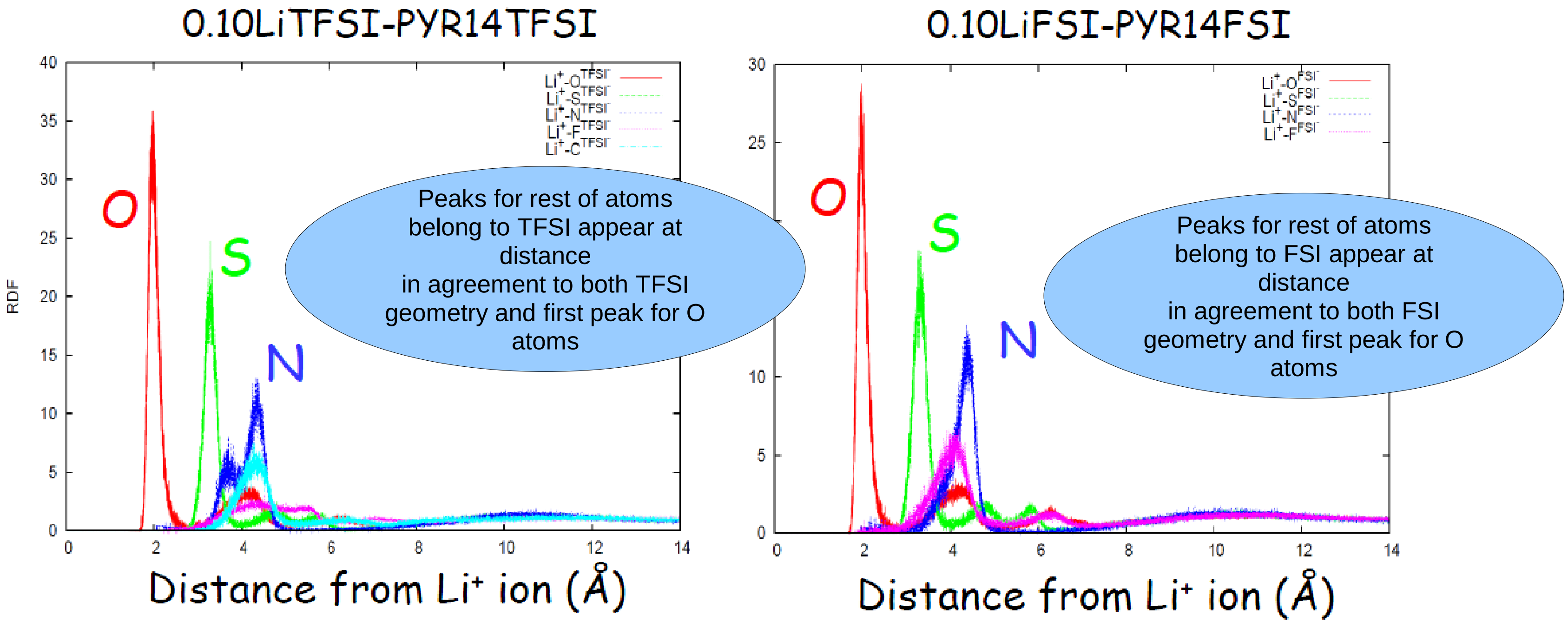
0.10LiFSI-PYR14FSI

In the first coordination shell, Li^+ is bonded to $(T)FSI^-$

III. RESULTS

• STRUCTURAL PROPERTIES : RADIAL DISTRIBUTION FUNCTIONS (RDF)

- RDF for Li+ cation and atoms belong to (T)FSI molecule :



Peaks for rest of atoms belong to TFSI appear at distance in agreement to both TFSI geometry and first peak for O atoms

Peaks for rest of atoms belong to FSI appear at distance in agreement to both FSI geometry and first peak for O atoms

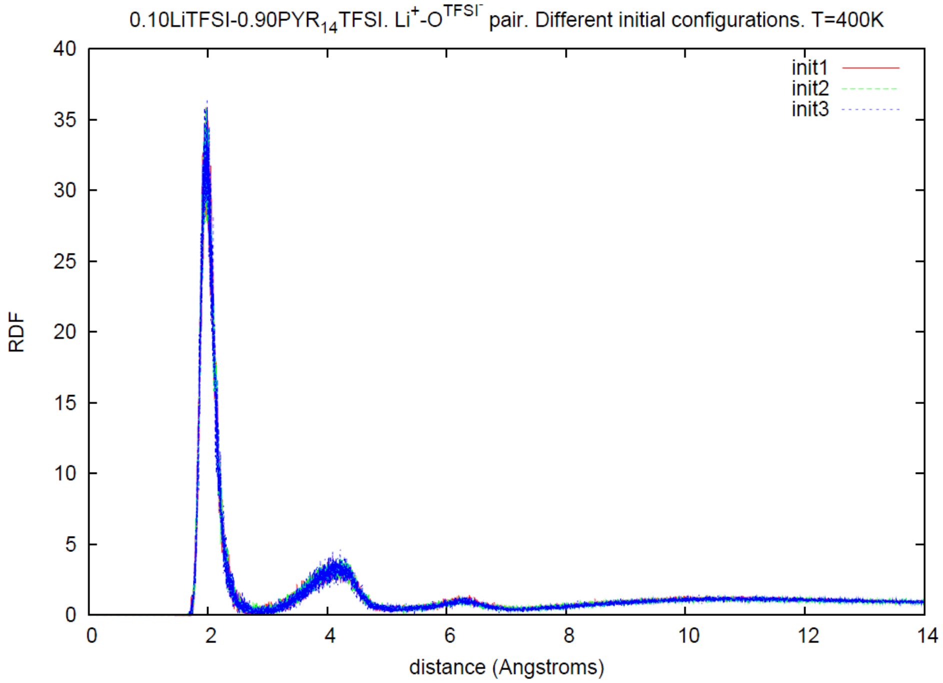
Li^+ is bonded to oxygen atoms of $(T)FSI^-$

III. RESULTS

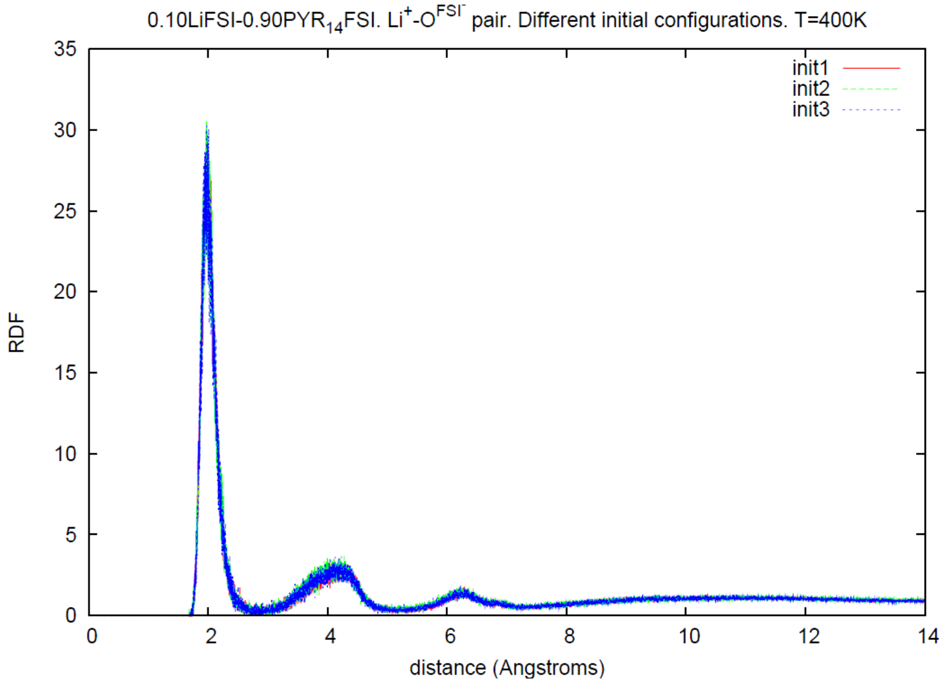
. STRUCTURAL PROPERTIES : RADIAL DISTRIBUTION FUNCTIONS (RDF)

- RDF for Li+ cation and O atom belongs to TFSI (FSI) molecule : excellent agreement is achieved for simulations from different initial configurations.

0.10LiTFSI-0.90PYR14TFSI



0.10LiFSI-0.90PYR14FSI

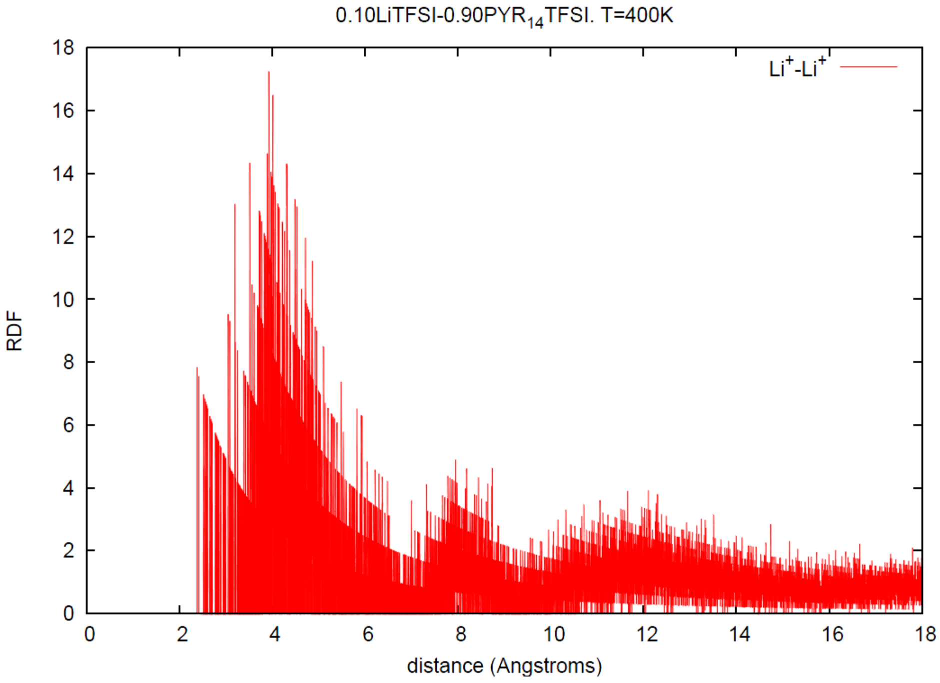


III. RESULTS

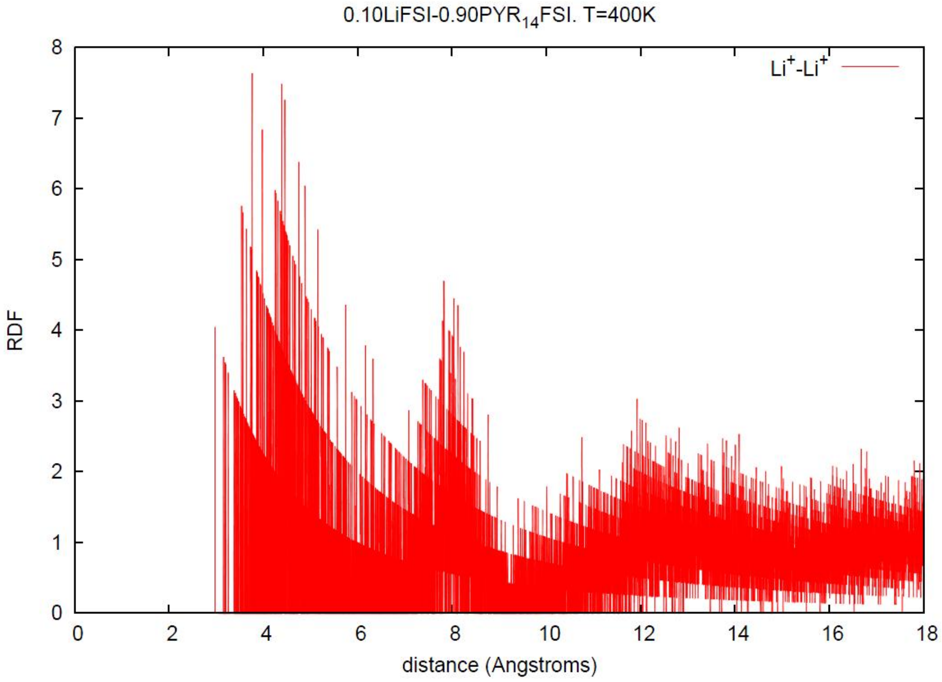
• STRUCTURAL PROPERTIES : RADIAL DISTRIBUTION FUNCTIONS (RDF)

- RDF for Li-Li cation :
  In a dilute solution of Li+ the relative positions of the Li+ vary strongly.

0.10LiTFSI-0.90PYR14TFSI

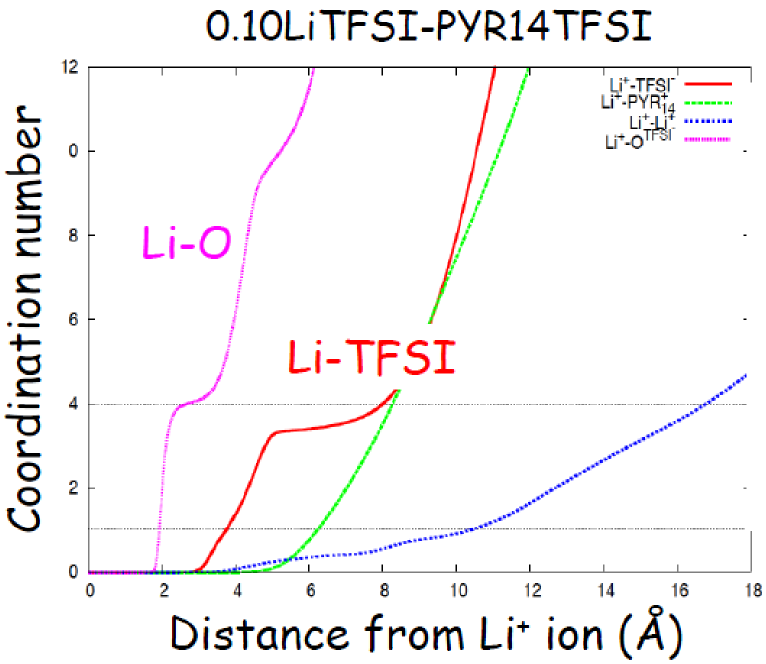


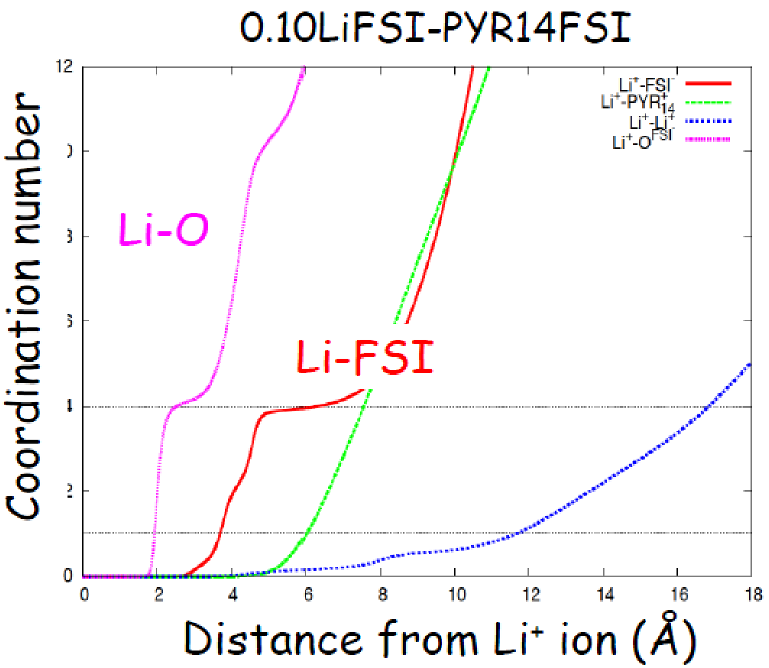
0.10LiFSI-0.90PYR14FSI



III. RESULTS

• STRUCTURAL PROPERTIES : COORDINATION NUMBER


0.10LiTFSI-PYR14TFSI


0.10LiFSI-PYR14FSI

Li⁺ is bonded to four O atoms belonging to four different (T)FSI molecules

III. RESULTS

• SUMMARY ON THE STRUCTURAL ANALYSIS

- Taking the end of strong peak for Li-TFSI and Li-FSI RDF into account, we find that Li cations are coordinated by around 4 (T)FSI molecules in ILs mixtures.

- Defining Li-O first coordination shell by a radius lower than 3 Angs. (the end of strong peak for Li-O RDF), we find that the Li cations are coordinated by around 4 O atoms.

- **Li+ is bonded to four O atoms belonging to four different (T)FSI molecules.**

- These results are in agreement to previous results for similar ILs mixtures[10].

[10] O. Borodin, G. D. Smith, and W. Henderson, *J. Chem. Phys. B,* 16789-16886 (**2006**)

III. RESULTS

• TRANSPORT PROPERTIES : SHEAR VISCOSITY

- Definition :

$$\boxed{\eta = \frac{V}{10k_B T} \sum_{\kappa\lambda = x,y,z} Q_{\kappa\lambda} \int_0^\infty \langle P_{\kappa\lambda}(t) P_{\kappa\lambda}(0) \rangle dt}$$

V =volume T =temperature k_B=Boltzmann constant

$\sum\limits_{\kappa,\lambda=x,y,z}$ =double sum over cartesian coordinates $Q_{\kappa\lambda}$=weight factor

$P_{\kappa\lambda}(t)$ =symmetrized traceless portion of stress tensor at time t

III. RESULTS

• TRANSPORT PROPERTIES : SHEAR VISCOSITY

- Implementation :

$$\eta = \lim_{t\to\infty} \eta(t) \text{ where } \eta(t) = \frac{V\Delta t}{10k_B T n N_{or}} \sum_{i=1}^{N_{or}} \left\{ \frac{2}{3} \sum_{\kappa} \left[J_{\kappa\kappa}(t;t_i)\right]^2 + \sum_{\kappa} \sum_{\lambda>\kappa} \left[J_{\kappa\lambda}(t;t_i)\right]^2 \right\}$$

N_{tot}=total number of discrete times

$N_{or} = \frac{N_{tot}}{2}$ =number of time origins Δt =time step

Discrete times $t_i = t_0 + (i-1)\Delta t$ where $i = 1, \ldots, N_{tot}$

Elapsed time $t = n\Delta t$ where $n = 1, \ldots, N_{or}$

Trapezoidal rule:

$$J_{\kappa\lambda}(t;t_i) = \frac{1}{2}P_{\kappa\lambda}(t_i) + P_{\kappa\lambda}(t_i+\Delta t) + P_{\kappa\lambda}(t_i+2\Delta t) + \ldots + P_{\kappa\lambda}(t_i+(n-1)\Delta t) + \frac{1}{2}P_{\kappa\lambda}(t_i+n\Delta t)$$

Simpson's rule:

$$\begin{aligned} J_{\kappa\lambda}(t;t_i) = \; & \frac{1}{3}P_{\kappa\lambda}(t_i) + \frac{4}{3}P_{\kappa\lambda}(t_i+\Delta t) + \frac{2}{3}P_{\kappa\lambda}(t_i+2\Delta t) + \frac{4}{3}P_{\kappa\lambda}(t_i+3\Delta t) + \ldots \\ + \; & \frac{2}{3}P_{\kappa\lambda}(t_i+(n-2)\Delta t) + \frac{4}{3}P_{\kappa\lambda}(t_i+(n-1)\Delta t) + \frac{1}{3}P_{\kappa\lambda}(t_i+n\Delta t) \end{aligned}$$

III. RESULTS

• TRANSPORT PROPERTIES : SHEAR VISCOSITY

- Because stress tensor is a strong oscillation function with respect to elapsed time, time integrals of this function doesn't convergence from numerical integration algorithms (i.e., Trapezoidal and Simpson's rules).

- Experimental results have been obtained at MUNSTER University.

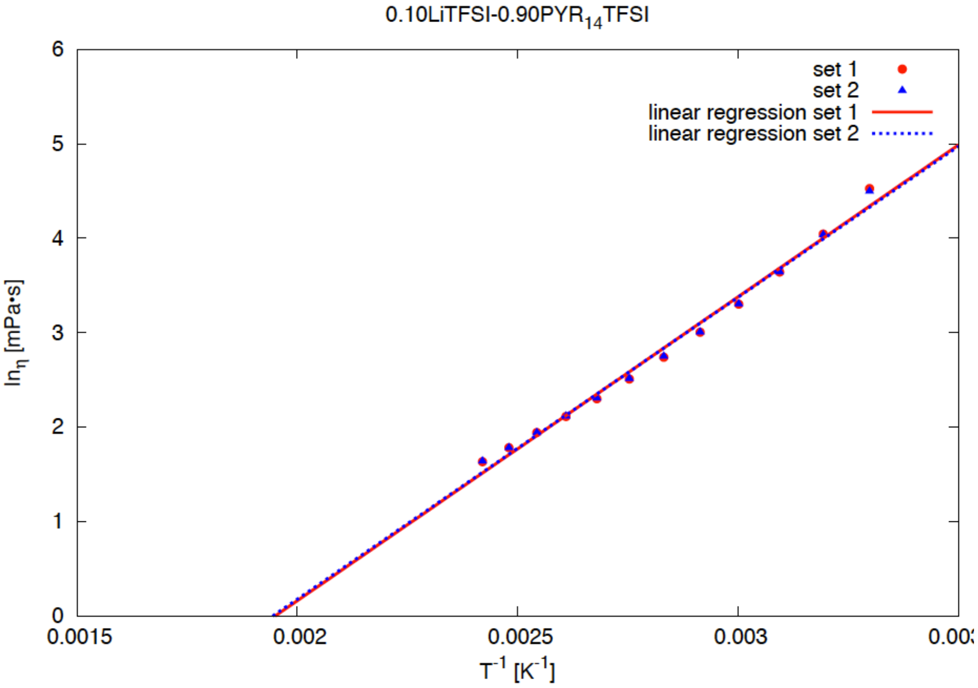
- Arrhenius model:

$$\boxed{ln\eta(T) = ln\eta_0 + \frac{E_a}{K_b T}}$$

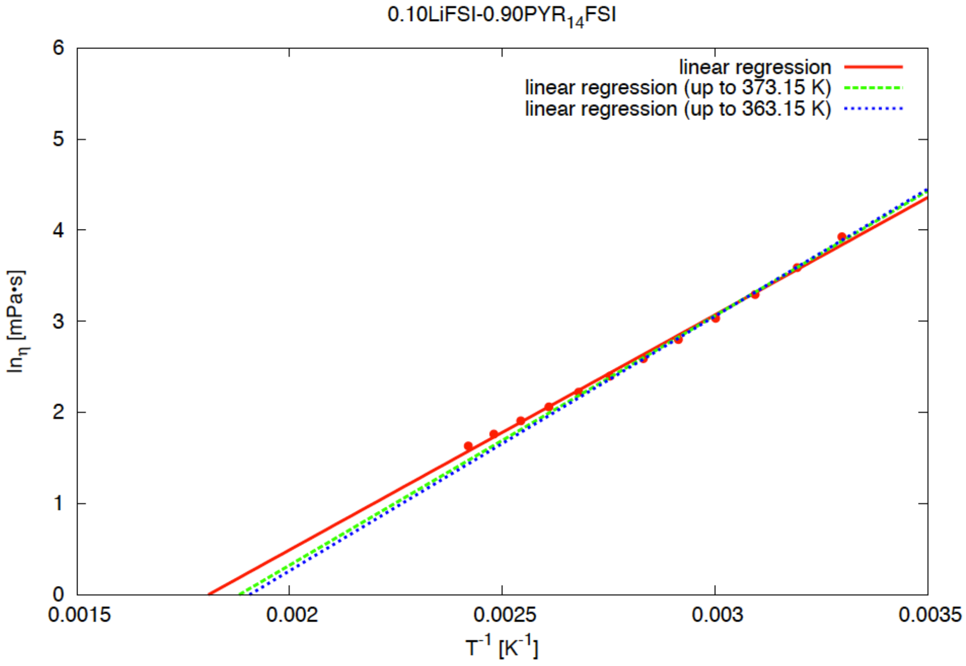
III. RESULTS

• TRANSPORT PROPERTIES : SHEAR VISCOSITY

0.10LiTFSI-0.90PYR14TFSI



0.10LiFSI-0.90PYR14FSI



III. RESULTS

• TRANSPORT PROPERTIES : SELF-DIFFUSION CONSTANTS

- Definition:

$$D_\alpha = \lim_{t\to\infty} \frac{1}{6t}\langle \frac{1}{N_\alpha}\sum_{i=1}^{N_\alpha}[\vec{r}_i(t)-\vec{r}_i(0)]^2\rangle$$

$\vec{r}_i(t)$ =cartesian vector position for i-molecule belong to α-type molecule at time t

- Implementation:

$$D_\alpha = \lim_{t\to\infty} D_\alpha(t) \quad \text{where} \quad D_\alpha(t)=\frac{1}{6t}\frac{1}{N_\alpha N_{or}}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_{or}}[\vec{r}_i(t_j+t)-\vec{r}_i(t_j)]^2$$

- Finite size correction[10]:

$$\Delta D = \frac{2.837 k_B T}{6\pi\eta L}$$

L =linear dimension of simulation periodic cell

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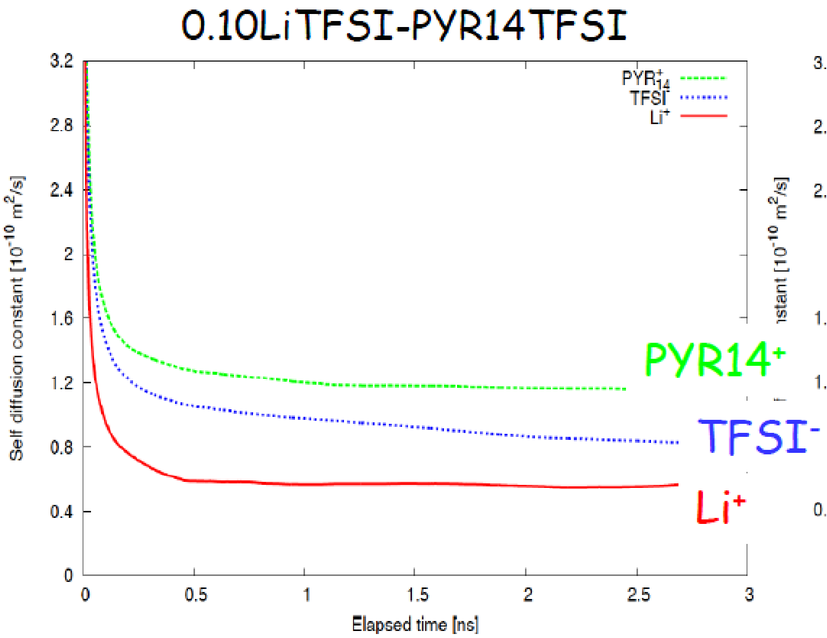
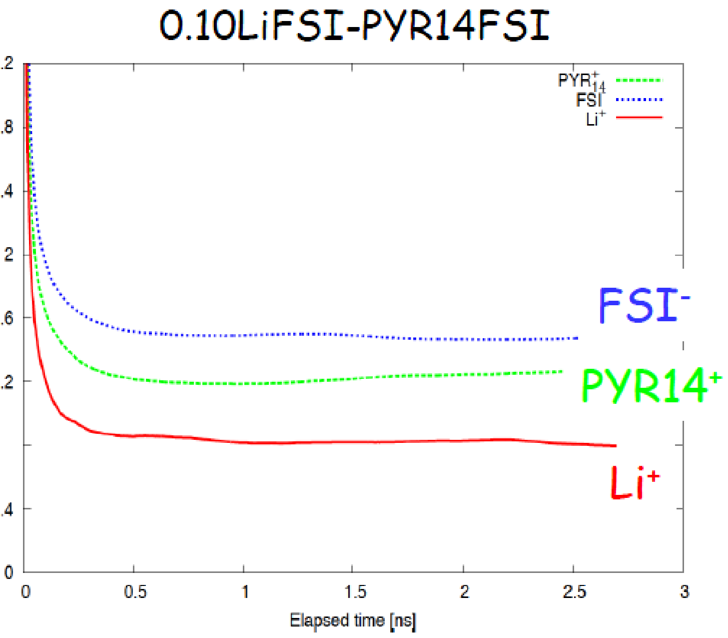
[10] B. Dunweg and K. Kremer, *J. Chem. Phys.* **99**, 6983-6997 (1993)

III. RESULTS

• TRANSPORT PROPERTIES : SELF-DIFFUSION CONSTANTS


0.10LiTFSI-PYR14TFSI


0.10LiFSI-PYR14FSI

Li$^+$ has the smallest diffusion constant :
Li$^+$ ions move surrounded by their anion shell

III. RESULTS

• TRANSPORT PROPERTIES : SELF-DIFFUSION CONSTANTS

- The diffusion constants were obtained from mean-square displacement by fitting a straight line.

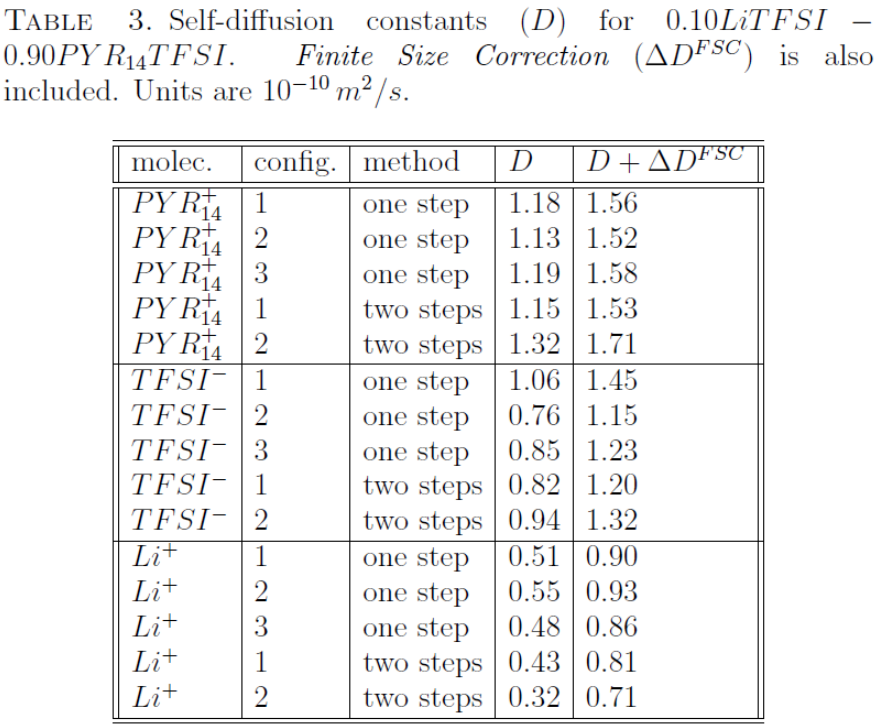


TABLE 3. Self-diffusion constants (D) for $0.10LiTFSI - 0.90PYR_{14}TFSI$. *Finite Size Correction* (ΔD^{FSC}) is also included. Units are $10^{-10}\, m^2/s$.

molec.	config.	method	D	$D + \Delta D^{FSC}$
PYR_{14}^+	1	one step	1.18	1.56
PYR_{14}^+	2	one step	1.13	1.52
PYR_{14}^+	3	one step	1.19	1.58
PYR_{14}^+	1	two steps	1.15	1.53
PYR_{14}^+	2	two steps	1.32	1.71
$TFSI^-$	1	one step	1.06	1.45
$TFSI^-$	2	one step	0.76	1.15
$TFSI^-$	3	one step	0.85	1.23
$TFSI^-$	1	two steps	0.82	1.20
$TFSI^-$	2	two steps	0.94	1.32
Li^+	1	one step	0.51	0.90
Li^+	2	one step	0.55	0.93
Li^+	3	one step	0.48	0.86
Li^+	1	two steps	0.43	0.81
Li^+	2	two steps	0.32	0.71

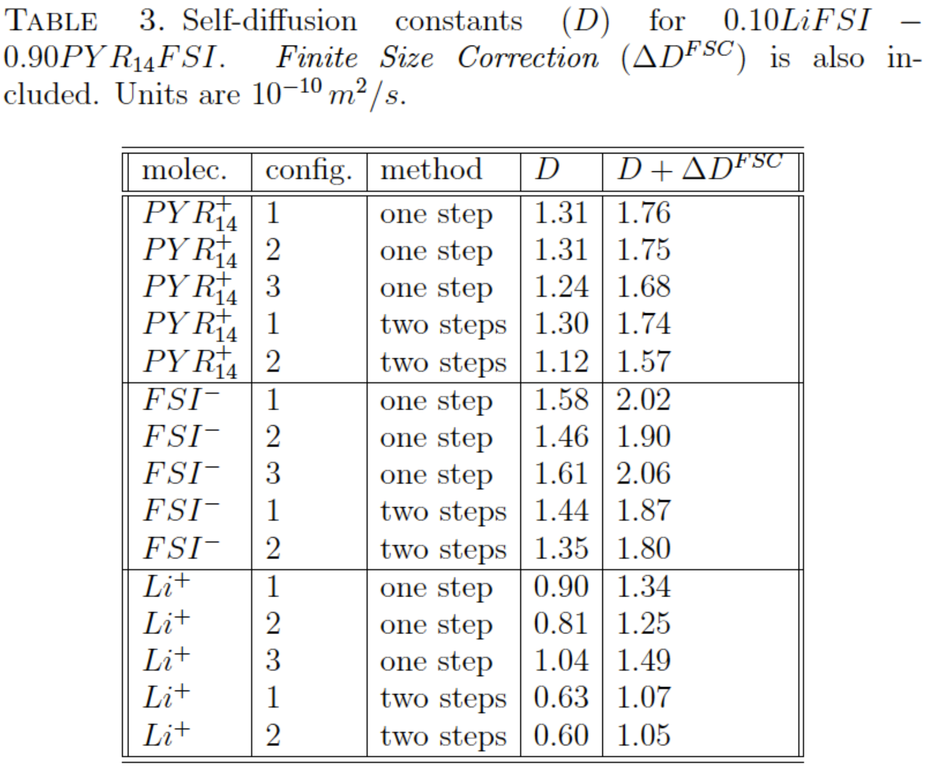


TABLE 3. Self-diffusion constants (D) for $0.10LiFSI - 0.90PYR_{14}FSI$. *Finite Size Correction* (ΔD^{FSC}) is also included. Units are $10^{-10}\, m^2/s$.

molec.	config.	method	D	$D + \Delta D^{FSC}$
PYR_{14}^+	1	one step	1.31	1.76
PYR_{14}^+	2	one step	1.31	1.75
PYR_{14}^+	3	one step	1.24	1.68
PYR_{14}^+	1	two steps	1.30	1.74
PYR_{14}^+	2	two steps	1.12	1.57
FSI^-	1	one step	1.58	2.02
FSI^-	2	one step	1.46	1.90
FSI^-	3	one step	1.61	2.06
FSI^-	1	two steps	1.44	1.87
FSI^-	2	two steps	1.35	1.80
Li^+	1	one step	0.90	1.34
Li^+	2	one step	0.81	1.25
Li^+	3	one step	1.04	1.49
Li^+	1	two steps	0.63	1.07
Li^+	2	two steps	0.60	1.05

III. RESULTS

. TRANSPORT PROPERTIES : IONIC CONDUCTIVITY

- Definition:

Charge transport due to self-diffusion:

$$\lambda_{uncorr} = \frac{1}{Vk_BT} \lim_{t\to\infty} \frac{1}{6t} \langle \frac{1}{N} \sum_{\alpha=1}^{N_{type}} \sum_{i=1}^{N_\alpha} q_\alpha^2 \left[\vec{r}_i(t) - \vec{r}_i(0)\right]^2 \rangle$$

q_α=charge of α-type molecule

Total charge transport :

$$\lambda = \frac{1}{Vk_BT} \lim_{t\to\infty} \frac{1}{6t} \langle \frac{1}{N} \left\{ \sum_{\alpha=1}^{N_{type}} \sum_{i=1}^{N_\alpha} q_\alpha \left[\vec{r}_i(t) - \vec{r}_i(0)\right] \cdot \sum_{\beta=1}^{N_{type}} \sum_{j=1}^{N_\beta} q_\beta \left[\vec{r}_j(t) - \vec{r}_j(0)\right] \right\} \rangle$$

III. RESULTS

• TRANSPORT PROPERTIES : IONIC CONDUCTIVITY

- Implementation:

Charge transport due to self-diffusion:

$$\lambda_{uncorr} = \lim_{t\to\infty} \lambda_{uncorr}(t) \quad \text{where} \qquad \lambda_{uncorr}(t) = \frac{1}{NVk_BT}\sum_{\alpha=1}^{N_{type}} q_\alpha^2 N_\alpha D_\alpha(t)$$

Total charge transport :

$$\lambda = \lim_{t\to\infty} \lambda(t) \quad \text{where} \qquad \lambda(t) = \frac{1}{6tVk_BTNN_{or}}\sum_{\alpha=1}^{N_{type}} q_\alpha \sum_{\beta=1}^{N_{type}} q_\beta \sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\alpha}\sum_{k=1}^{N_{or}} [\vec{r}_i(t_k+t)-\vec{r}_i(t_k)]\cdot[\vec{r}_j(t_k+t)-\vec{r}_j(t_k)]$$

III. RESULTS

. TRANSPORT PROPERTIES : IONIC CONDUCTIVITY

- Ionic conductivity can be estimated from charge transport due to self-diffusion and degree of uncorrelated ion motion.

$$\gamma_d(t) = \frac{\lambda(t)}{\lambda_{uncorr}(t)}$$

TABLE 4. Degree of uncorrelated ion motion (α_d) for $0.10LiTFSI - 0.90PYR_{14}TFSI$. Average obtained up to times 5% (2%) of the total simulation run.

config.	method	α_d
1	one step	0.56 (0.55)
1	two steps	0.59 (0.53)
2	one step	0.59 (0.54)
2	two steps	0.55 (0.55)
3	one step	0.60 (0.53)
3	two steps	0.58 (0.54)

$$< \lambda_{uncorr} >= 12.88\, mS/cm$$

$$< \lambda >= 7.47\,(6.96)\, mS/cm$$

TABLE 4. Degree of uncorrelated ion motion (α_d) for $0.10LiFSI - 0.90PYR_{14}FSI$. Average obtained up to times 5% (2%) of the total simulation run.

config.	method	α_d
1	one step	0.60 (0.55)
1	two steps	0.63 (0.58)
2	one step	0.87 (0.69)
2	two steps	0.67 (0.60)
3	one step	0.67 (0.58)

$$< \lambda_{uncorr} >= 16.63\, mS/cm$$

$$< \lambda >= 11.47\,(9.98)\, mS/cm$$

III. RESULTS

- **SUMMARY ON THE TRANSPORT ANALYSIS**

  - **FSC is an important contribution for self-diffusion constants**.

  - **Li^+diffusion constant : 0.10LiFSI-0.90PYR14FSI > 0.10LiTFSI-0.90PYR14TFSI.**

  - **Ionic conductivity : 0.10LiFSI-0.90PYR14FSI > 0.10LiTFSI-0.90PYR14TFSI.**

III. RESULTS

• MECHANISM OF THE Li^+ CATION TRANSPORT

- In principle, there are two possible mechanisms of the Li^+ transport:

  - * **Vehicular mechanism** → Li^+ cations move primarily with their coordination shells as $Li[(T)FSI]_4$ complex.
  - * **Structure-diffusion mechanism** → Li+ cations move primarily by exchanging $(T)FSI^-$ molecules in their first coordination shell.

- One way to quantify the contribution of the vehicular mechanism to the Li^+ transport is to calculate the lifetime of the $Li[(T)FSI]_4$ coordinations and how far the $Li[(T)FSI]_4$ complex moves before Li^+ exchanges $(T)FSI^-$ anions in its first coordination shell.

III. RESULTS

- **MECHANISM OF THE Li$^+$ CATION TRANSPORT**

  - **Lifetime correlation function**:

    * Definition

$$P_{Li-(T)FSI}(t) = \frac{\langle \frac{1}{N_{Li}N_{(T)FSI}} \sum_{i=1}^{N_{Li}} \sum_{j=1}^{N_{(T)FSI}} H_{ij}(t)H_{ij}(0)\rangle}{\langle \frac{1}{N_{Li}N_{(T)FSI}} \sum_{i=1}^{N_{Li}} \sum_{j=1}^{N_{(T)FSI}} H_{ij}(0)\rangle}$$

$$H_{ij}(t) = 1 \Leftrightarrow \left| \vec{r}_i^{\,Li}(t) - \vec{r}_j^{\,(T)FSI}(t) \right| \leq 5.6\mathring{A}$$

$$H_{ij}(t) = 0 \text{ otherwise}$$

III. RESULTS

• MECHANISM OF THE Li$^+$ CATION TRANSPORT

- **Lifetime correlation function**:
  * Implementation

$$P_{Li-(T)FSI}(t) = \frac{\sum_{k=1}^{N_{or}} \sum_{i=1}^{N_{Li}} \sum_{j=1}^{N_{(T)FSI}} H_{ij}(t_k + t) H_{ij}(t_k)}{\sum_{k=1}^{N_{or}} \sum_{i=1}^{N_{Li}} \sum_{j=1}^{N_{(T)FSI}} H_{ij}(t_k)}$$

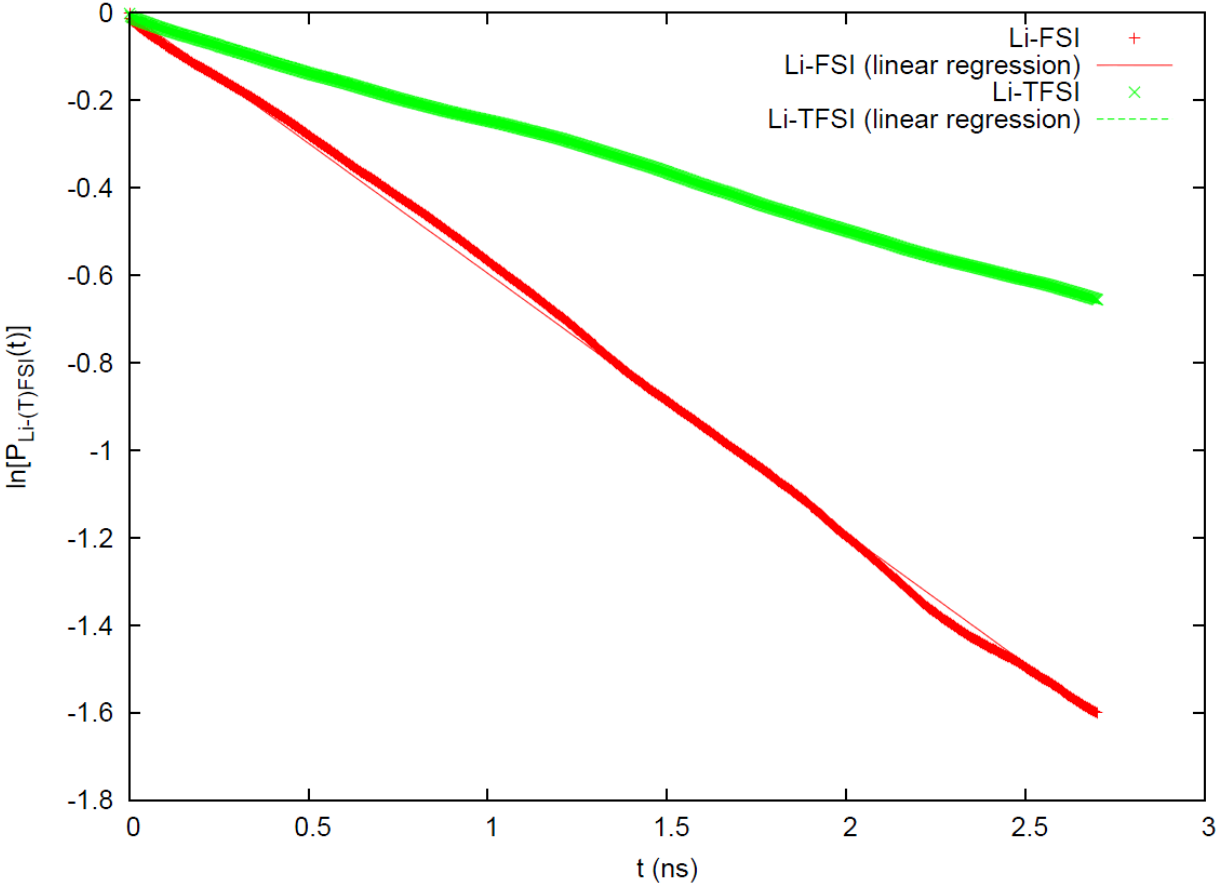
- **Residence time for lifetime correlation function (Rt):**

$$ln\left[P_{Li-(T)FSI}(t)\right] = -\frac{t}{Rt}$$

III. RESULTS

• MECHANISM OF THE Li$^+$ CATION TRANSPORT

- Residence time for lifetime correlation function (Rt):



III. RESULTS

• MECHANISM OF THE Li$^+$ CATION TRANSPORT

- Residence time for lifetime correlation function (Rt):

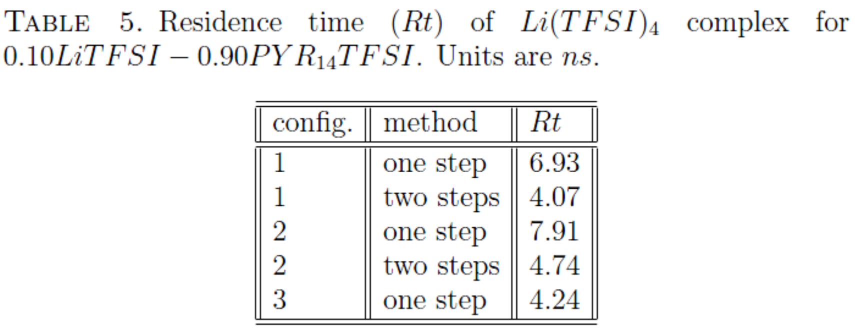


TABLE 5. Residence time (Rt) of $Li(TFSI)_4$ complex for $0.10LiTFSI - 0.90PYR_{14}TFSI$. Units are ns.

config.	method	Rt
1	one step	6.93
1	two steps	4.07
2	one step	7.91
2	two steps	4.74
3	one step	4.24

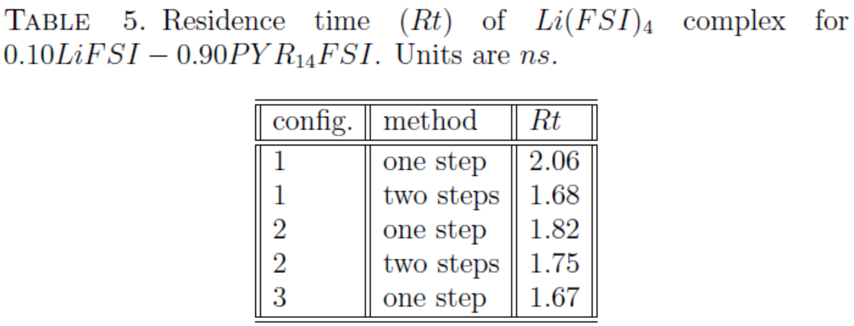


TABLE 5. Residence time (Rt) of $Li(FSI)_4$ complex for $0.10LiFSI - 0.90PYR_{14}FSI$. Units are ns.

config.	method	Rt
1	one step	2.06
1	two steps	1.68
2	one step	1.82
2	two steps	1.75
3	one step	1.67

- Radius of gyration (Rg):

* Rg allows to estimate the size of a molecule and it can be obtained from MD simulations.

<Rg(TFSI)> = 2.60 Angs. <Rg(FSI)>=2.00 Angs.

III. RESULTS

- **MECHANISM OF THE Li^+ CATION TRANSPORT**

  - **Using self-diffusion coefficient data and residence times, we estimate that an Li^+ cation on average moves a distance of 1.39 (1.74) FSI^- ($TFSI^-$) diameters (diameter is defined as two radii of gyration) before it exchanges a $(T)FSI^-$ anion in its first coordination shell. These numbers suggest that there is a significant contribution to the Li^+ transport mechanism from the structure-diffusion in which Li^+ cations move by exchanging $(T)FSI^-$ anions.**

  - These results are in agreement to previous results for similar ILs mixtures[10].

THANK YOU FOR YOUR ATTENTION!