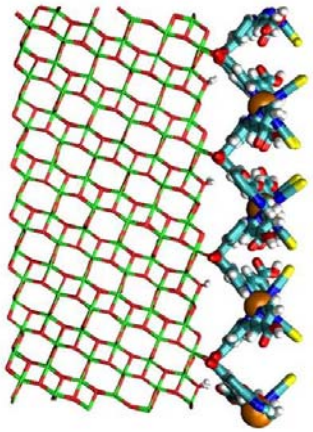
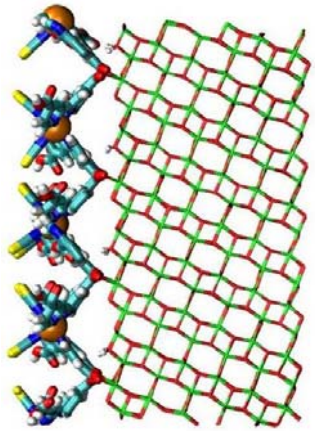
Molecular Aspects of Solid State and Interfacial Electrochemistry
26-31 August, Dubna



Molecular Dynamics Simulation as a Powerful Tool to Investigate the Structure of Interfaces and Heterogeneous Processes



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Moscow, Russia

Plan.

Basics of the MD simulation.

Research projects:

- Interface structure of ionic liquids at a solid electrode surface.
- Influence of cations on the TiO_2/electrolyte interface structure.

Rare events simulation (reaction free energy surface, rate constant):

- Umbrella sampling
- Constrained dynamics
- Activated dynamics simulations

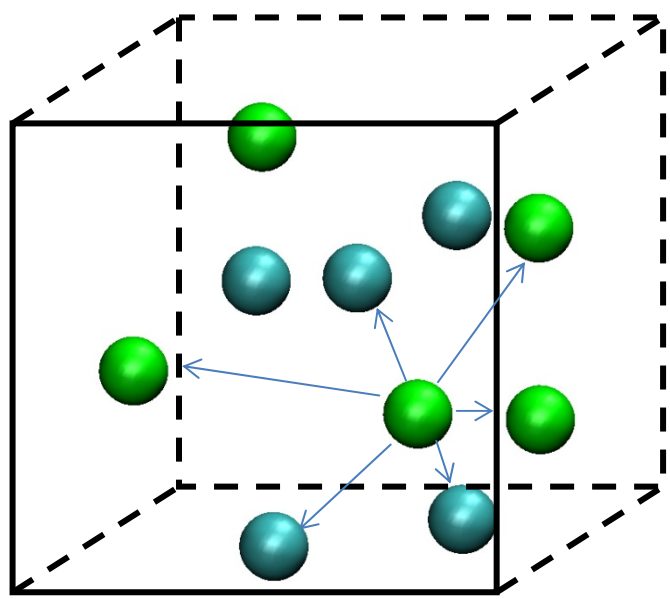
MD simulation basics.

Numerical integration of Newton's equations of motion for a system of N interacting particles:

$$\begin{cases} m_i \dfrac{dv_i(t)}{dt} = F_i(r_1,\ldots,r_N), \quad \dfrac{dr_i(t)}{dt} = v_i(t) \\ r_i(t=0) = r_i^0, \quad v_i(t=0) = v_i^0 \quad i = 1,\ldots,N \end{cases}$$

$$F_i = -\frac{\partial U(r_1,\ldots,r_N)}{\partial r_i}$$

Properties are determined by a **force field**!



Quantum chemistry → Force field development ← Experiment

↓

MD simulations

↓

Property prediction
(structure, thermodynamics, dynamics, kinetics)

What is required for a good algorithm?

- It should satisfy the conservation laws for energy and momentum.
- It should de time reversible.
- The algorithm should be relatively fast and accurate.

Verlet leapfrog algorithm.

$$\begin{cases} v_i(t+\frac{\Delta t}{2}) = v_i(t-\frac{\Delta t}{2}) + \frac{F_i(t)}{m_i}\Delta t \\ r_i(t+\Delta t) = r_i(t) + v_i(t+\frac{\Delta t}{2})\Delta t \end{cases}$$

Integration timestep:

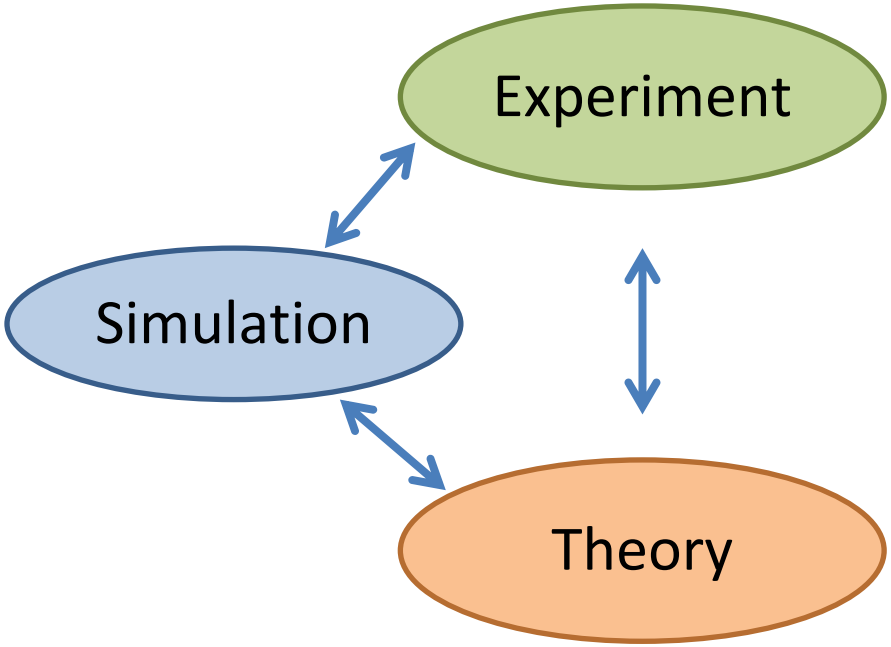
Translation Δt ~ 10 fs

Flexible molecules, rigid bonds Δt ~ 2fs

Flexible molecules and bonds Δt ~ 1fs

System size: N ~ $10^4 \div 10^6$ particles.
Accessible timescale: τ ~ 10÷100 ns.

Why do we need atomistic simulations?



- for understanding experimental observations
- for obtaining molecular level information that can't be found experimentally
- for checking theoretical results
- for study conditions which are not accessible experimentally

Why use molecular dynamics?

Molecular dynamics vs. **Quantum mechanics/Quantum MD**

Larger system — More accurate

Longer timescale

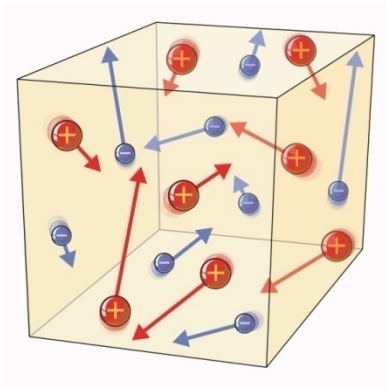
Molecular dynamics vs. **Monte Carlo method**

Nonequilibrium processes

Dynamic properties

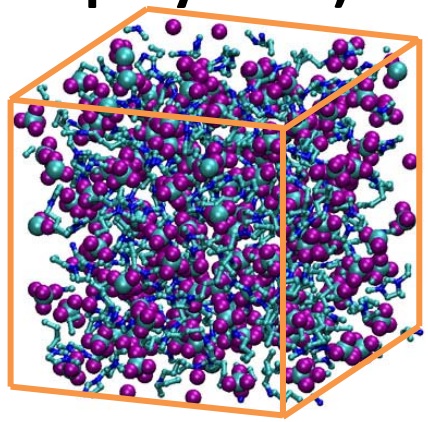
MD applications

Plasma science

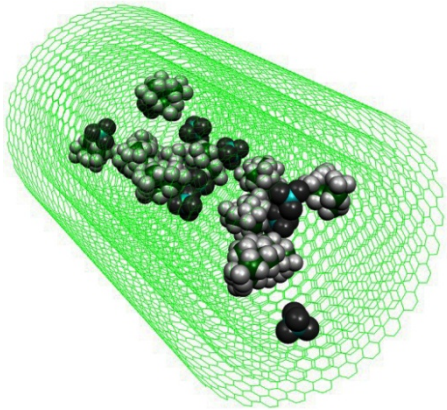


Macromolecules, biophysics

Condensed matter (crystals, liquids, polymers)

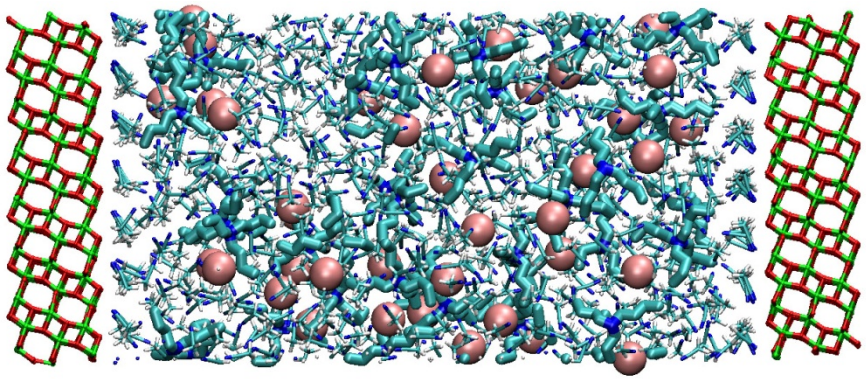


Material science



Kalugin et. al,
Carbon Nanotubes

Interfaces



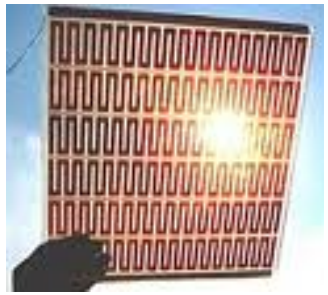
Double layer in ionic liquids.
Challenge for theory.
Routine for MD simulation.

Properties and applications of Ionic liquids.

Ionic liquid is an organic salt with melting point around room temperature.

1. Electrochemical stability.
2. Thermal stability.
3. Inflammable, nonvolatile, nontoxic.
4. Possibility of adjustment the ionic liquid properties.

Supercapacitors


Dye sensitized solar cells

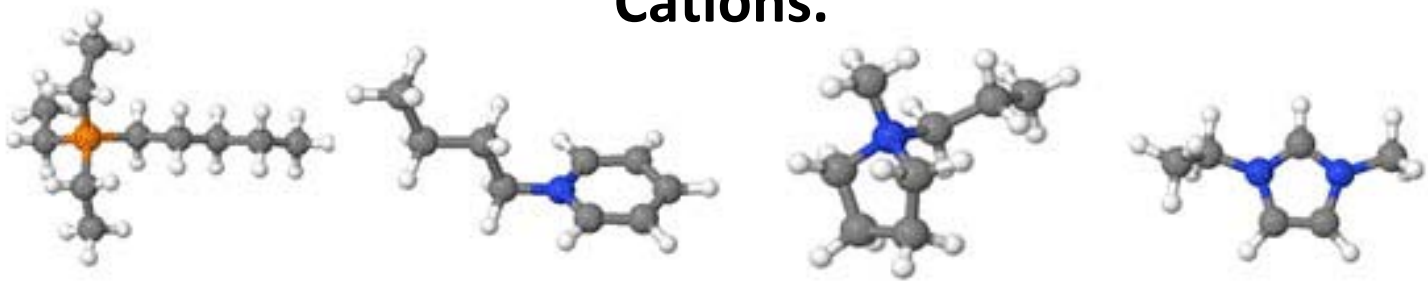
Fuel cells


Heterogeneous catalysis

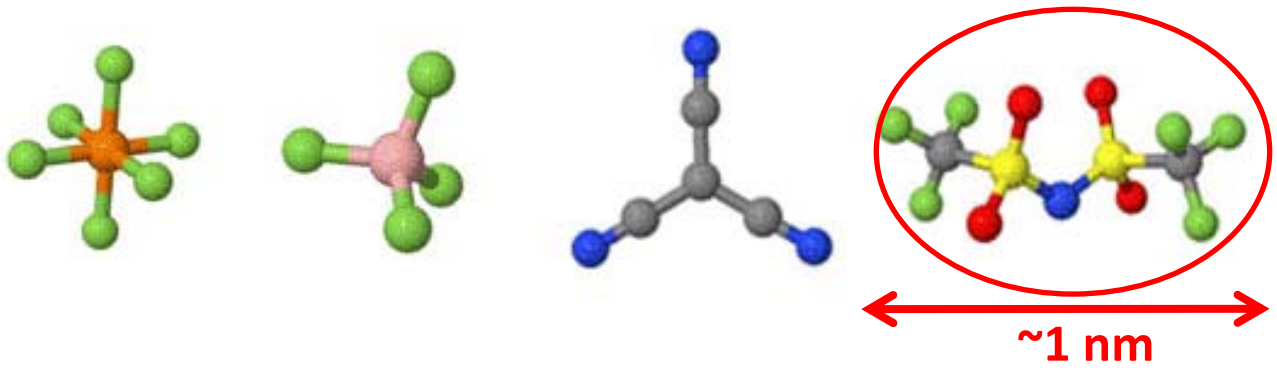
Theory of the double layer in ionic liquids must be built!

Types of ionic liquids.

Cations.



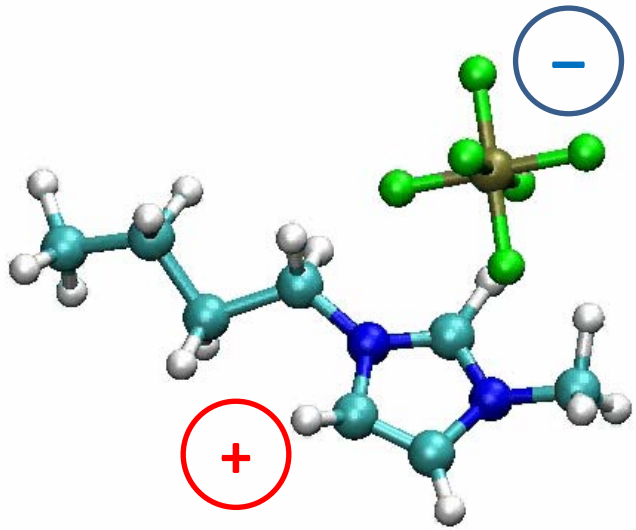
Anions.



$n_{ions} \sim 10^{21}$ cm^{-3}

The theory of the double layer must properly takes into account ions' structures and ion-ion interactions!

Ionic liquid [BMIM][PF_6]. The force field.

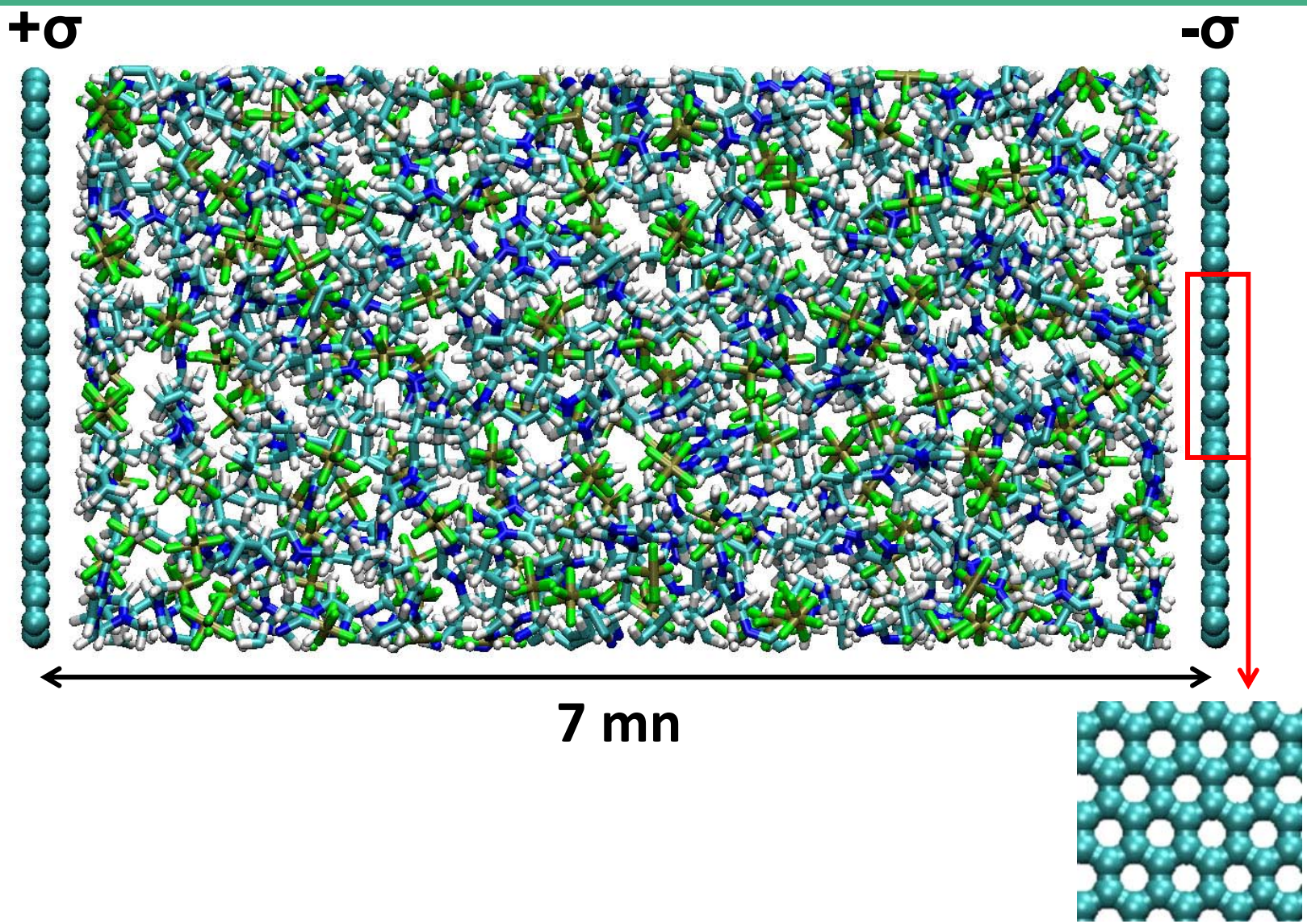


The AMBER-based force field[1]:

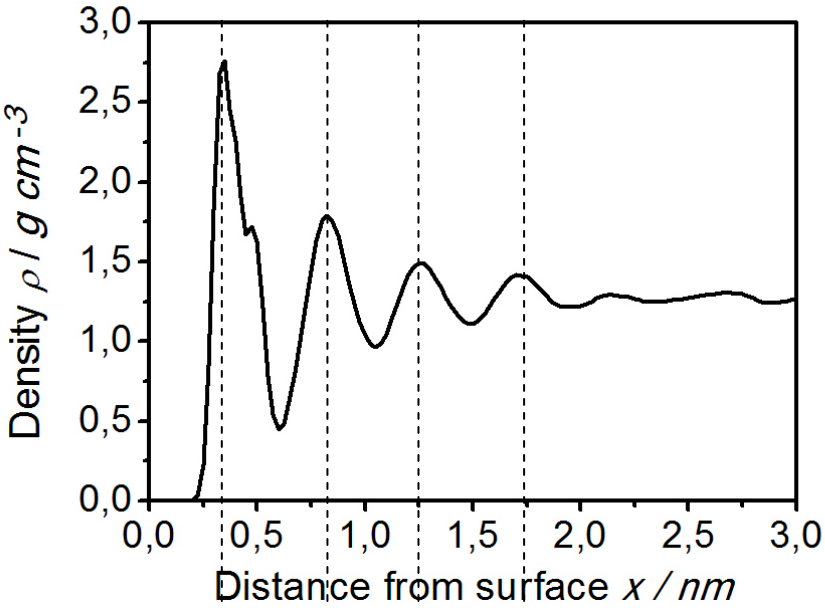
$$E_{tot} = \sum_{bonds} K_r (r - r_{eq})^2 + \sum_{angles} K_\theta (\theta - \theta_{eq})^2 + \sum_{angles} \frac{V_n}{2} (1 + \cos(n\phi - \gamma)) + \sum_{i<j} \left(\frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}} \right)$$

[1]S.A. Kislenko et al., *Phys. Chem. Chem. Phys.*, 2009, 11, 5584.

3D view of typical simulation boxes.

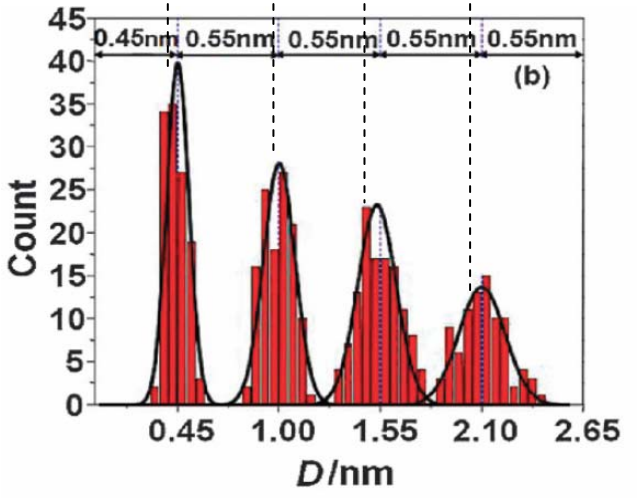


Ionic liquid interface structure near an uncharged surface.



MD simulation

S.A. Kislenko et al., *PCCP* , 2009, 11, 5584.

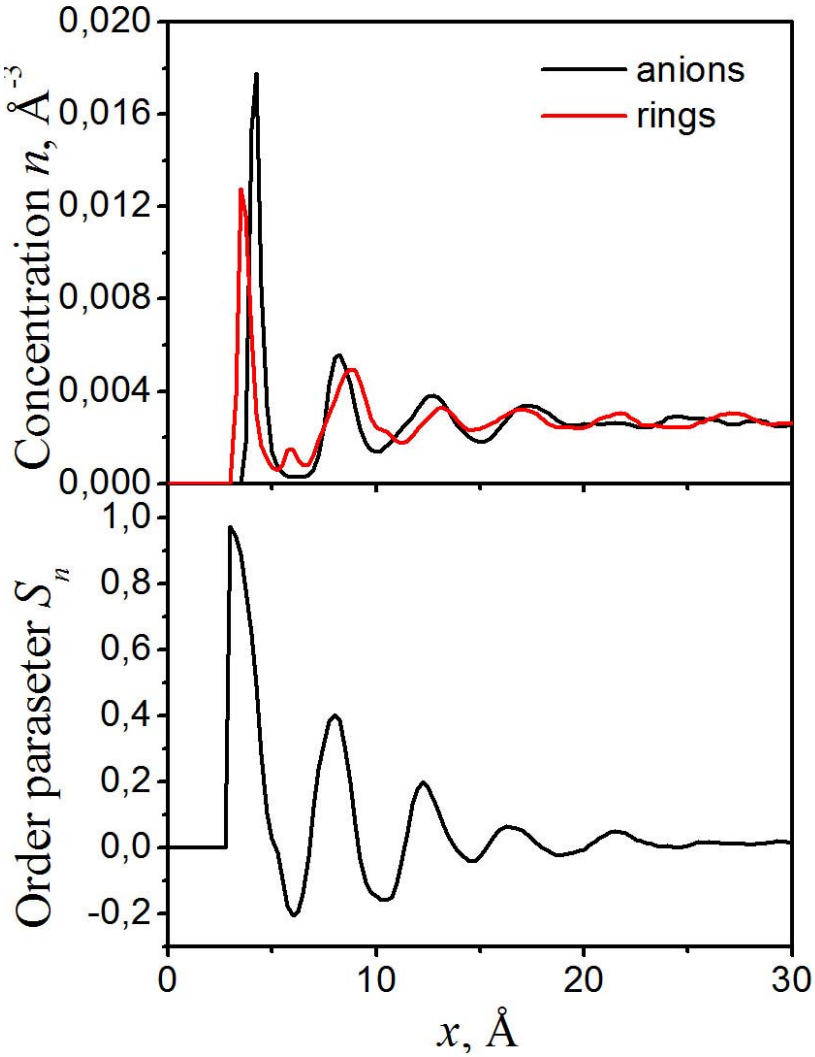


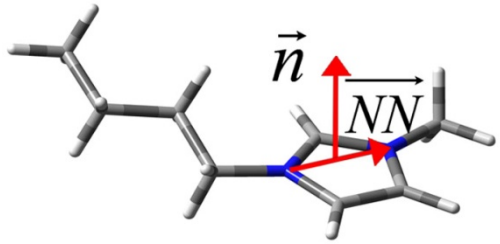
Experiment

Au(111)/[BMIM][PF_6]

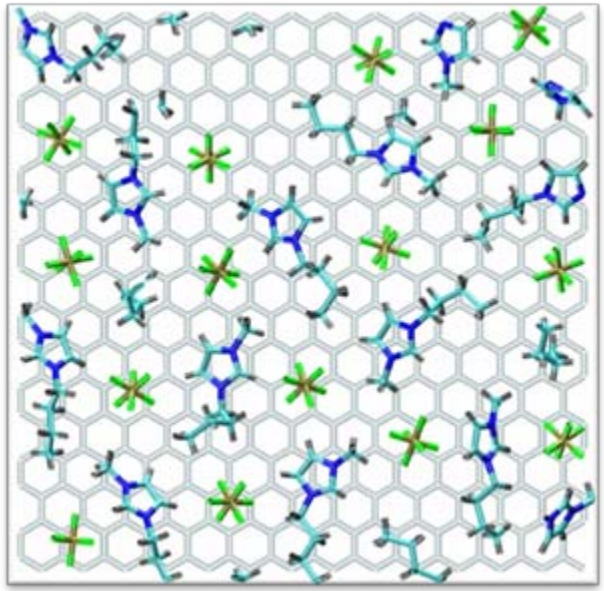
Xiao Zhang et al., *Chem. Commun.*, 2012, 48, 582.

Ionic liquid interface structure near an uncharged surface.

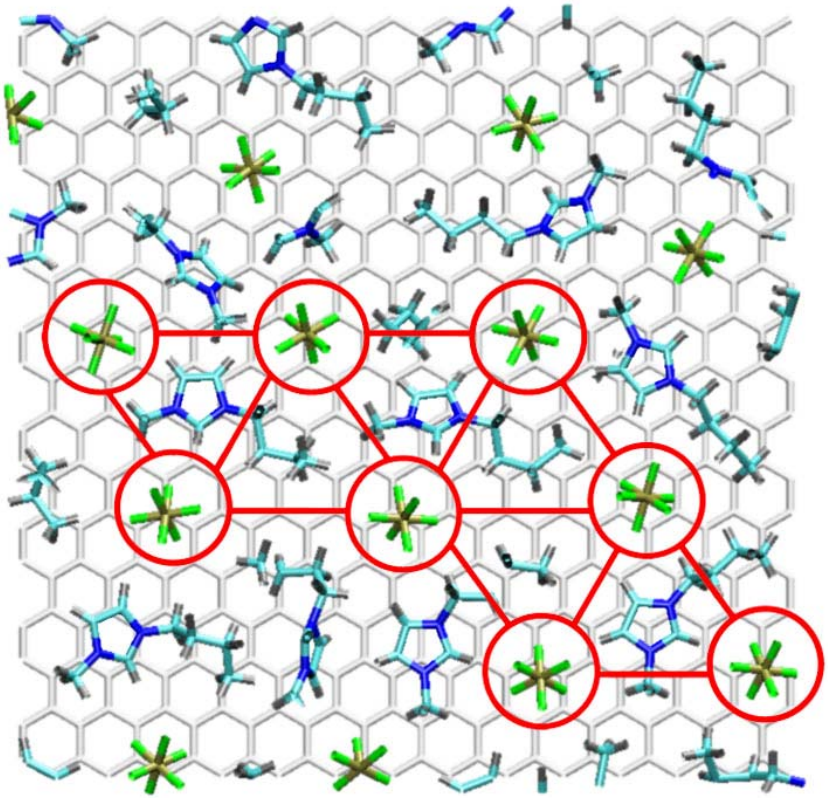


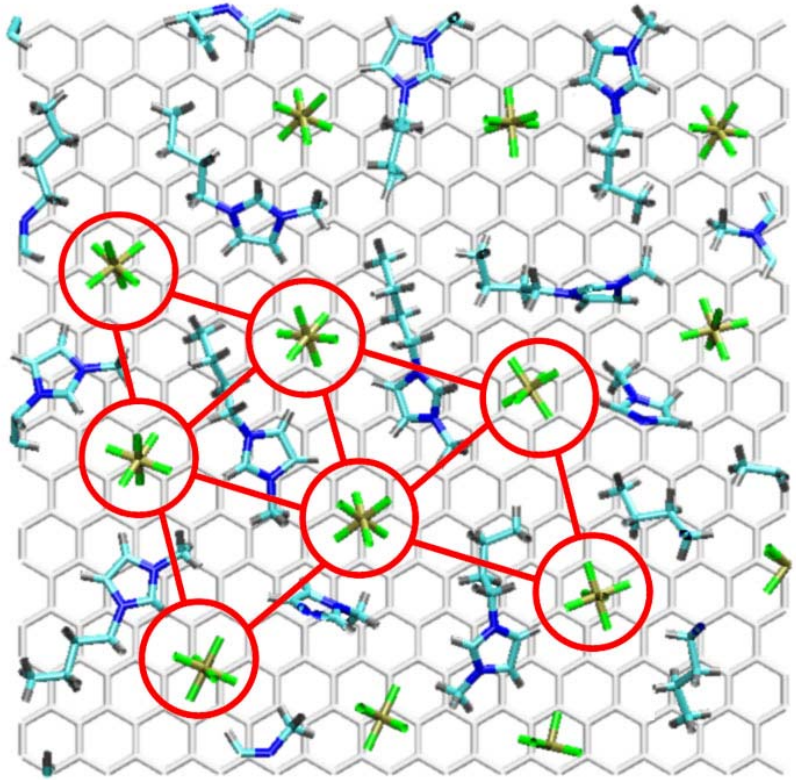


$$S = \left\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \right\rangle$$



Ion adsorption and formation of the 2D molecular clusters.





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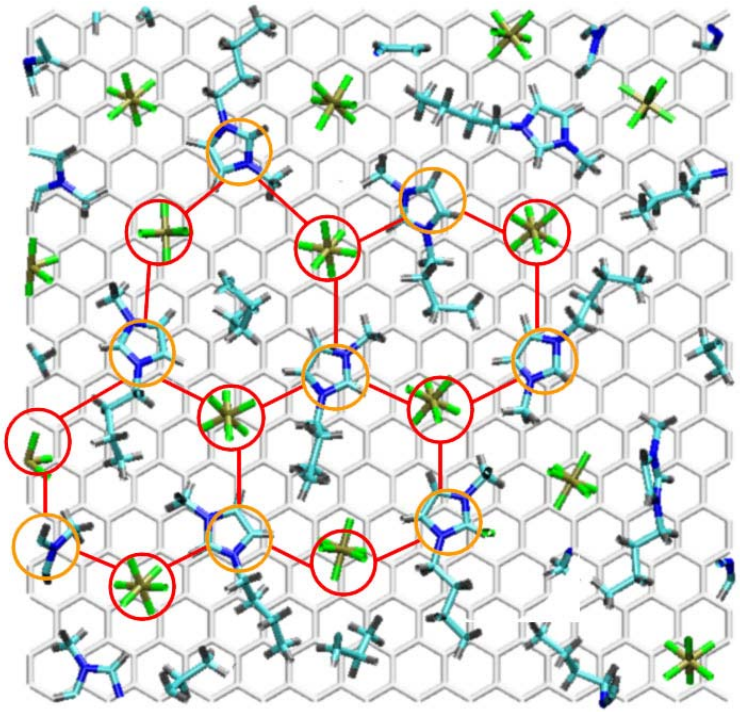
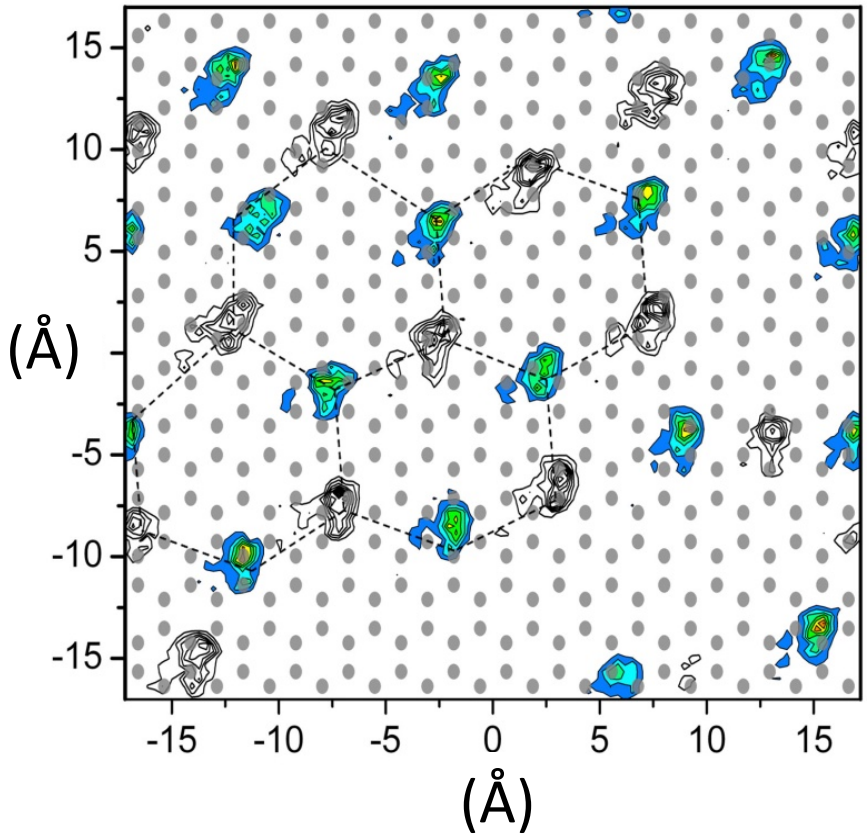
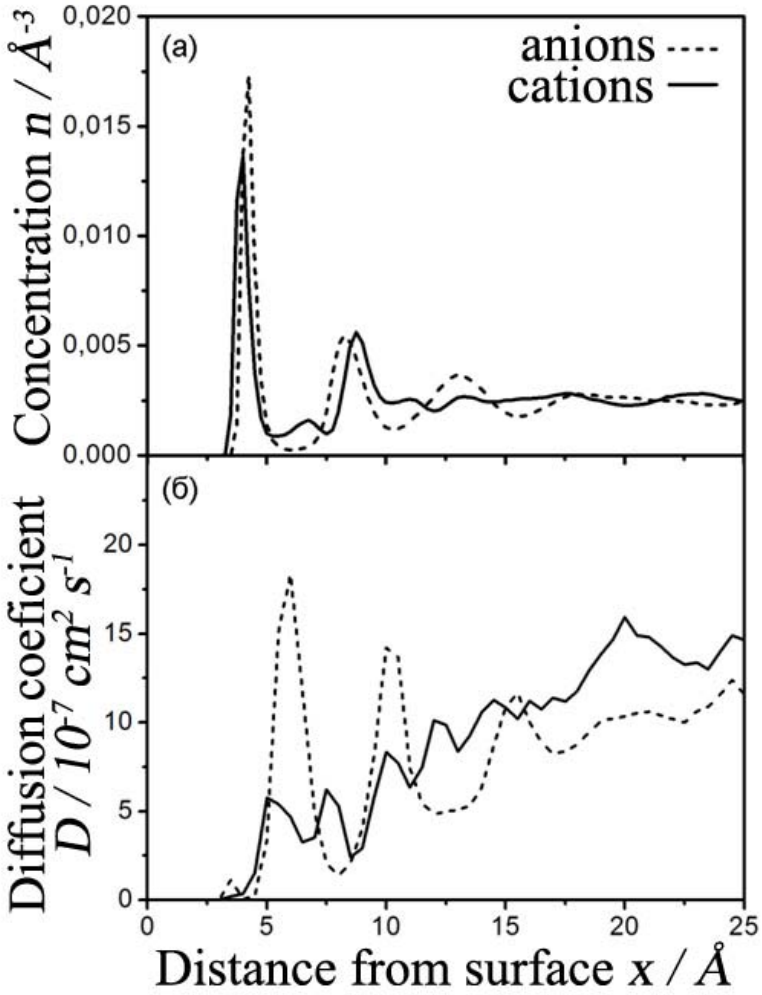


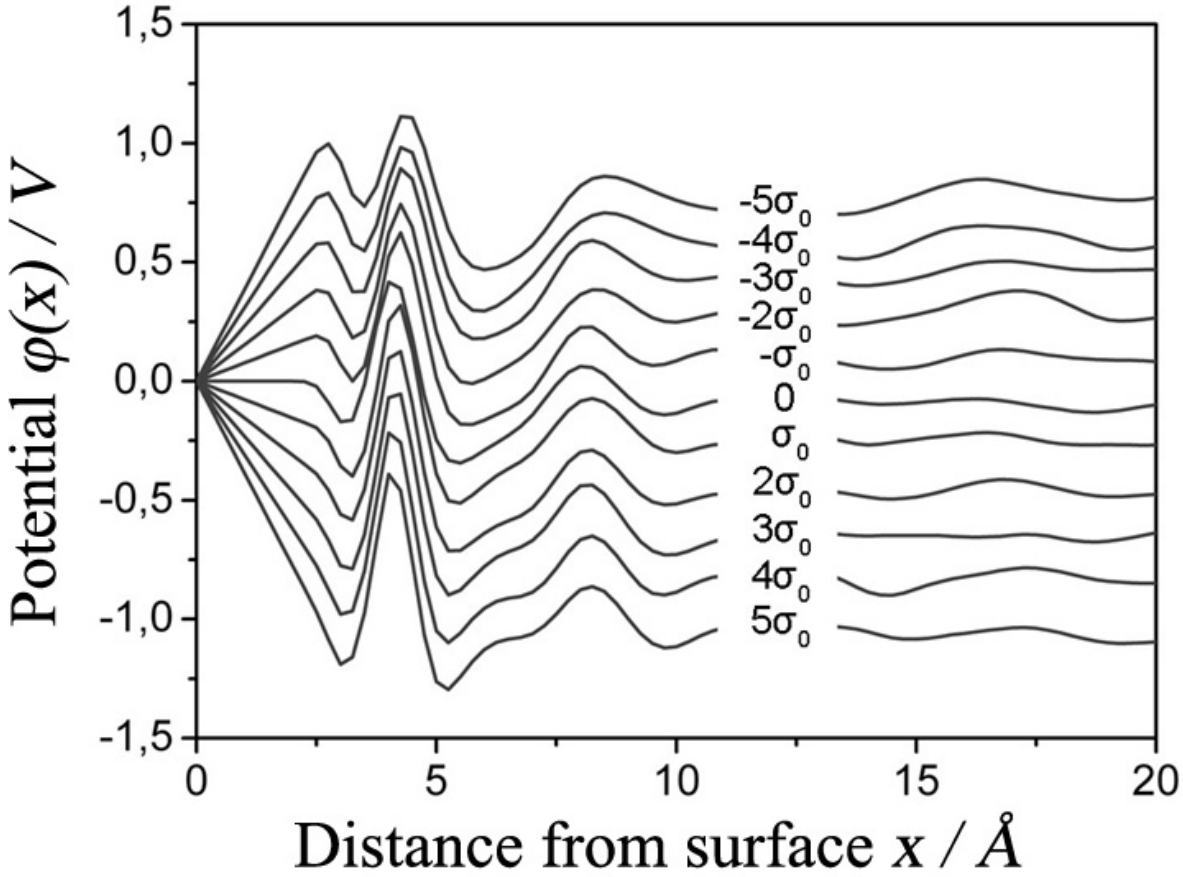


local self-diffusion coefficients of ions and its spatial correlation.



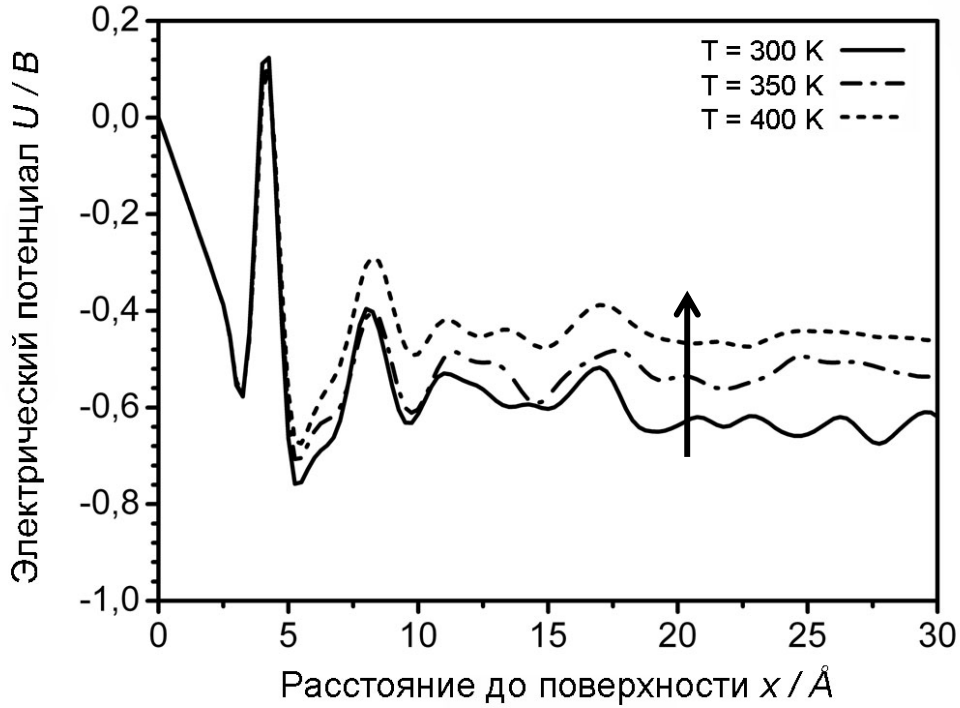
$$\langle (x(t) - x(t_0))^2 \rangle \propto 2D_x t$$

Dependences of the electric potential on the distance to the charged surface.



$\sigma_0 = 0.34 \cdot 10^{-6}$ C/cm^2

The influence of temperature on the screening potential.



$$C = \frac{c}{\Delta U}$$

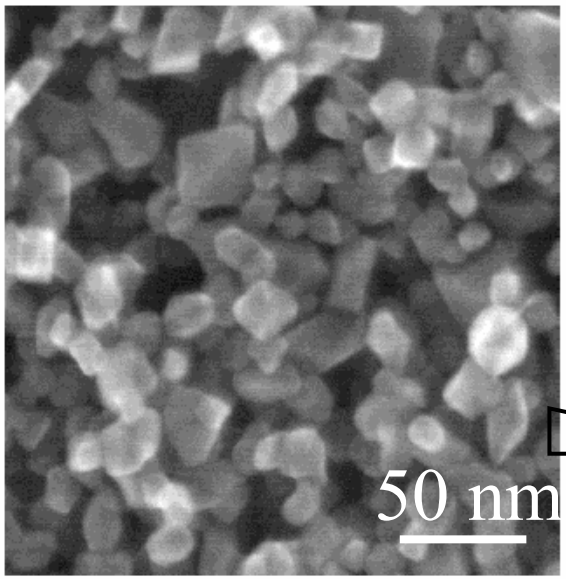
Increase of the capacitance *C* of the double layer in ionic liquids.
In ideal plasma the capacitance decrease with temperature $\sim 1/\sqrt{T}$

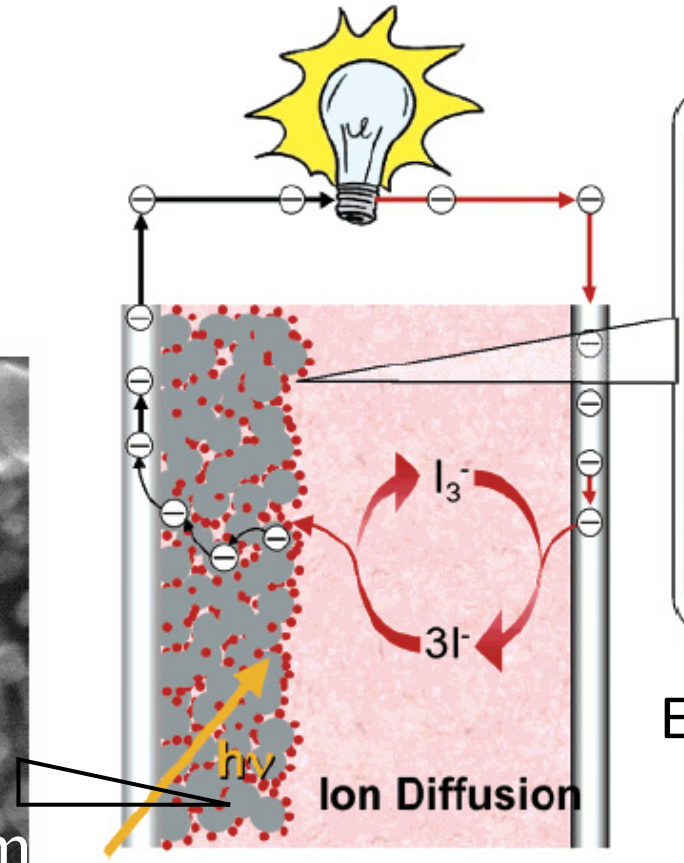
1. Lockett V., J. Phys. Chem. C, 2008, **112**, 7486.
2. Silva F., J. Electroanal. Chem., 2008, **622**, 153.

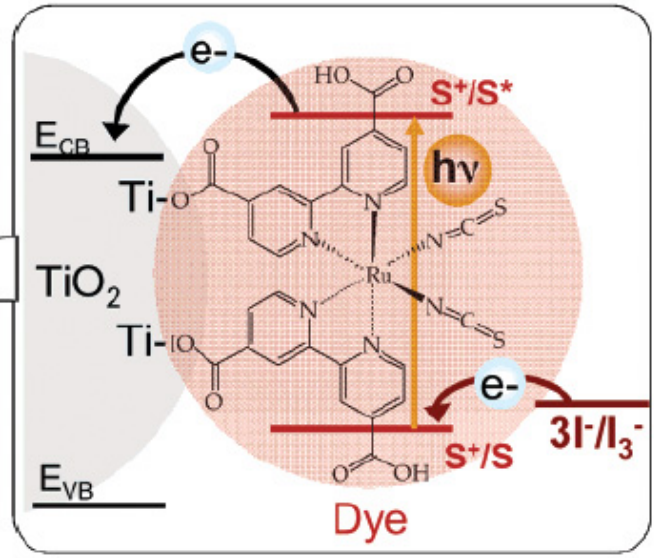
Influence of cations on the structure of the TiO_2/electrolyte interface.
Topics of Relevance to Dye-Sensitized Solar Cells (DSSCs).

Principle of operation of the DSSCs.

TiO_2 nanocrystals







Efficiency record 12.3%.

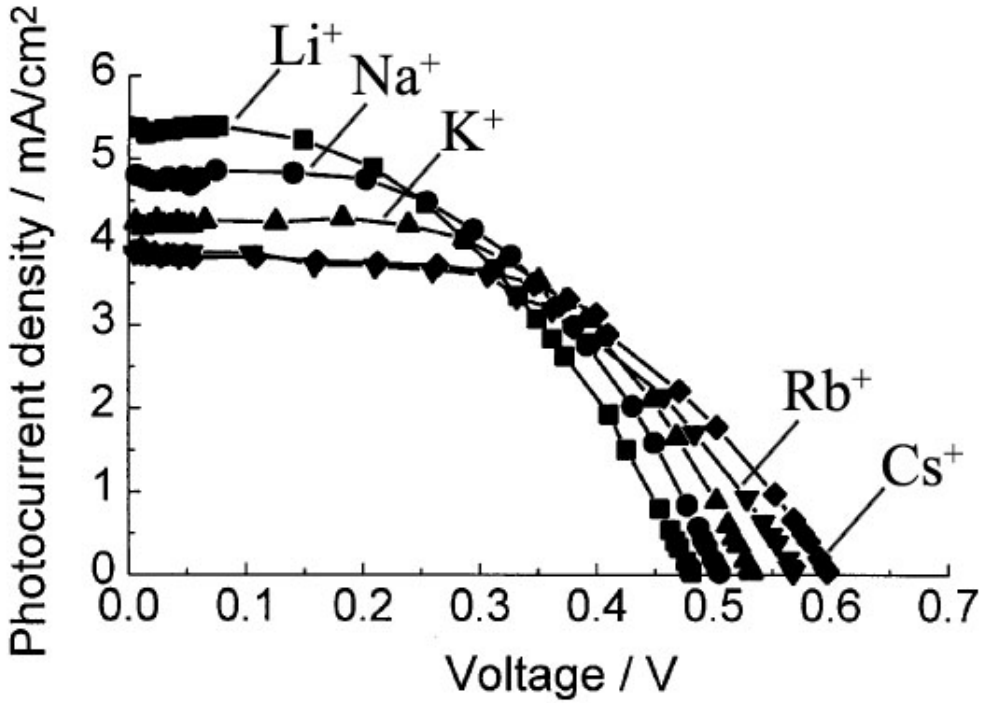
Almost all performance determining processes occur at the interface!

⇩

Optimization of the interface as a strategy to improve DSSCs efficiency.

M. Grätzel, *J. Photochem. Photobiol. A: Chemistry*, 2004, 164, 3.
B. Hardin, *Nature photonics*, 2012, 6, 162.

Influence of cations on the DSSCs performance.

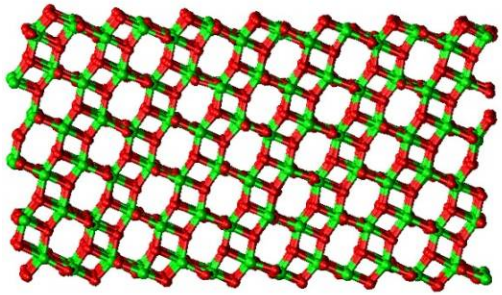
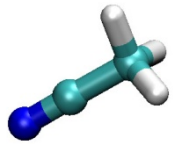


It has been observed experimentally that cations effect on the kinetics of electron injection and recombination, kinetics of dye regeneration, electron transport properties.

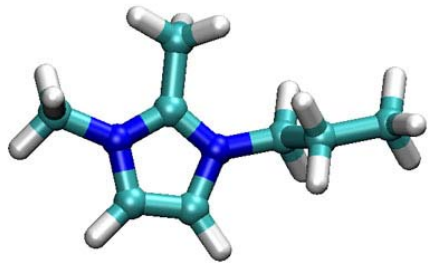
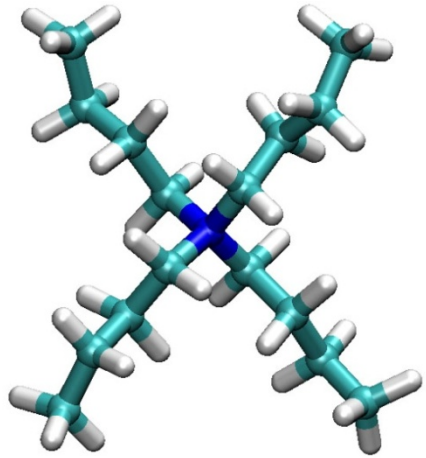
To improve an efficiency of the DSSCs the detailed picture of the interface processes should de constructed!

Yao Liu, *Solar Energy Materials and Solar Cells*, 1998, 55, 267.

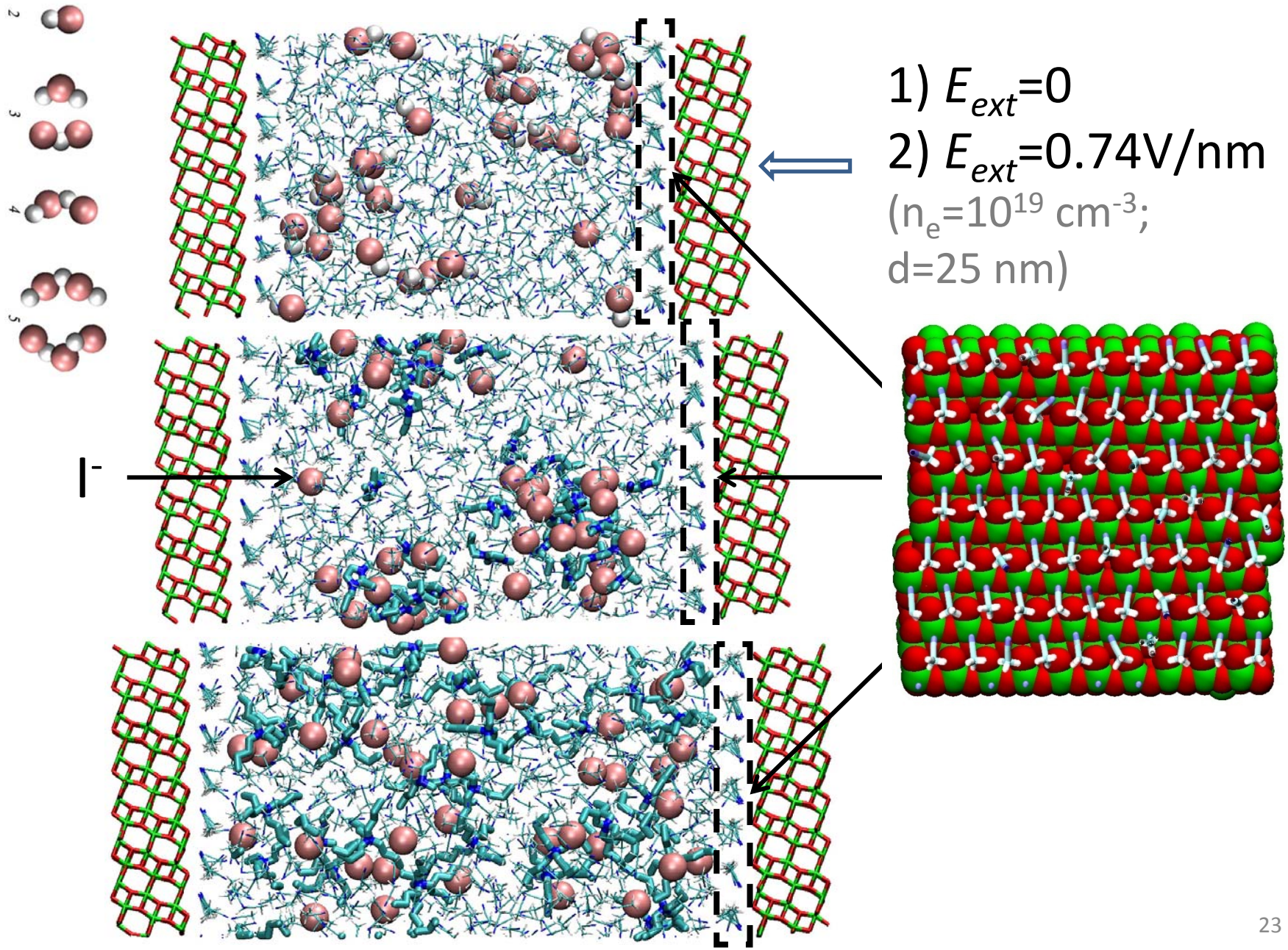
Simulated system.

Surface	Electrolyte
 TiO_2 anatase (101) surface	 0.7M + [X]I Acetonitryle-based electrolytes containing different iodide salts.

Cations

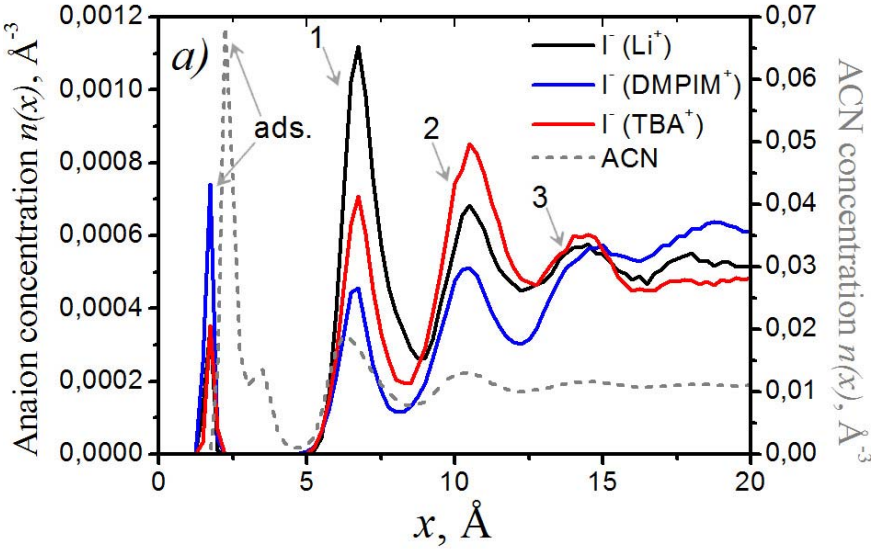
Li^+	$[DMPIM]^+$	$[TBA]^+$
		

Simulation box.

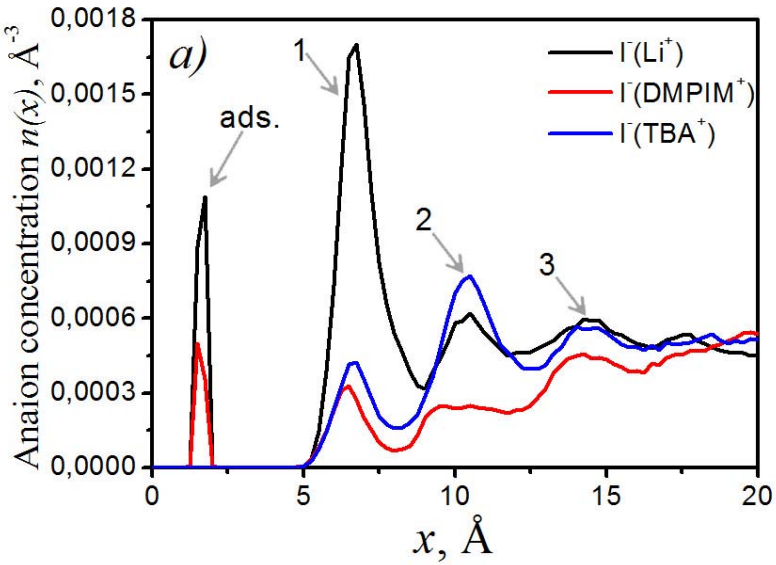


I^- anion distributions at the interface.

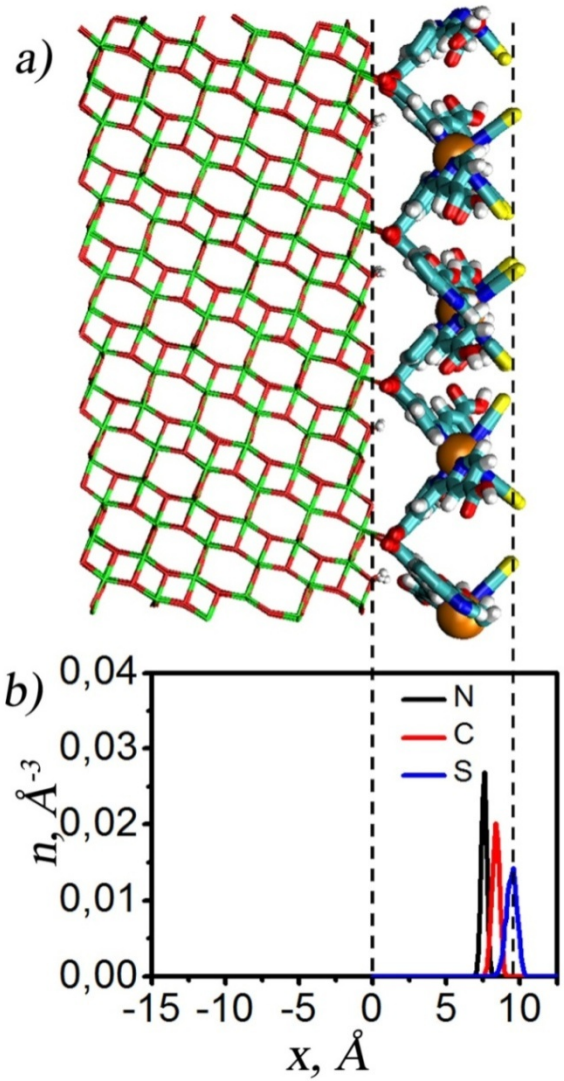
E_{ext}=0



E_{ext}=0.74



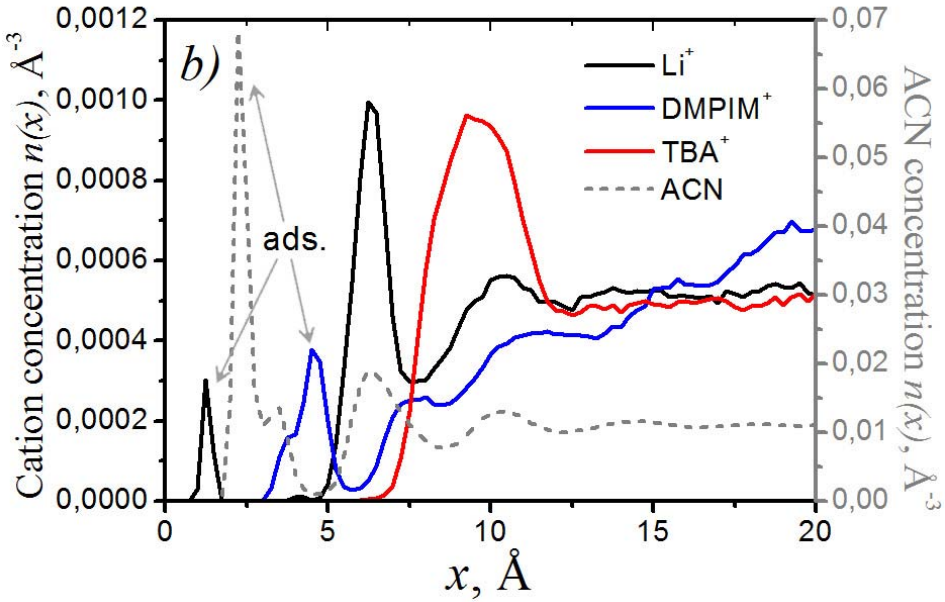
N3 dye



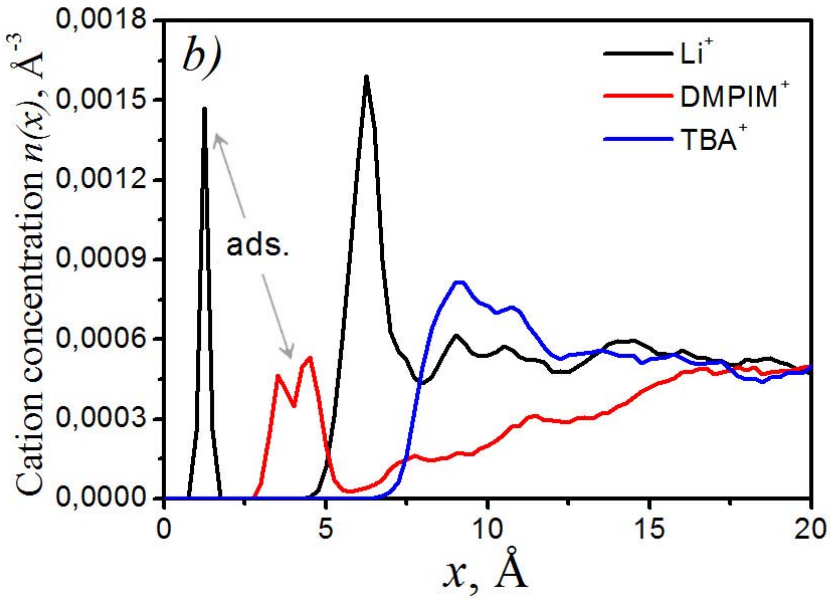
Cation effects on I^- distribution. That is the mechanism (as we suppose) by which cations influence the regeneration kinetics of a dye molecule.

Cation distributions at the interface.

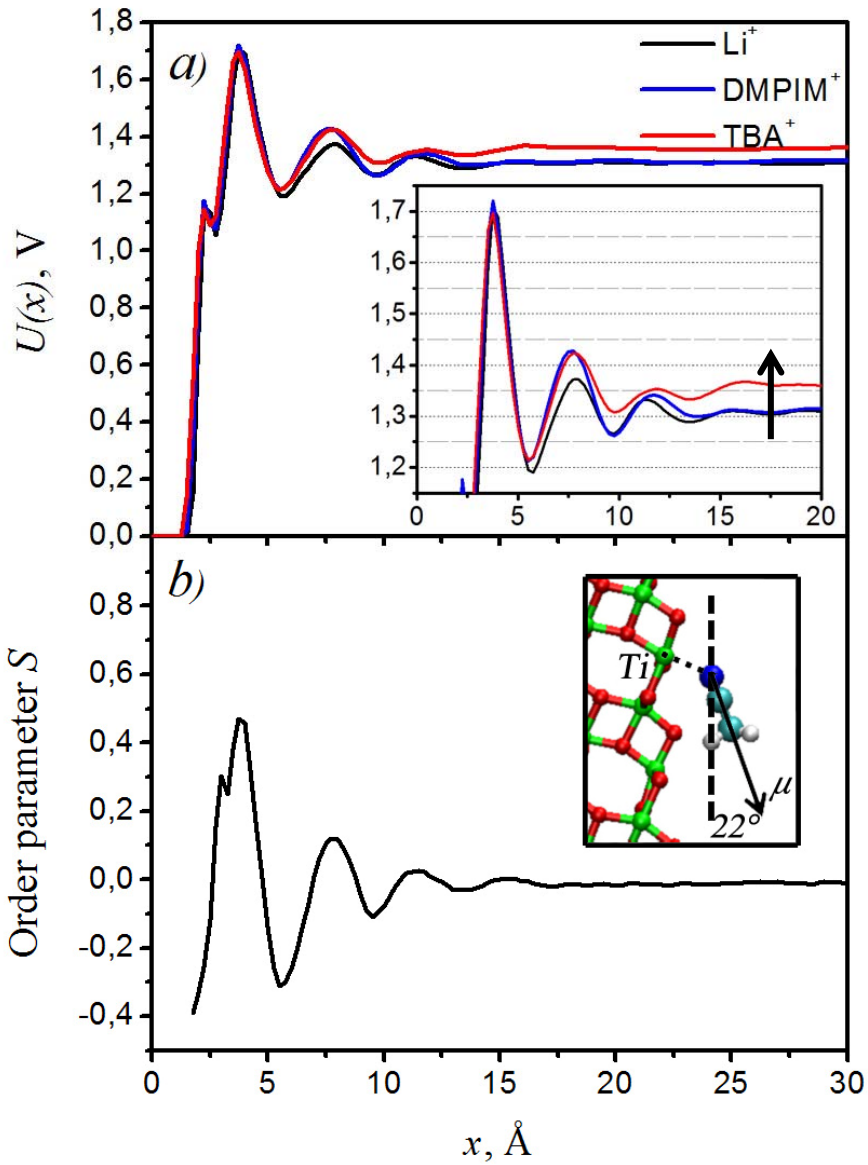
E_{ext}=0



E_{ext}=0.74



Electric potential across the interface.



Experiment

	J_{sc}/mA /cm^2	V_{oc}/V
$DMPIm^+$	8.5	0.75
TBA^+	6.8	0.83

Shogo Nakade, *J. Phys. Chem. B*, 2005, 109, 3480.

Investigation of rare events by MD simulation.

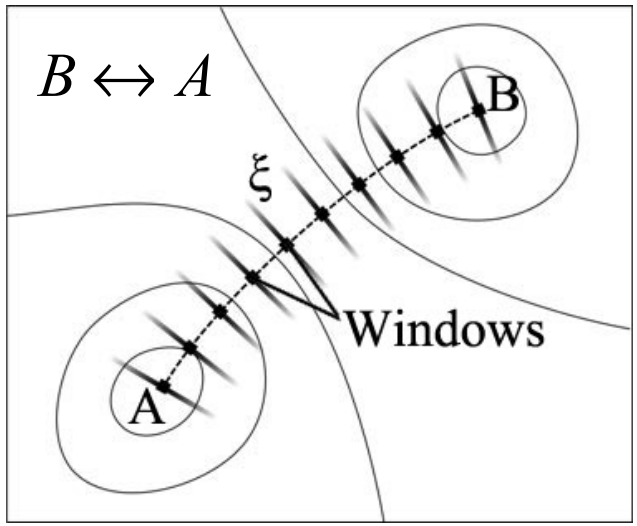
Umbrella sampling.

For fast processes (in comparison to simulation timescale):

Free energy along the reaction coordinate:

$$A(\xi) = - kT \ln P(\xi)$$

Rate constant: $k_{A \to B} = 1/\tau$



$$E^b(r) = E^u(r) + \omega_i(\xi) \qquad \omega_i(\xi) = K/2(\xi - \xi_i)^2$$

$$\Downarrow$$

$$P_i^b(\xi)$$

$$\Downarrow$$

$$A_i(\xi) = -kT \ln P_i^b(\xi) - \omega_i(\xi) + F_i \Rightarrow A(\xi)$$

Umbrella sampling.

Methods to analyze umbrella sampling simulations:

- Weighted Histogram Analysis Method
- Umbrella Integration

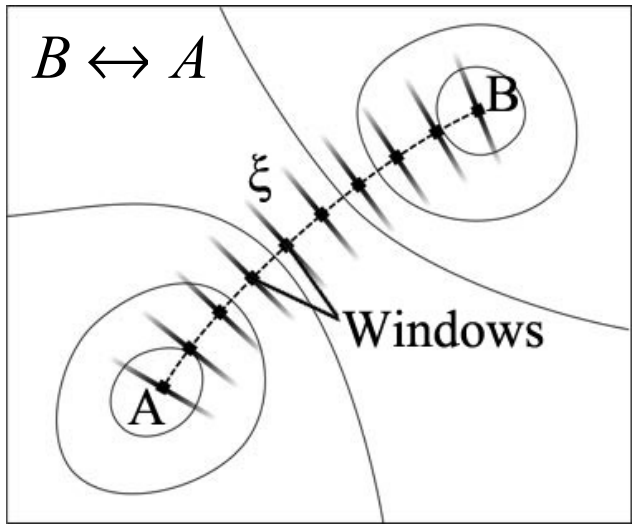
$$A_i(\xi) = -kT \ln P_i^b(\xi) - \omega_i(\xi) + F_i \quad \Leftrightarrow \quad \frac{\partial A_i^u(\xi)}{\partial \xi} = -kT \frac{\partial \ln P_i^b(\xi)}{\partial \xi} - \frac{d\omega_i}{d\xi}$$

$$P_i^b(\xi) = \frac{1}{\sigma_i \sqrt{2\pi}} \exp\left[-\frac{1}{2} \left(\frac{\xi - \bar{\xi}_i}{\sigma_i} \right)^2 \right]$$

$$\frac{\partial A_i^u(\xi)}{\partial \xi} = -kT \frac{\xi - \bar{\xi}_i}{\sigma_i^2} - K(\xi - \xi_i)$$

$$\frac{\partial A}{\partial \xi} = \sum_i^{windows} p_i(\xi) \frac{\partial A_i^u}{\partial \xi} \qquad p_i(\xi) = \frac{N_i p_i^b(\xi)}{\sum_i N_i p_i^b(\xi)} \quad \Rightarrow \quad A(\xi)$$

Constraint dynamics. Thermodynamics integration.



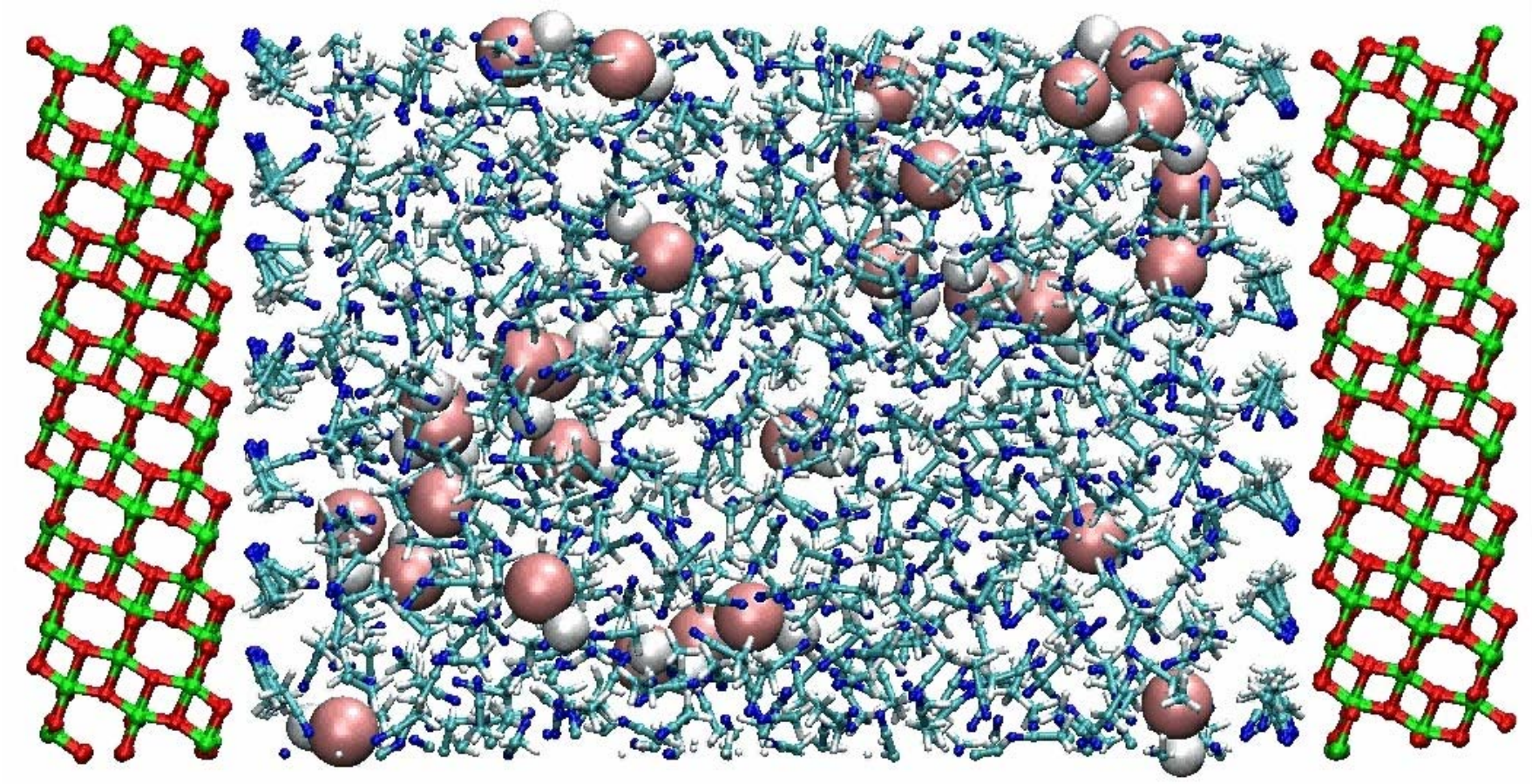
Potential of mean force:

$$\Delta A_{A\to B} = \int_{\xi_A}^{\xi_B} \left\langle \frac{\partial E}{\partial \xi} \right\rangle_{\xi'} d\xi' = \int_{\xi_A}^{\xi_B} \langle F \rangle_{\xi'} d\xi'$$

With an additional term correcting for incomplete momentum sampling, the so-called metric-tensor correction[1,2].

[1]M. Sprik, *J. Chem. Phys.*, 1998, 109, 7737.
[2] W. K. den Otter, *J. Chem. Phys.*, 1998, 109, 4139.

Adsorption kinetics of Li^+ ions on the TiO_2(101) surface.

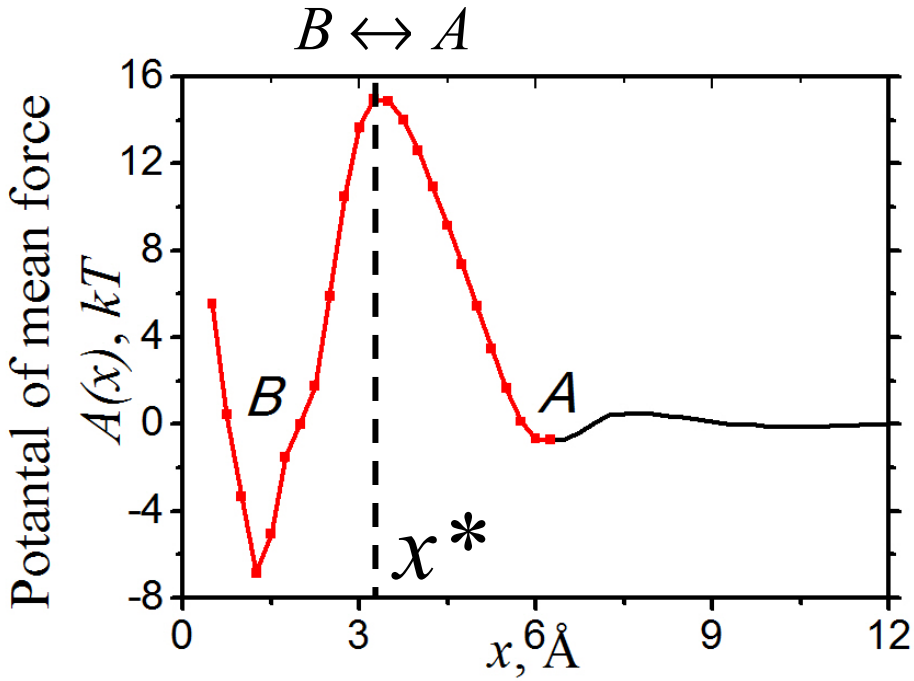


ξ Reaction coordinate ⇩

Elementary act of adsorption/desorption of Li^+ ions is the rare event.

$\tau = 1/k_{ads} >> 10$ ns

Adsorption kinetics of Li^+ ions on the TiO_2(101) surface.

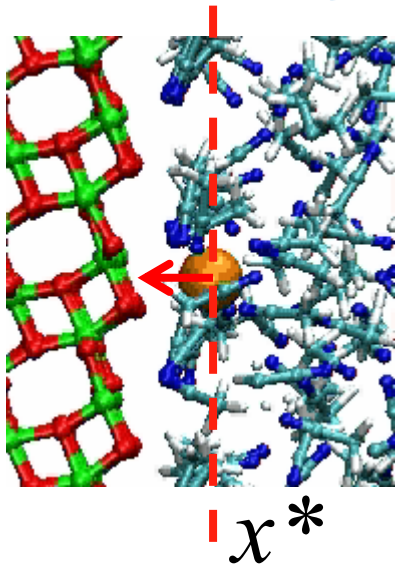


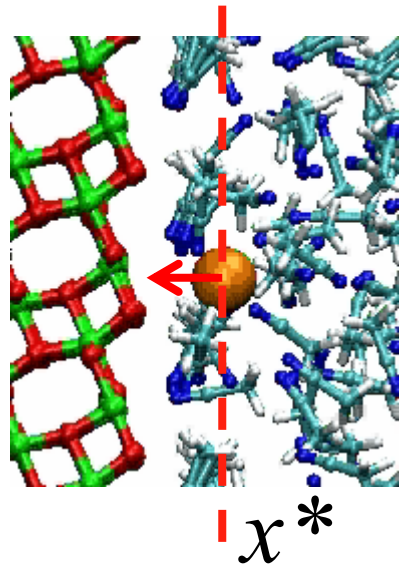
$$k_{A\to B}^{TST} = \sqrt{\frac{kT}{2\pi m}} \frac{\exp(-E_a / kT)}{\int_A \exp(-A(x)/kT)dx}$$

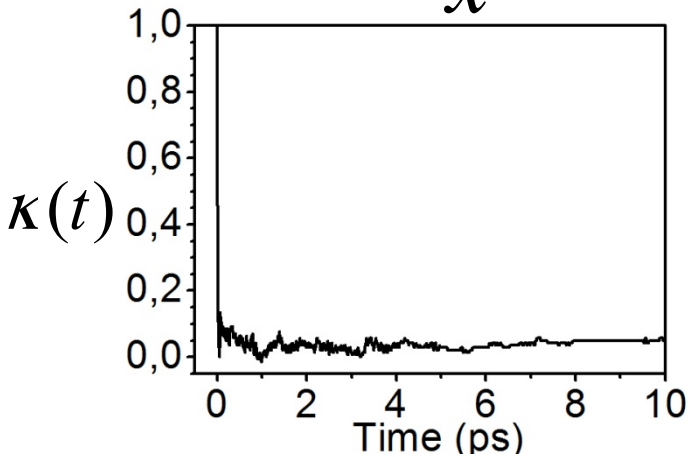
$$k_{A\to B} = \kappa \cdot k_{A\to B}^{TST} \qquad \kappa < 1$$

Transmission coefficient

Transmission coefficient. Activated dynamics simulations.







$k_{A\to B}=1.1\cdot10^{4}\text{c}^{-1}$; $\tau\sim 100$мкс

$k_{B\to A}=0.21\ \text{c}^{-1}$; $\tau\sim 5$c

$$\kappa(t)=\frac{k(t)}{k^{\mathrm{TST}}}=\frac{\langle\delta\,(x(0)-x^{\ddagger})\,v_x(0)\Theta(x(t)-x^{\ddagger})\rangle}{\langle\delta(x(0)-x^{\ddagger})v_x(0)\Theta\,(v_x(0))\rangle}$$

D. Chandler, Introduction to statistical mechanics, 1987