Vacuum-Liquid Interface of Imidazolium-Based Ionic Liquids from Atomistic Simulations and High-Resolution Rutherford Backscattering Spectroscopy

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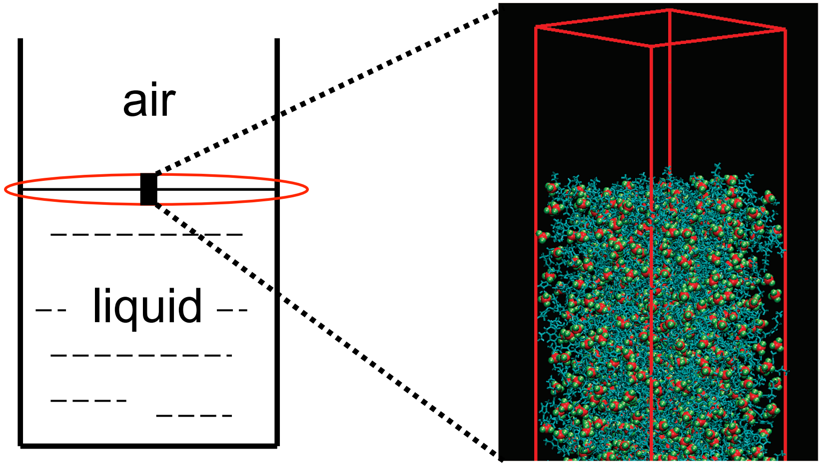
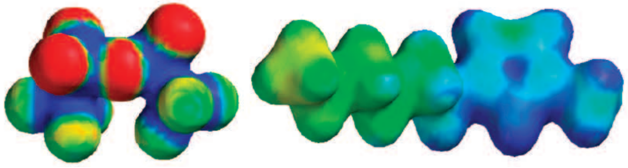
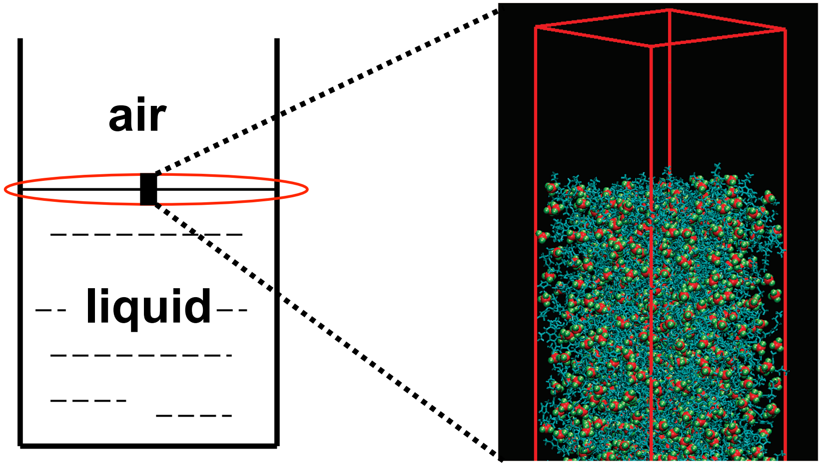


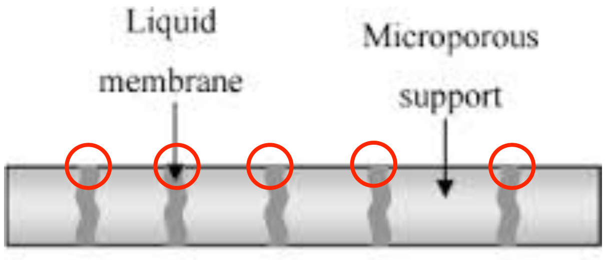


Fluid-Fluid Interfaces



- Fluid-fluid interfaces play a key role in various physical and chemical processes (adsorption, liquid-liquid extraction, heterogeneous catalysis, chromatography, or drug delivery).
- Physical properties such as density, solubility or dielectric constant change abruptly, yet continuously, in the vicinity of the interfaces.
- The molecules located at the interface experience a markedly different local environment wrt bulk phases.
- Single-particle properties such as orientation, diffusion constant or binding energy of the interfacial molecules are markedly different than those of the bulk phases.

Molecular Transport across Liquid Membrane



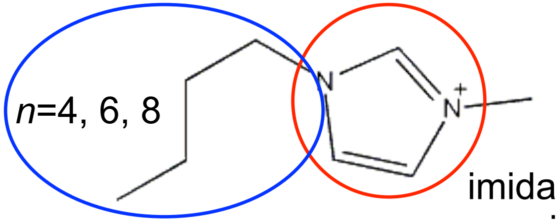
- solubility of molecules
- diffusion
  - ➢ diffusion in bulk phase
  - ➢ **interfacial transport – *mass transfer resistance***

What can be addressed

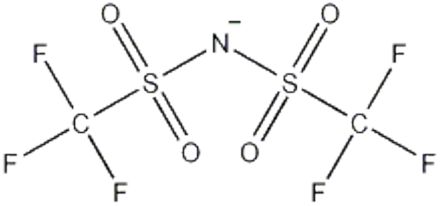
- ○ **Size of the interfacial region?**
- ○ **Ions density and concentration at the interfacial region?**
- ○ **Any preferential orientation of ions at the interfacial region?**
- ○ **Relation of the interfacial ions structure with surface tension?**

Imidazolium-Based Ionic Liquids

$C_n$mim$^+$



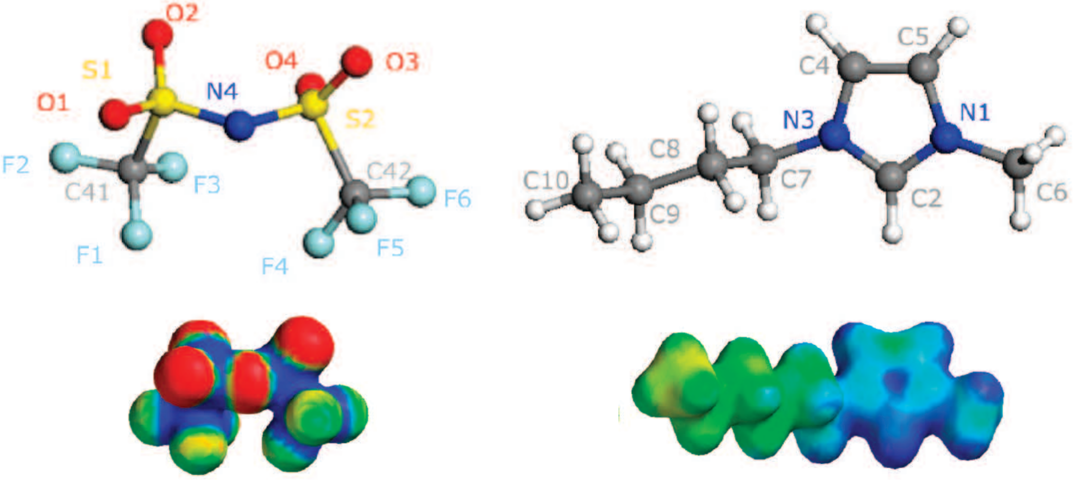
tfsi$^-$



Atomic Models of Ions

Flexible All-Atom Models

[C_4mim][tfsi]



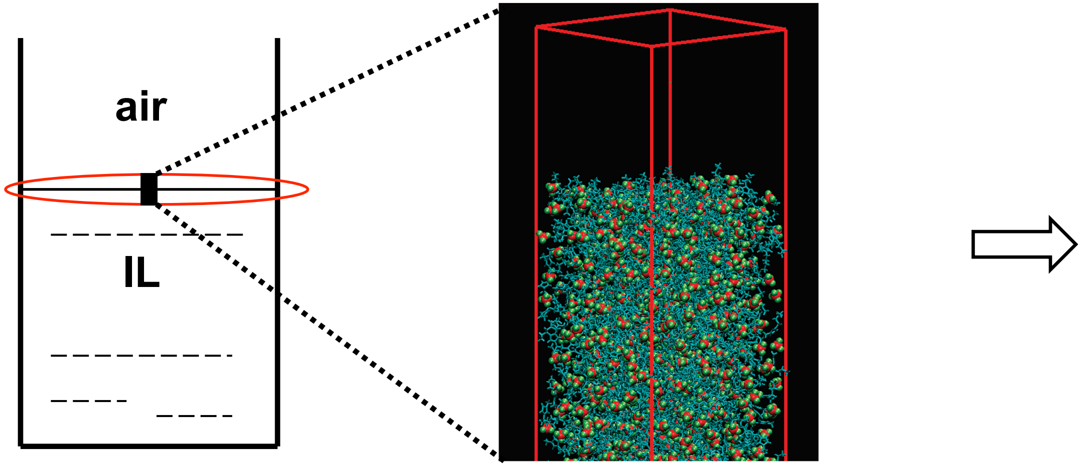
Termodynamic Properties @ *T*=300K & *P*=1bar

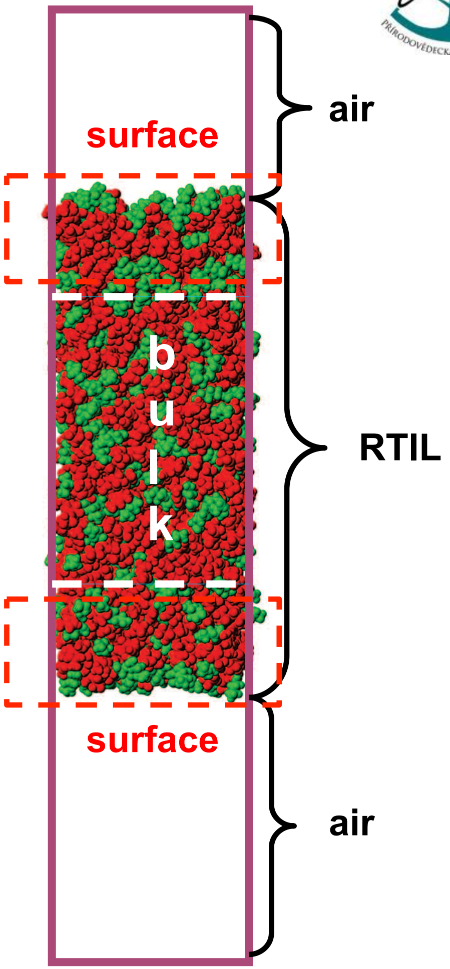
RTILs	ρ^{sim} (kg/m^3)	ρ^{exp} (kg/m^3)	$\Delta\rho$ (%)	ΔH_v^{sim} (kJ/mol)	ΔH_v^{exp} (kJ/mol)	ΔH_v (%)
[C_4mim][tfsi]	1461.6(55)	1436.2(6)	1.7	133.1(20)	134(3)	-0.1
[C_6mim][tfsi]	1394.9(48)	1364.0(26)	2.2	140.2(32)	139(2)	0.9
[C_8mim][tfsi]	1338.5(42)	1320.0(50)	1.4	147.0(38)	149(2)	-1.3

M. Lísal et al., *PCCP* **14**, 5164, 2012

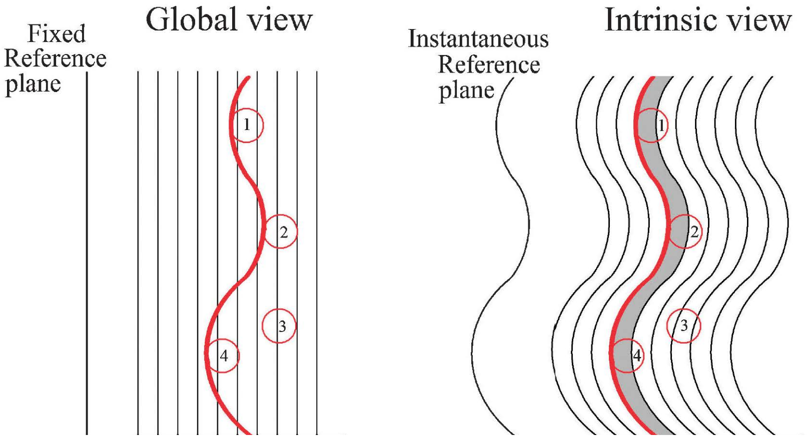
Molecular Dynamics Simulations

Simulation Set-up

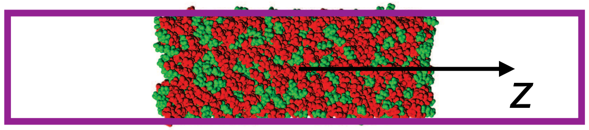




Intrinsic Approach-Based Post-Processing



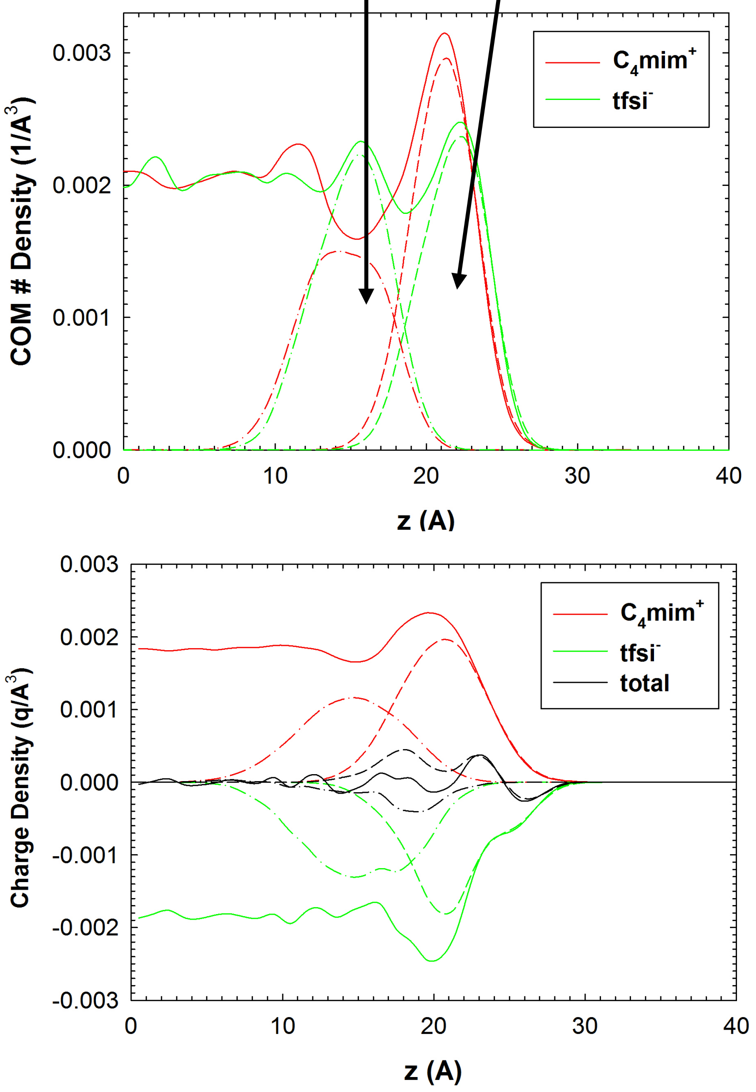
Ions Density Profiles



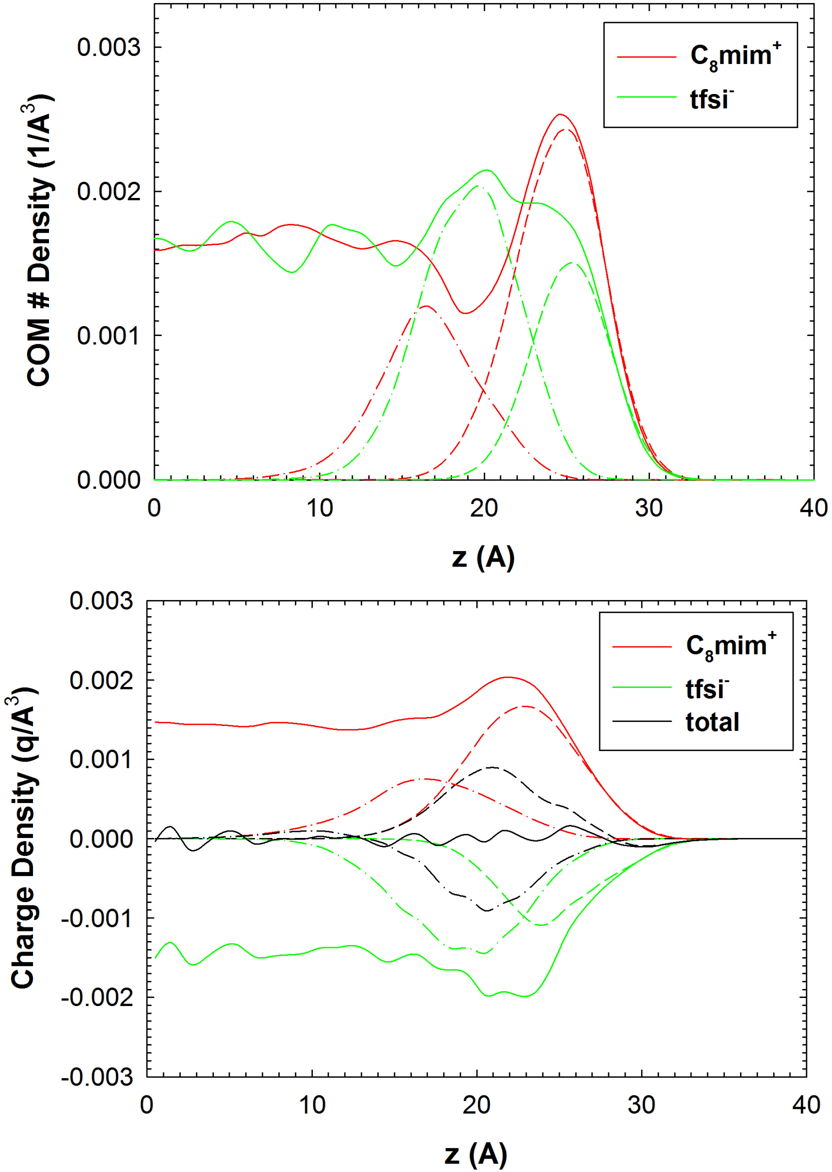
[C_4mim][tfsi]

Sub-Interfacial Layer

Interfacial Layer



[C_8mim][tfsi]



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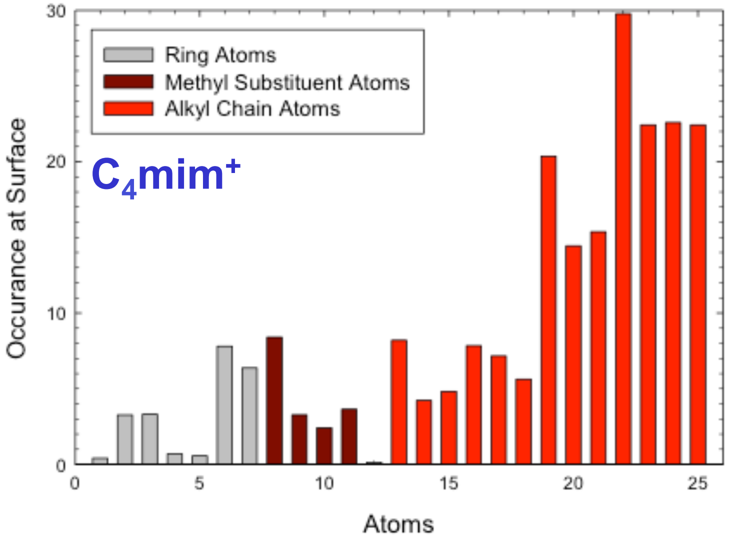
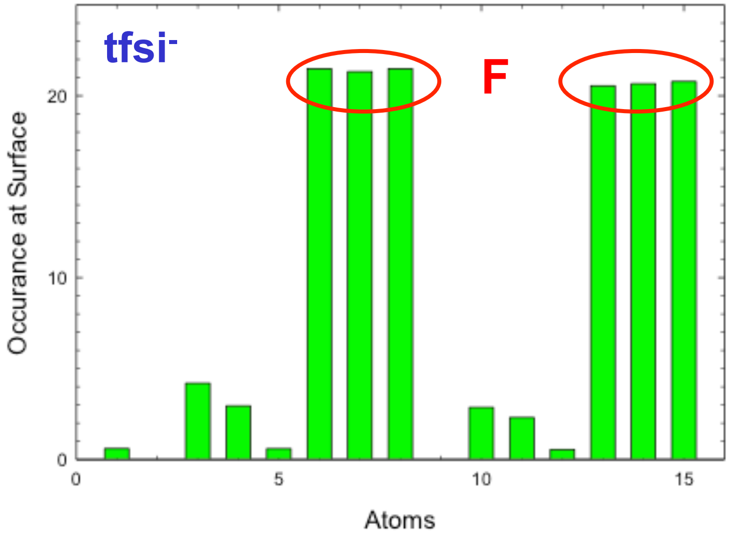
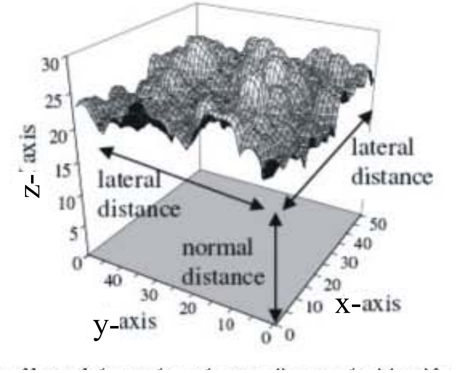
Surface Roughness

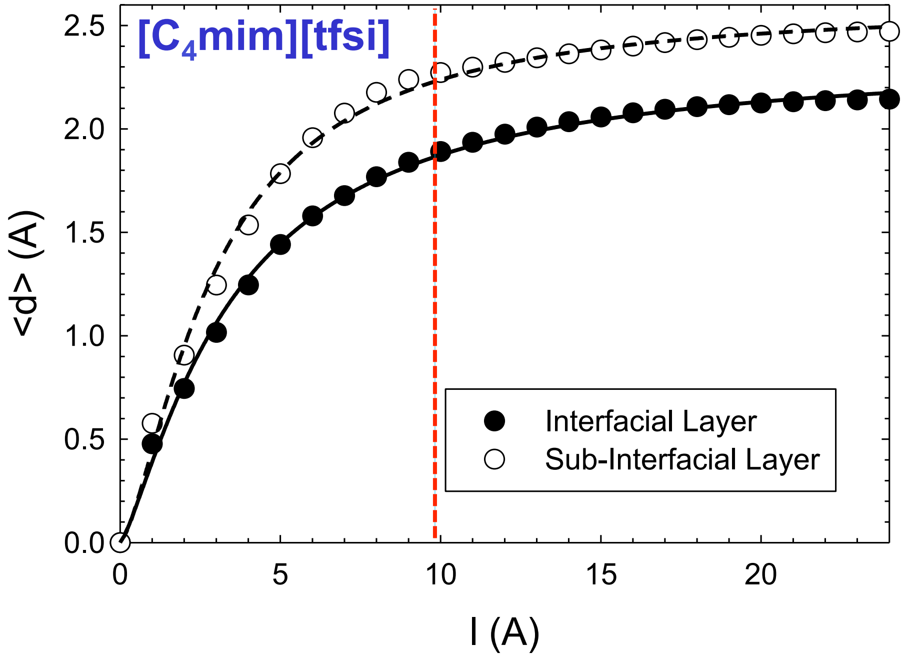
Surface Atoms





Surface Characterization



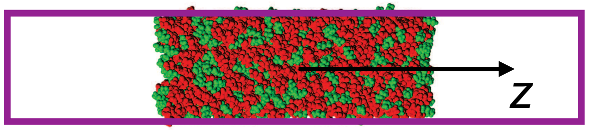


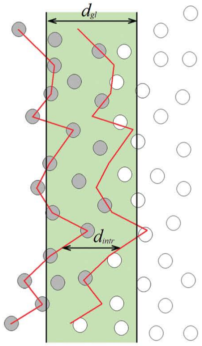
M. Lísal et al., *PCCP* **14**, 5164, 2012
M. Lísal et al., *J. Chem. Phys.* **139**, 014704, 2013

Summary of Findings #1

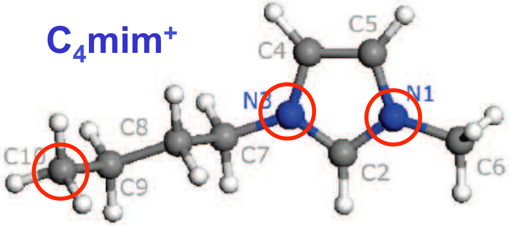
- an enhancement of ions density in the interfacial layer
- surplus of the cations wrt the anions in the interfacial layer
- the cation surplus is balanced by surplus of the anions in the sub-interfacial layer
- the cation surplus increases with increase in the cation tail length
- surface of the interfacial layer is smoother than the surface of the sub-interfacial layer which indicates a closer packing of the cations in the interfacial layer
- roughness of the surfaces of the interfacial and sub-interfacial layers increased with the increase in the cation tail length which suggests a less dense packing of ions in the surface layers of systems with longer cation tails

Interfacial-Layer Atomic Density Profiles

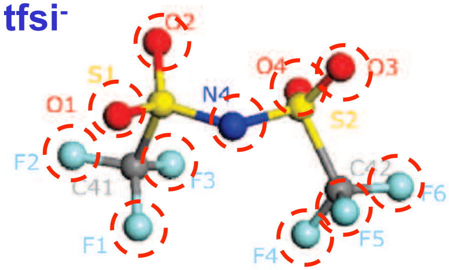


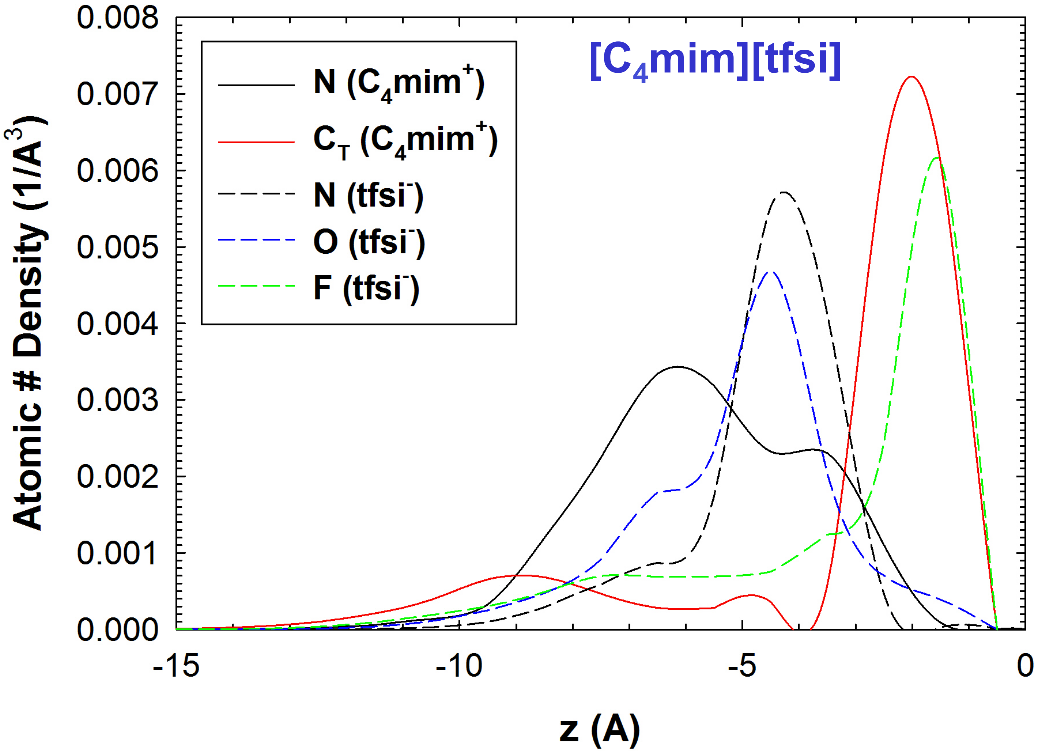


C_4mim^+



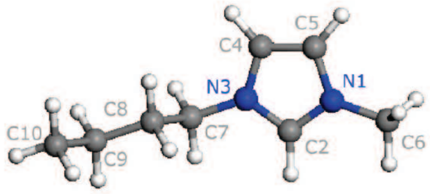
$tfsi^-$



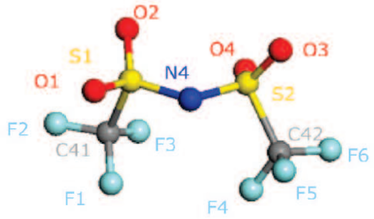


Preferential Orientations of Ions

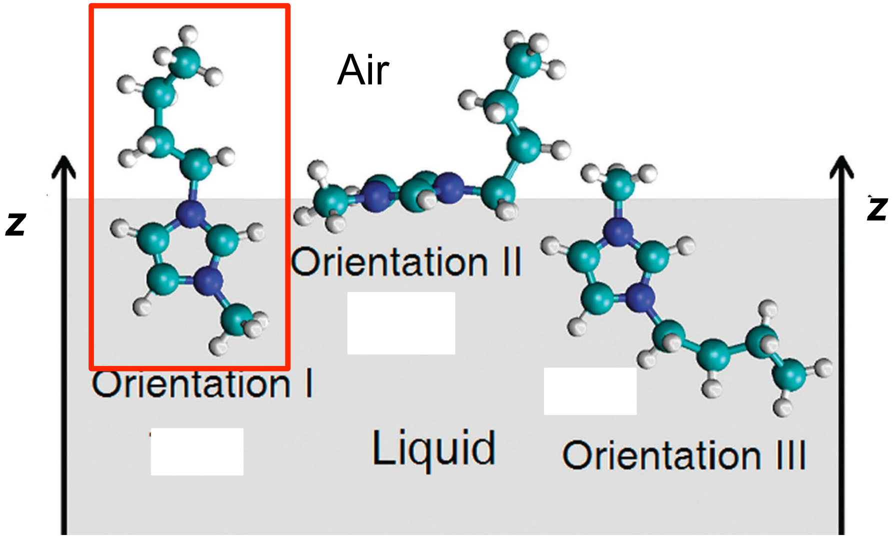
$C_n$mim$^+$



tfsi$^-$

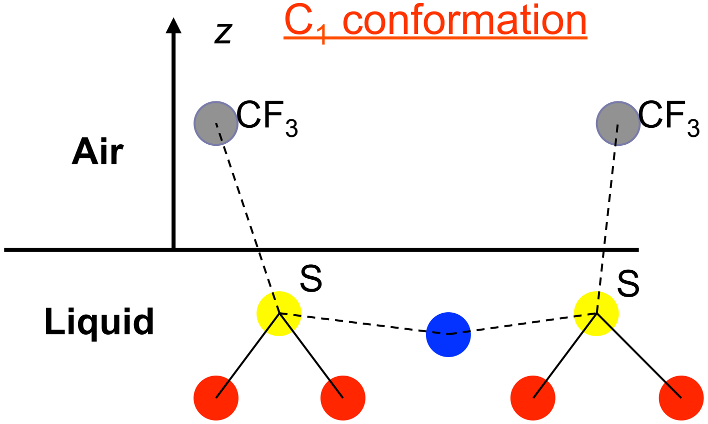


Preferential Orientations



Preferential Orientation

C_1 conformation



!!! Bulk: C_2 conformation !!!

M. Lísal et al., *PCCP* **14**, 5164, 2012.

Surface Tension

Effect of Anion Size

γ_{MeOH}~22mN/m

$\gamma_{acetone}$~24mN/m

$\gamma_{n\text{-}alkanes}$~(21-23)mN/m

<

RTILs	γ^{sim} (mN/m)	γ^{exp} (mN/m)	$\Delta\gamma$ (%)
$[C_4mim][tfsi]$	33.6(33)	32.66(70)	3.0
$[C_4mim][Br]$	39.4(29)	43	-8.0

< γ_{water}~72mN/m

Effect of Alkyl Tail Length

RTILs	γ^{sim} (mN/m)	γ^{exp} (mN/m)	$\Delta\gamma$ (%)
$[C_4mim][tfsi]$	33.6(33)	32.66(70)	3.0
$[C_6mim][tfsi]$	33.4(37)	31.45(70)	6.0
$[C_8mim][tfsi]$	35.5(40)	31.03(59)	12.6

M. Lísal et al., *PCCP* **14**, 5164, 2012
M. Lísal et al., *J. Mol. Liq.* **189**, 85, 2014
M. Lísal et al., *J. Chem. Phys.* **139**, 014704, 2013

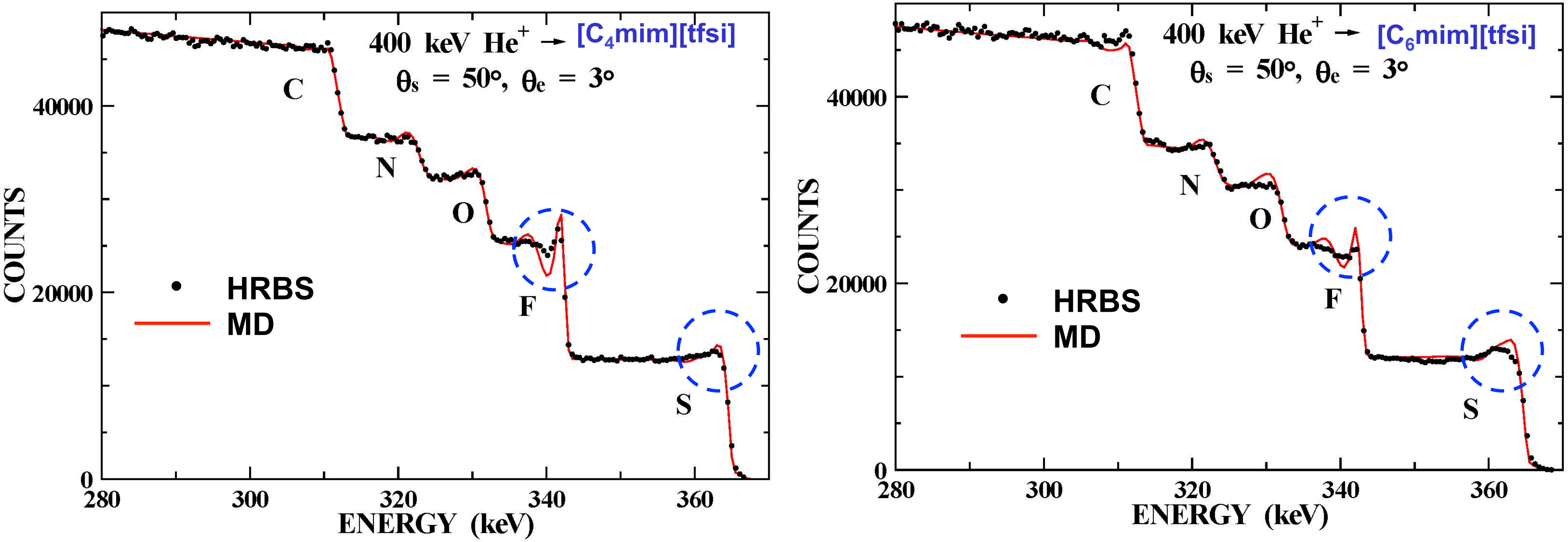
Summary of Findings #2

- cation and anion have preferential orientations simultaneously in the interfacial layer
- cation alkyl tails protrude to the vapor phase irrespective of the tail length
- a less dominant cation orientation with the alkyl tails pointing toward the liquid
- CF_3 groups of tfsi$^-$ point toward the vapor phase, C_1 conformation
- cation and anion show only a weak preferential orientation in the sub-interfacial layer
- surface tension decreases with increasing cation alkyl tails

Comparison with HRBS

- High-Resolution Rutheford Backscattering Spectroscopy (HRBS)[1] (Kenji Kimura's group, Kyoto, Japan)
- HRBS provides elemental depth profiles with a sub-nanometer depth resolution

HRBS Energy Spectra



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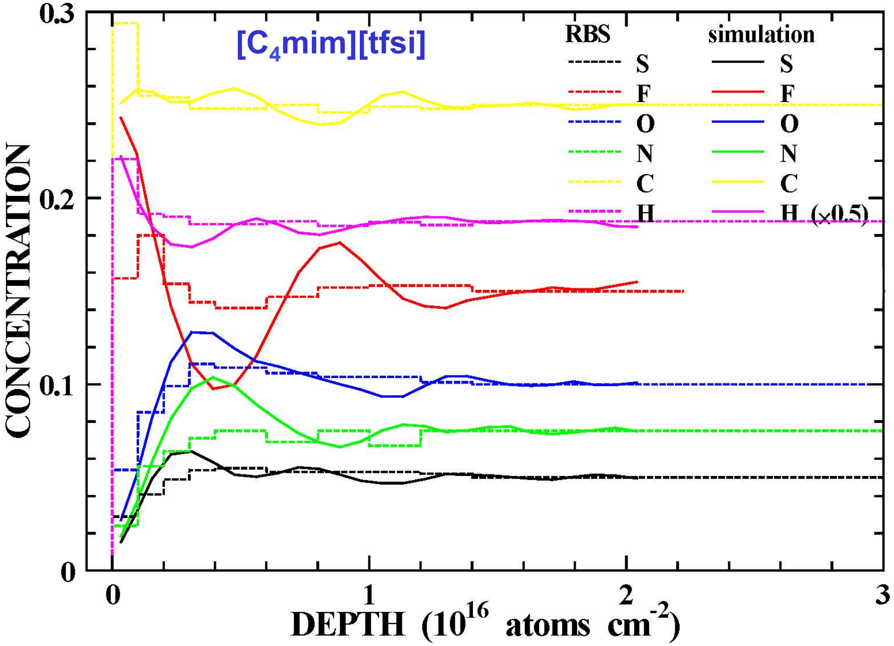
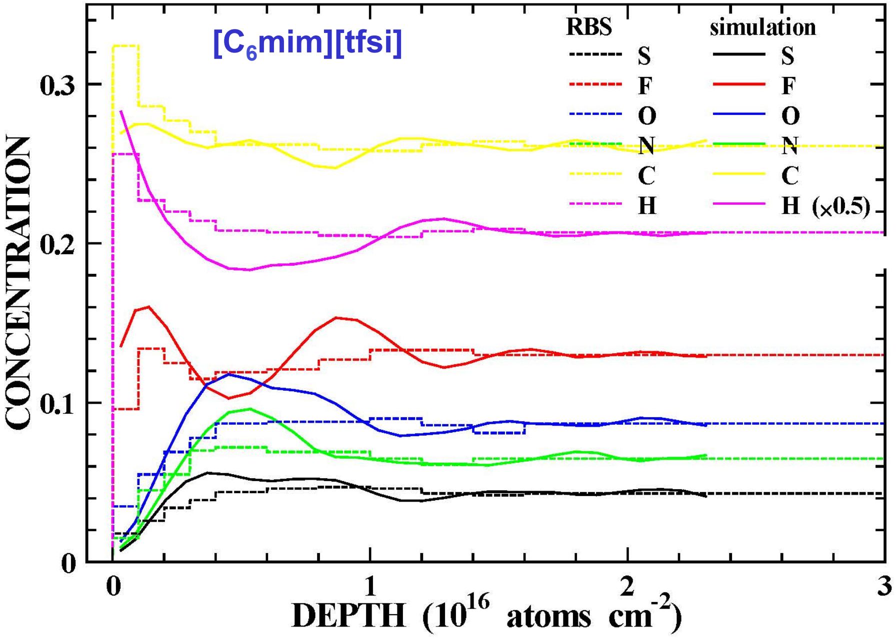
[1] K. Nakajima et al., *J. Chem. Phys.* **133**, 044702, 2010

Comparison with HRBS (cont'd)

HRBS Elemental Depth Profiles





K. Nakajima et al., *J. Chem. Phys.* **133**, 044702, 2010

Summary: HRBS vs. MD [C$_n$mim][tfsi]

Rutherford Backscattering Spectroscopy

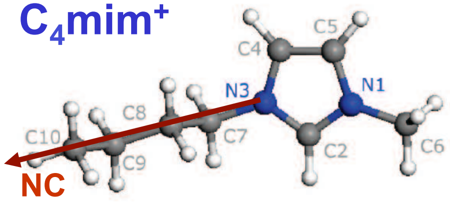
- The surface is shared almost equally by C$_n$mim$^+$ and tfsi$^-$.
- At the surface, both C$_n$mim$^+$ and tfsi$^-$ have preferential orientations simultaneously.
- The alkyl tails of C$_n$mim$^+$ protrude to the air irrespective of the tail length.
- CF$_3$ groups of tfsi$^-$ point toward the air.
- tfsi$^-$ in the sub-interfacial layer show a weak preferential orientation.

Molecular Dynamics Combined with Intrinsic Analysis

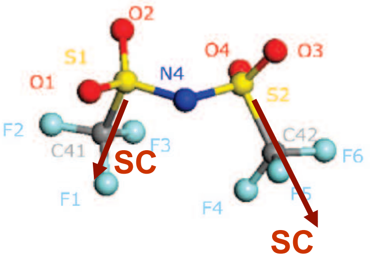
- The surface shows surplus of C$_n$mim$^+$ wrt tfsi$^-$ and the surplus increases with the cation tail length; the surplus is balanced in the sub-interfacial layer.
- At the surface, both C$_n$mim$^+$ and tfsi$^-$ have preferential orientations simultaneously.
- The alkyl tails of C$_n$mim$^+$ protrude to the air irrespective of the tail length; a less dominant orientation with the alkyl tails pointing toward the liquid.
- CF$_3$ groups of tfsi$^-$ point toward the air.
- Both C$_n$mim$^+$ and tfsi$^-$ in the sub-interfacial layer show a weak preferential orientation.

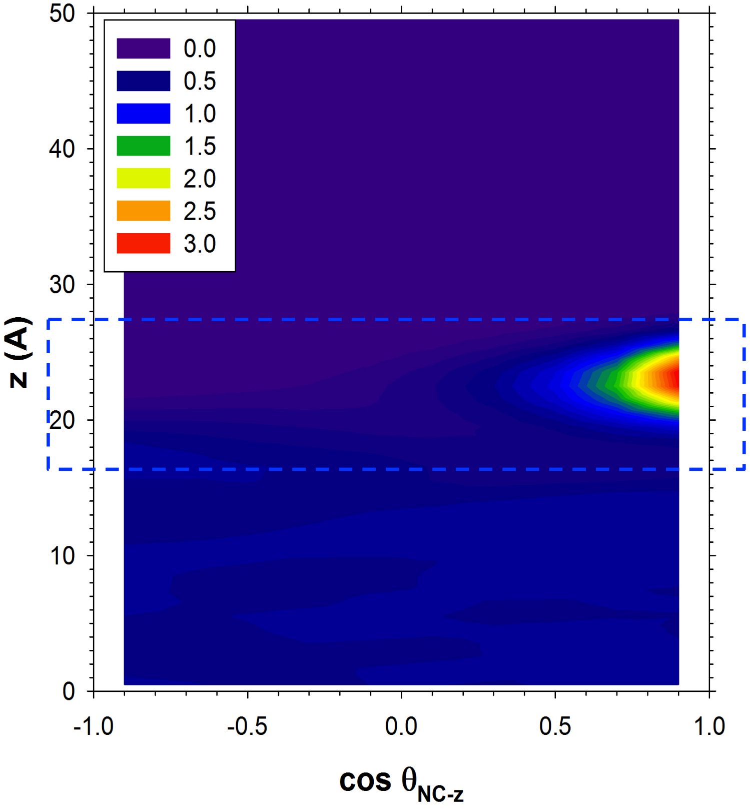
Orientations of Ions

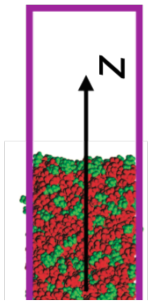
C_4mim^+

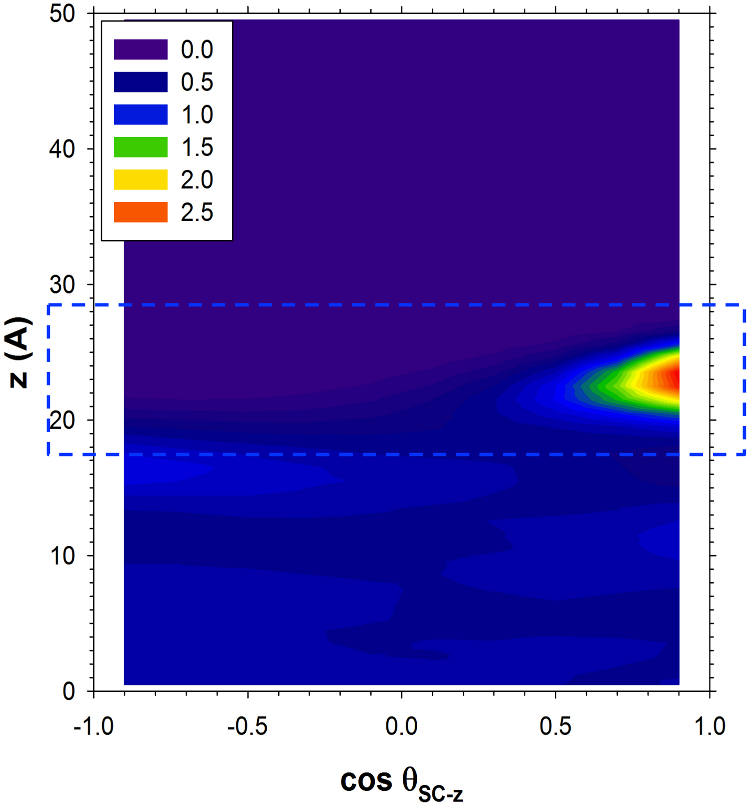


$tfsi^-$









M. Lísal et al., *PCCP* **14**, 5164, 2012