Influence of the Size of Cation on the Structure and Tribological Properties of Ionic Liquids Studied with Molecular Dynamics

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Outline of the talk

A) Introduction

- A1) Overview of ionic liquids (ILs)
- A2) Motivation for studying ILs
- A3) Models of ILs and methods applied

B) Key results

- B1) Bulk ILs
  - B1.1) Relaxed structure of bulk ILs
  - B1.2) NEMD shearing simulations
- B2) Confined ILs
  - B2.1) Equilibrium behaviour of confined ILs
  - B2.2) Cyclic extension-compression of confined ILs
  - B2.3) Tribological behaviour of confined ILs

C) Conclusions

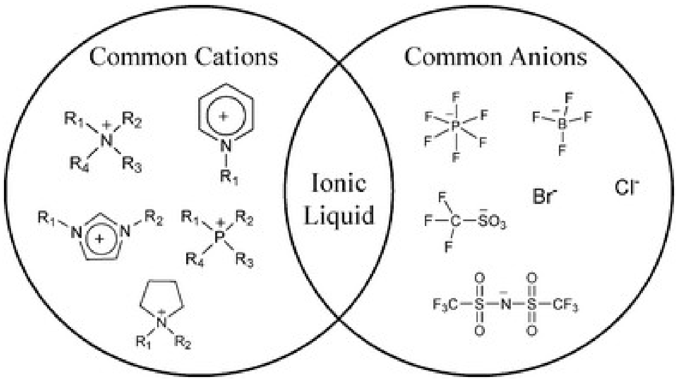
Physico-chemical characteristics of ionic liquids

- ILs are salts composed of large asymmetric organic cationic and anionic molecules

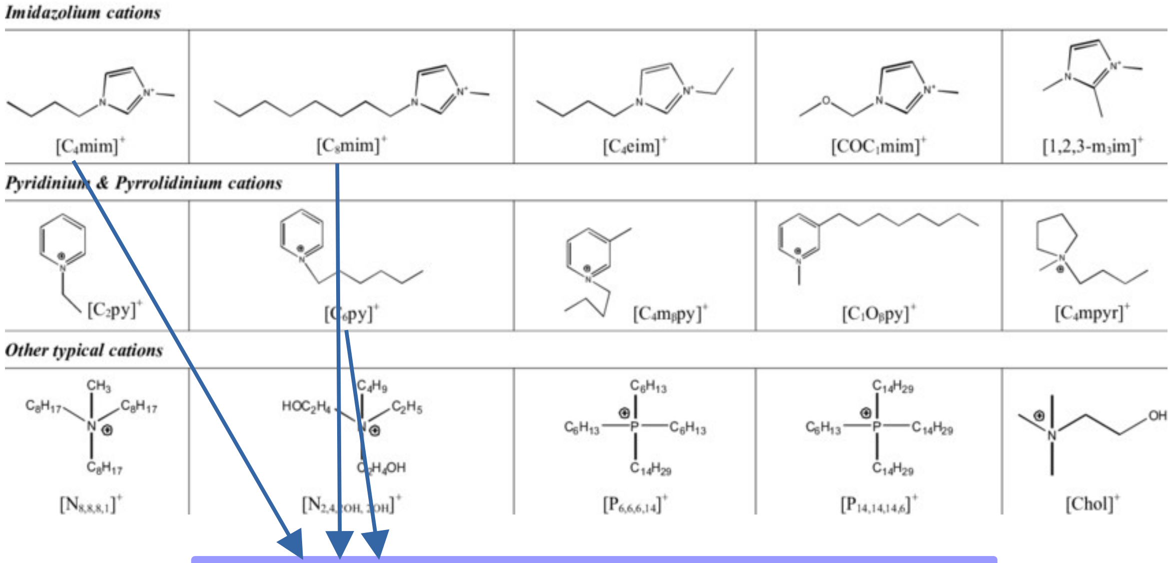
  → liquid state even at room temperature
  → high temperature stability and low vapour pressure

- Externally controllable lubricating characteristics via application of confining solid plates and external electric fields

  → formation of alternating cationic-anionic layers



Overview of common cations and anions in ILs



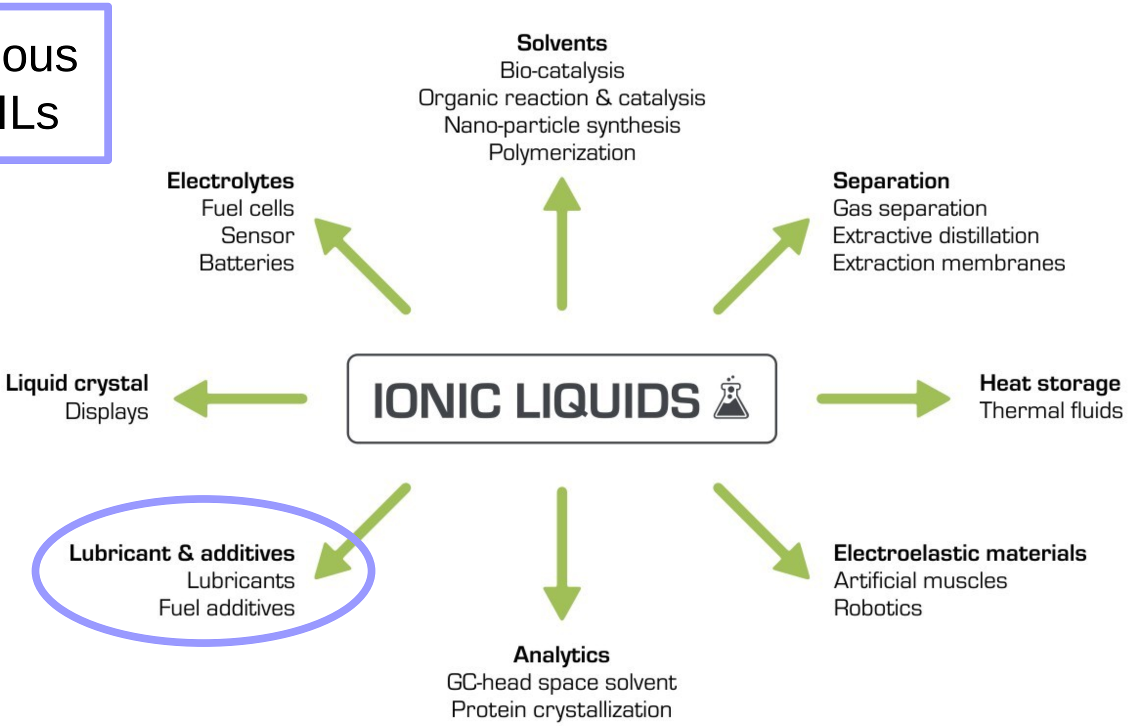
Overview of typical cations showing the variety of alkyl chain length

ILs as lubricants – computational nanotribology

- Nanotribology: friction, lubrication and wear at nanoscale
- Ionic Liquids (ILs): high quality lubricants with wide applications

  → relevant from fundamental and industrial aspects (designer liquids)
- Experimental results: decrease of friction and wear by adding ILs and mixing them with synthetic oils: friction coefficient decreases for 60%, while wear level decreases for three orders of magnitude

Overview of various applications of ILs



Solvents
Bio-catalysis
Organic reaction & catalysis
Nano-particle synthesis
Polymerization

Electrolytes
Fuel cells
Sensor
Batteries

Separation
Gas separation
Extractive distillation
Extraction membranes

Liquid crystal
Displays

IONIC LIQUIDS

Heat storage
Thermal fluids

Lubricant & additives
Lubricants
Fuel additives

Electroelastic materials
Artificial muscles
Robotics

Analytics
GC-head space solvent
Protein crystallization

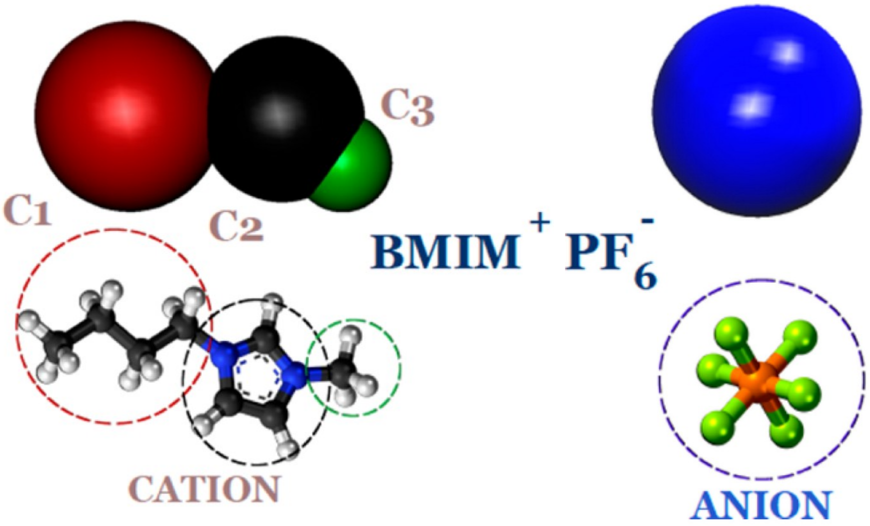
Modeling the ionic liquids

- Goals of our study on ILs:

  1) structural properties of bulk and confined ILs
  2) nanoscopic lubrication with confined ILs as lubricants

- Time-scale and length-scale of the system: nanoseconds and nanometers
  - → Coarse–Grained (CG) model of ionic liquids is adequate
  - → Interatomic potentials (Lennard–Jones (LJ) and Coulombic potential)

- Realization: Molecular dynamics simulations of modelled ILs

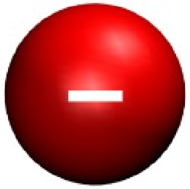


Example of ionic molecules’ coarse-graining:

Cation/anion are represented with three/one charged Lennard-Jones spheres

Tailed models (TM) of ionic liquids

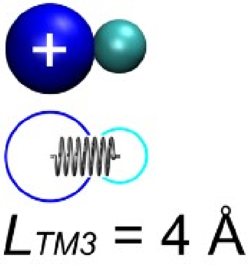
(a) anion

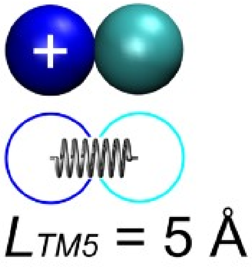


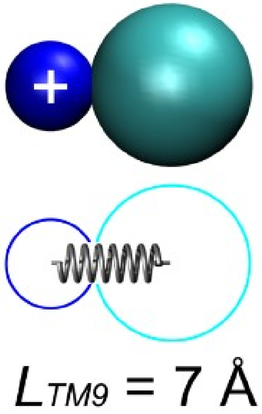
Anion is represented by one charged LJ sphere

$\sigma_A = 10\,\mathring{A}$

(b) TM3 cation/tail TM5 cation/tail TM9 cation/tail







Tail smaller than cation

Same size of tail and cation

Tail larger than cation

$\sigma_C = 5\,\mathring{A}$

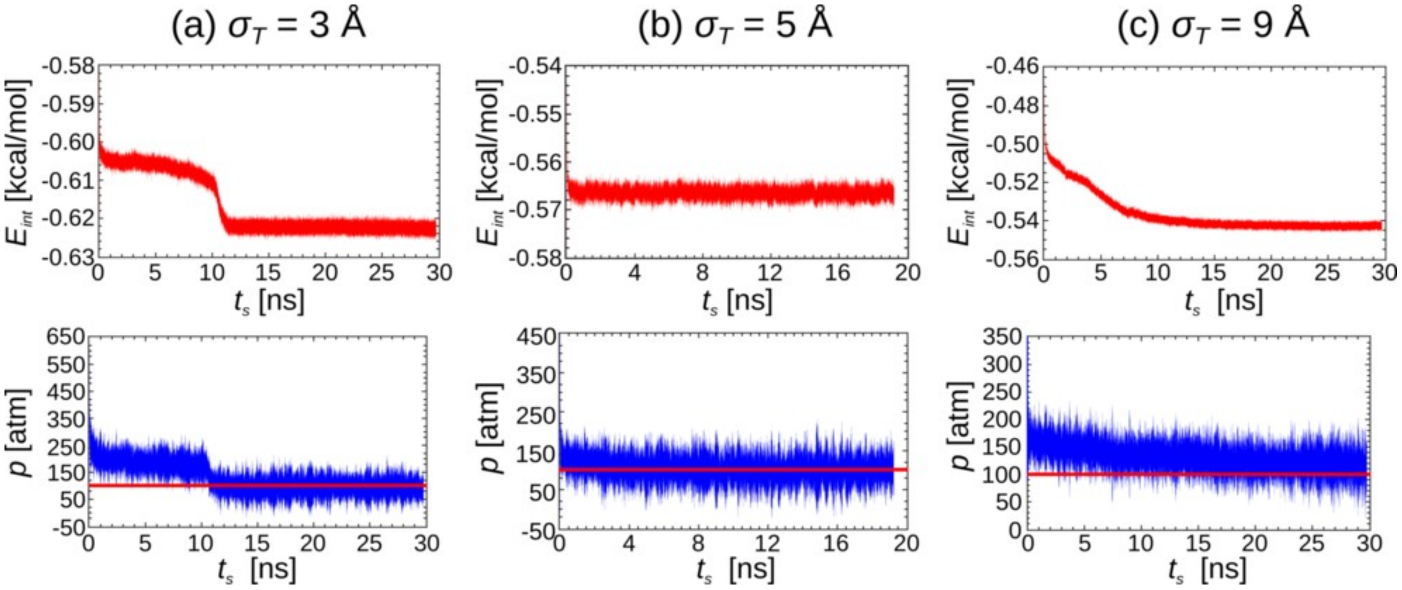
$\sigma_T^{TM3} = 3\,\mathring{A}$

$\sigma_T^{TM5} = 5\,\mathring{A}$

$\sigma_T^{TM9} = 9\,\mathring{A}$

Cation is represented by a neutral tail attached to a cationic head
Sizes of neutral tail → modeling three different alkyl chain lengths

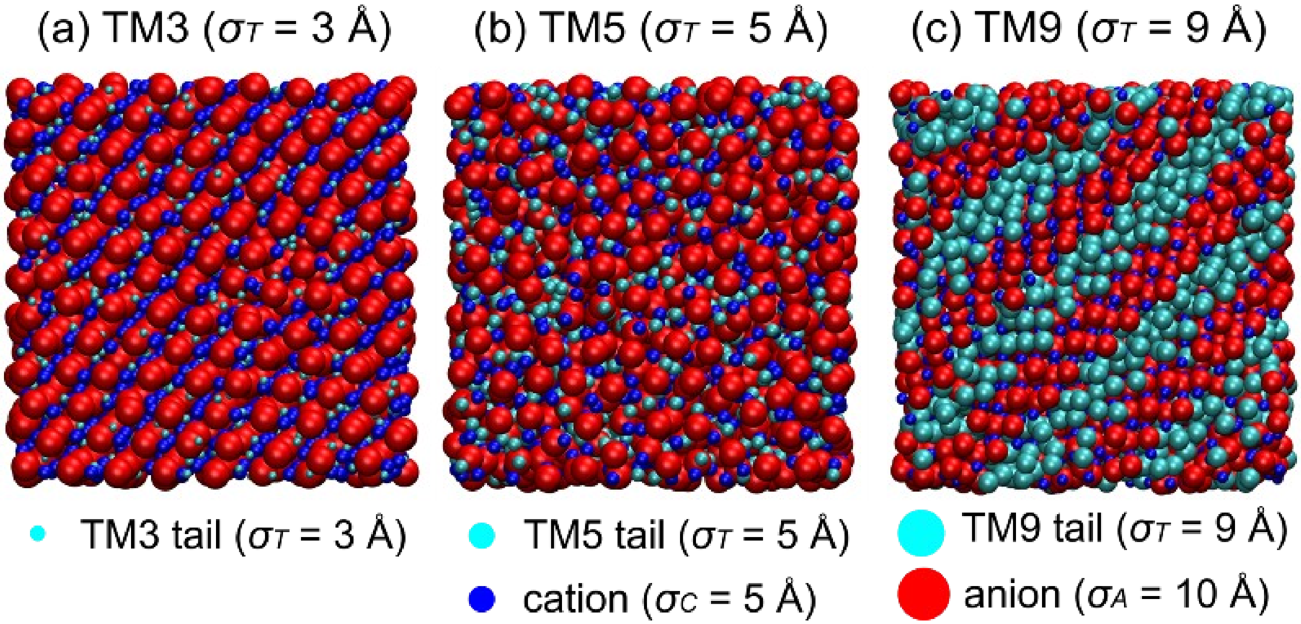
Relaxed structure of bulk ILs


(a) σ_T = 3 Å

(b) σ_T = 5 Å

(c) σ_T = 9 Å

Time relaxation
of internal energy
and pressure
for three
TM models

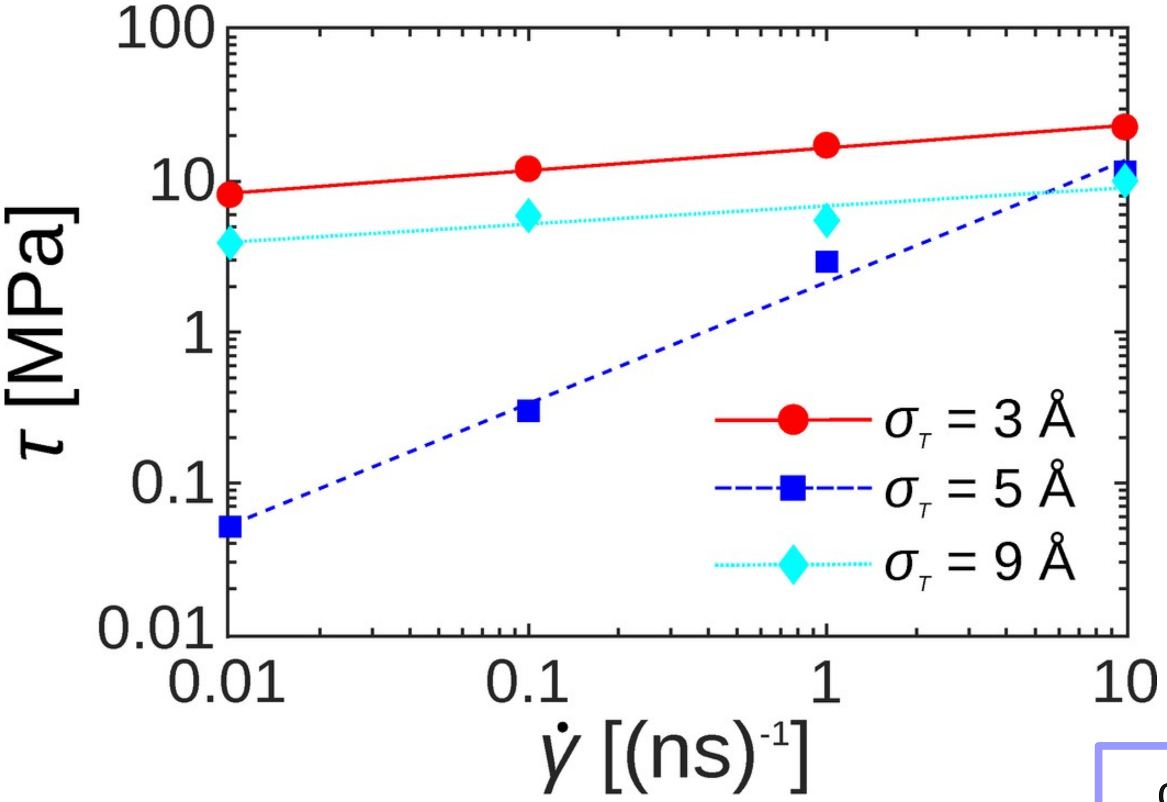

(a) TM3 (σ_T = 3 Å)

(b) TM5 (σ_T = 5 Å)

(c) TM9 (σ_T = 9 Å)

Relaxed structure
of three TM models

NEMD shearing simulations of bulk ILs



Average shear stress τ
as a function of
shear rate $\dot{\gamma}$
of bulk TM ILs

● ■ ◆ NEMD shearing simulations

— - - - ······ Fit with relation (1)

(1) $\tau = \eta \cdot \dot{\gamma}^{\alpha}$

(2) $\eta^{GK} = \frac{V}{k_B T} \int_0^{\infty} dt \langle \tau(0) \tau(t) \rangle$

ordered structure: TM3, TM9

$\alpha_{TM3} = 0.15 \pm 0.02$

$\alpha_{TM9} = 0.12 \pm 0.04$

$\eta^{GK}_{TM3} = 4.72\, mPas$

$\eta^{GK}_{TM9} = 1.67\, mPas$

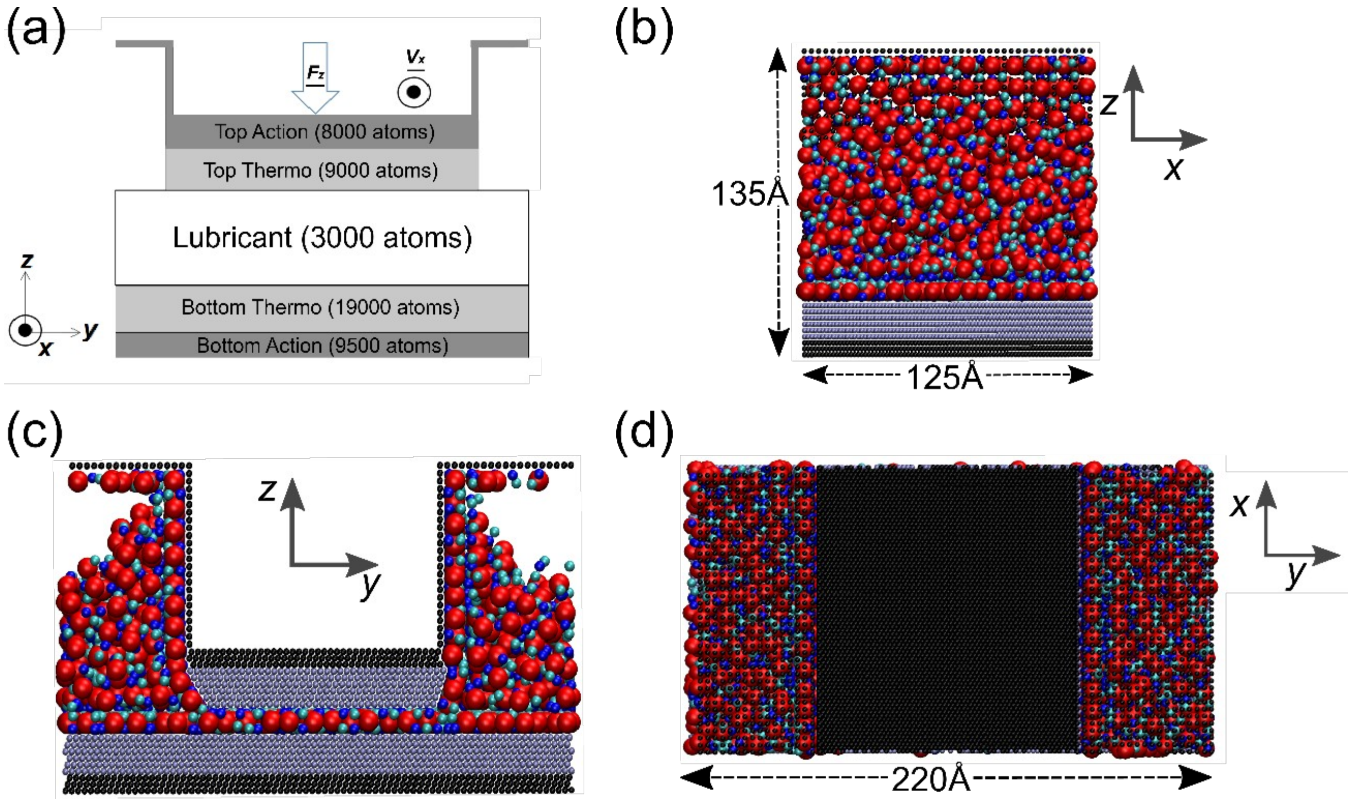
$\alpha \approx 1$

liquid: TM5

$\alpha_{TM5} = 0.8 \pm 0.1$

$\eta^{GK}_{TM5} = 0.61\, mPas$

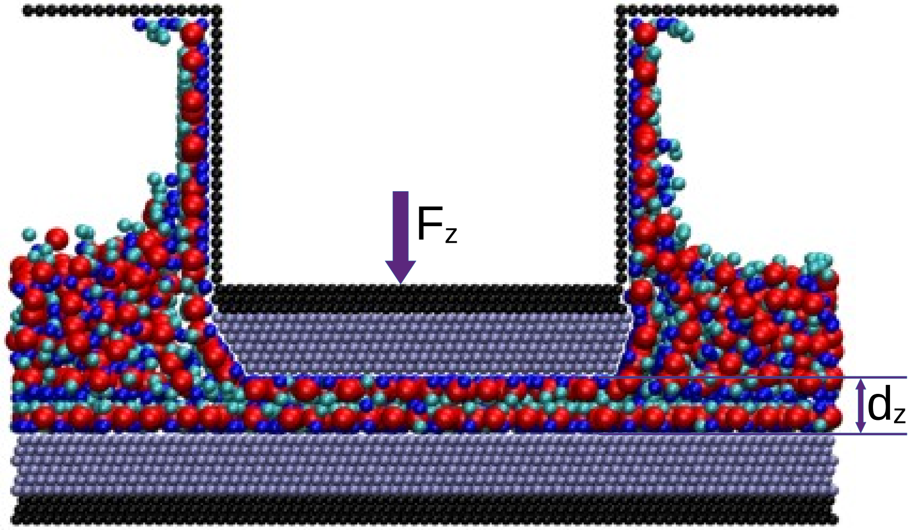
Simulation setup of confined ILs



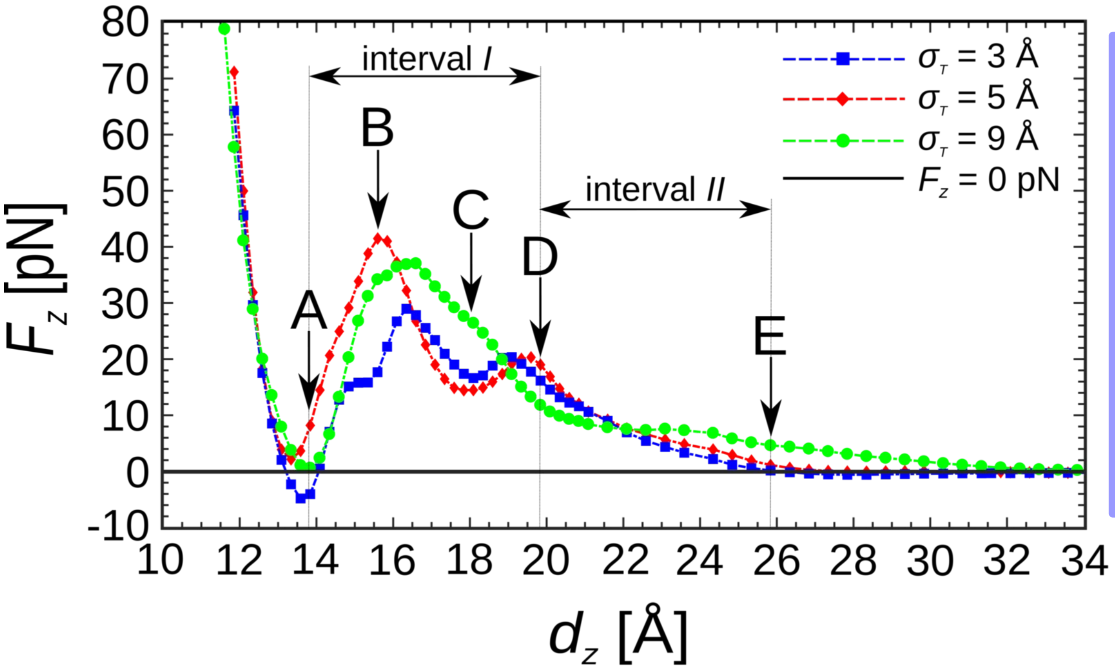
(a) Schematic of the MD simulation setup
(b) VMD snapshot of the xz cross-section
(c) VMD snapshot of the yz cross-section
(d) VMD snapshot of the xy cross-section

VMD = Visual Molecular Dynamics, a program for visualization

Equilibrium behaviour of confined ILs



Example of IL confined between
Top and Bottom plate
with normal load and
inter-plate distance indicated
Smooth and easy compression of
IL ↔ its equilibrium behaviour

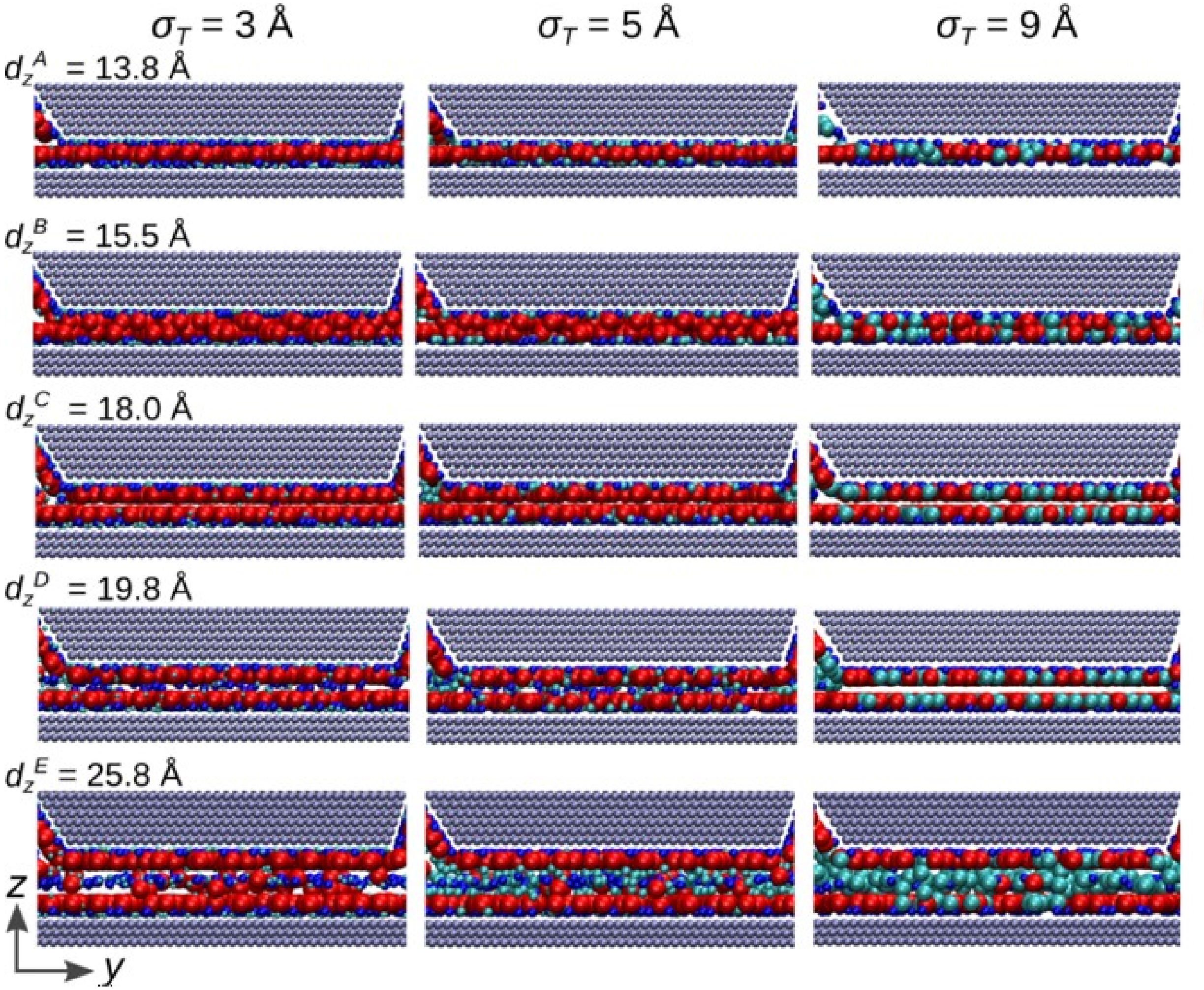


Dependence of normal load F_z
acting between IL and Top plate
on inter-plate distance d_z

Static force-distance characteristic

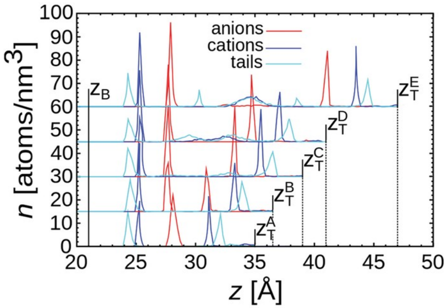
Characteristic points:
Interval I: {A, B, C, D}
Interval II: {D, E}

Configurations in static force-distance characteristic

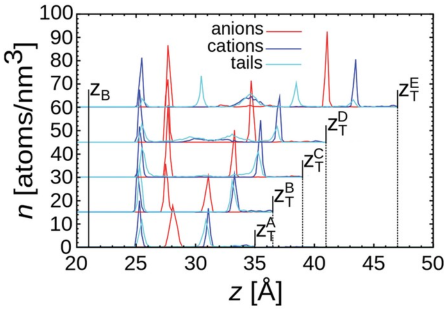


VMD snapshots of system configurations in characteristic points {A, B, C, D, E} in the yz cross-section

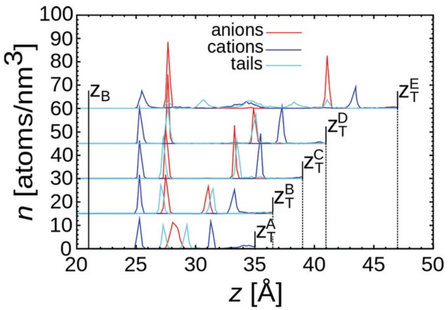
(a) TM3 ($\sigma_T = 3$ [Å])



(b) TM5 ($\sigma_T = 5$ [Å])

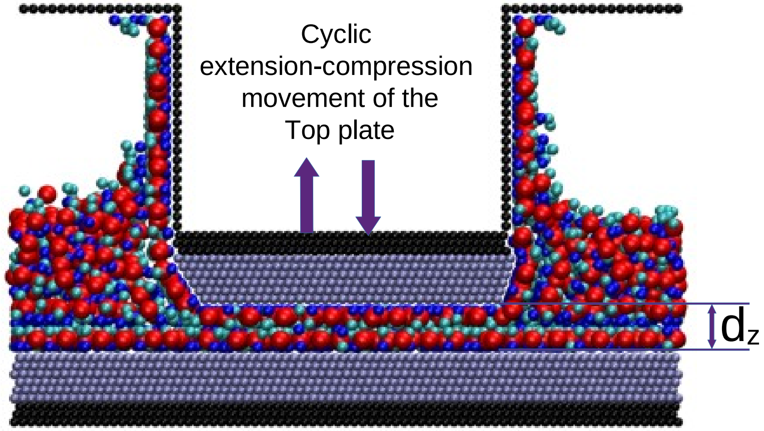


(c) TM9 ($\sigma_T = 9$ [Å])



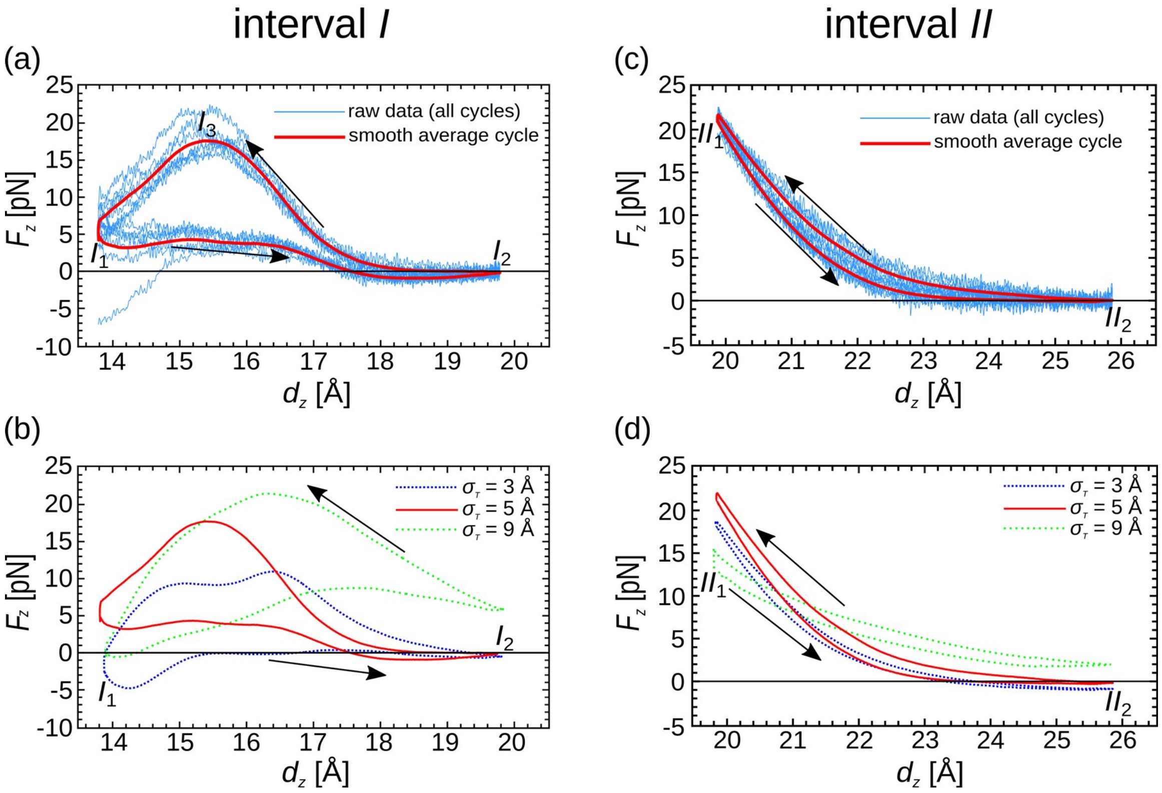
Ionic density distributions along the z-axis

Cyclic extension-compression of confined ILs



Quick and sharp extension-compression of IL ↔ its dynamic behaviour

We applied in total 10 cycles and computed a smooth average cycle


interval *I*

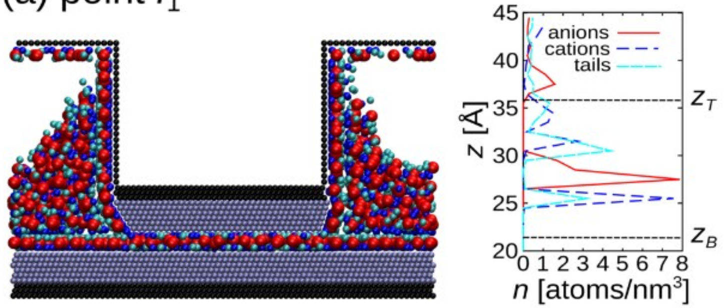
interval *II*

Dependence of normal load F_z acting between IL and Top plate on inter-plate distance d_z

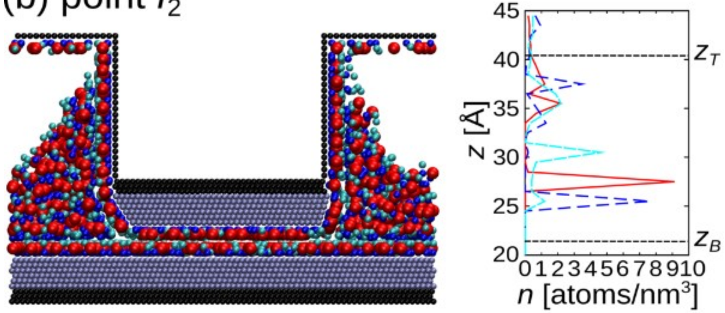
Dynamic force-distance characteristic

Configurations in dynamic force-distance characteristic

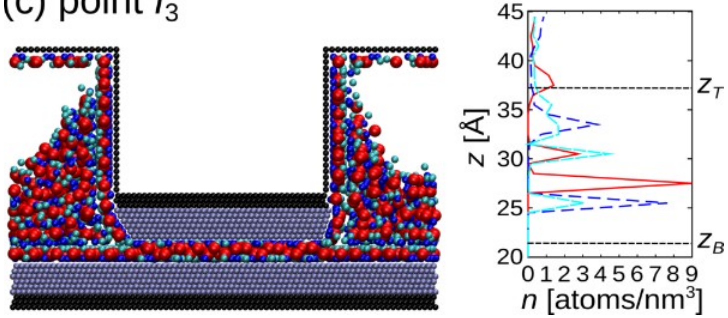
(a) point I_1



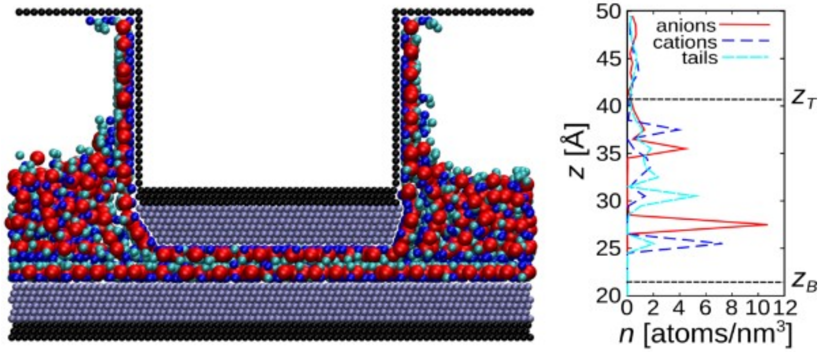
(b) point I_2



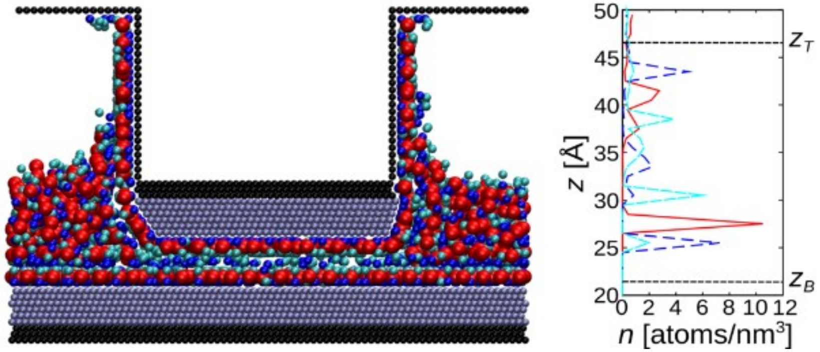
(c) point I_3



(a) point II_1

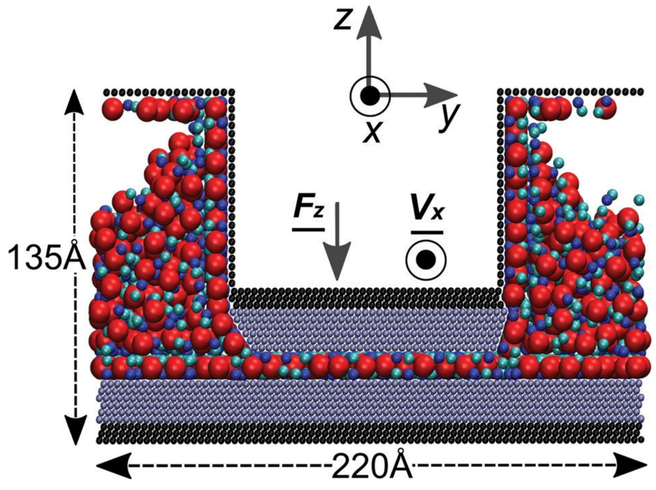


(b) point II_2

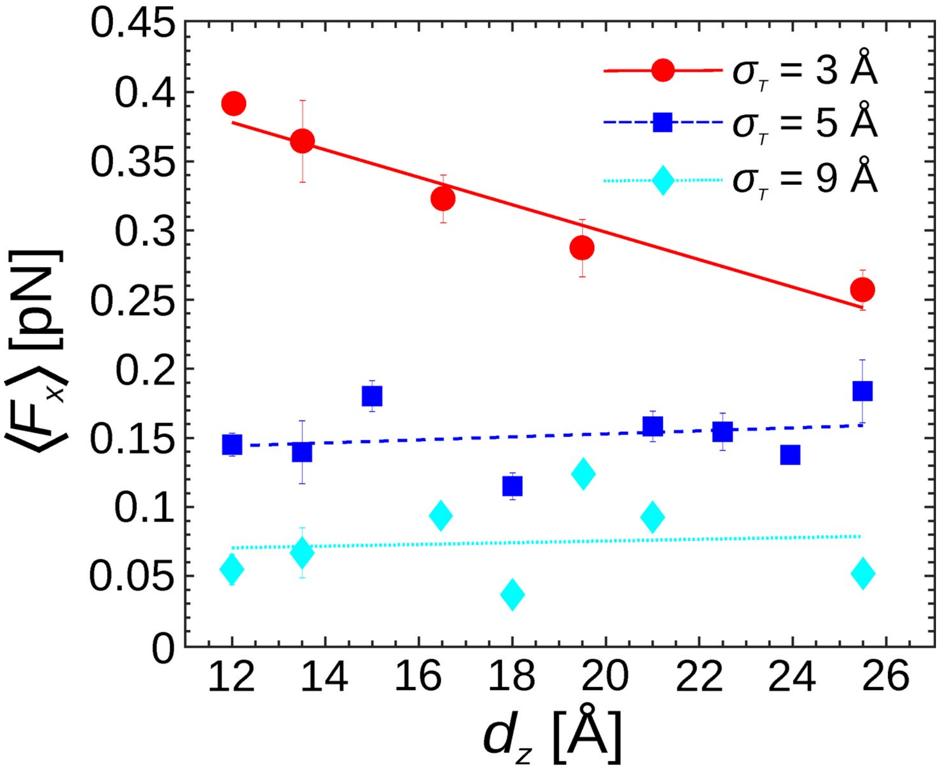


Snapshots of system configurations at characteristic points of intervals *I* and *II* with corresponding ionic density distribution along the z-axis

Tribological behaviour of confined ILs



Example of a configuration with sliding velocity V_x imposed on the Top plate



Dependence of friction force F_x acting on the Top plate on inter-plate distance d_z

Conclusions

- A mutual feature of all modeled ILs is formation of the fixed layers of ions along the solid plates due to strong ions-plate LJ interaction

  → consequence of the fixed layer stability is steep rise of the normal force at small interplate gaps

- This is an effect useful for preventing solid-solid contact and wear
- A high load-sustending capability requires strong adsorption of the lubricant to the surface of confining solid plates, while low friction requires low viscosity
- The obtained results confirm that the behaviour of ILs in confinement can be unrelated to their bulk behaviour

  → matching simultaneously, typically contradicting, low friction and pronounced anti–wear performance

- General conclusion:

Design of optimal IL lubricants should take into account nanoscale properties of lubricating thin films, in which the effects of molecular-level processes are pronounced and highly relevant

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with major R&D laboratories.

Topic: novel surfaces & magnetic materials,
python coding and use of super computers

Funding framework:
EU RISE project (2021-2025)

Deadline: open
Start date: anytime

Location:
Belgrade (Serbia) / Zaragoza (Spain) /
/ Nancy (France) / Valparaizo (Chile)

contact: igor@ipb.ac.rs (expressions of interest); mdasic@ipb.ac.rs
website: ultimate-i.eu

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THANK YOU FOR YOUR ATTENTION!

ХВАЛА НА ПАЖЊИ!