

Mass transport at electrified ionic liquid–electrode interfaces

*Vladislav Ivaništšev^a, Luis M. Varela^b,
Ruth M. Lynden-Bell^c and Maxim V. Fedorov^d*

^a University of Tartu, vi@ut.ee

^b Universidade de Santiago de Compostela

^c University of Cambridge

^d Strathclyde University

Table of contents

Applications

Interface

Chemical space

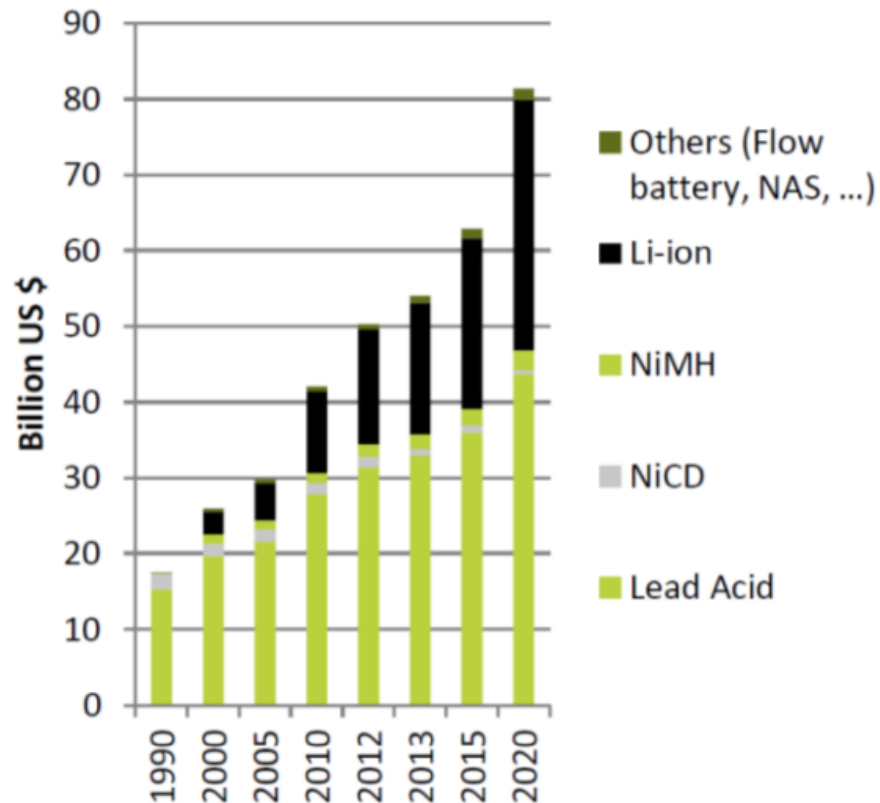
Computer simulations

Results

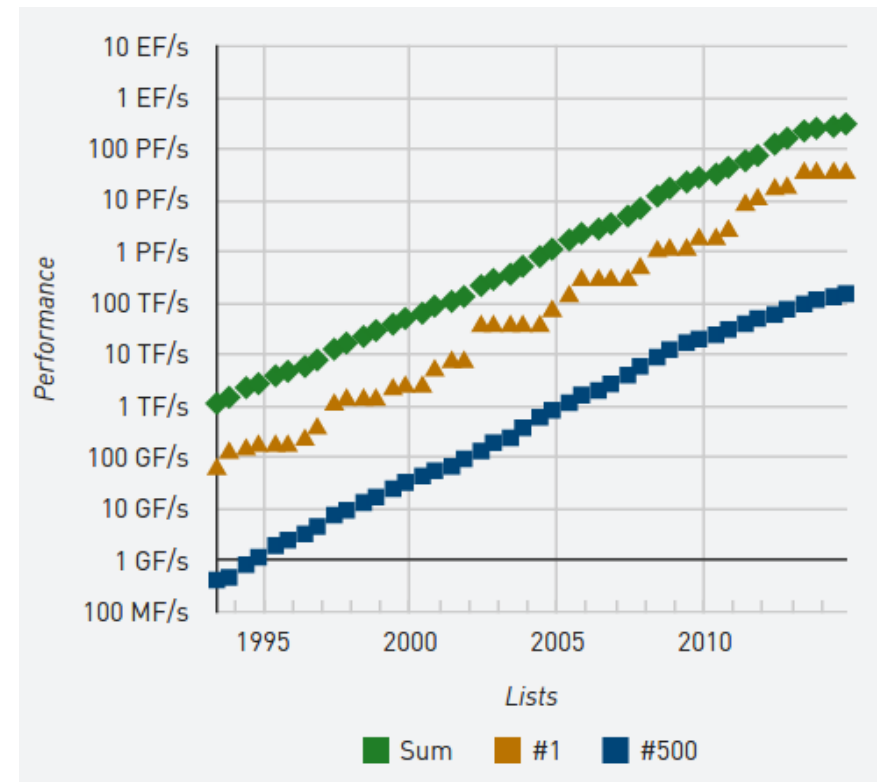
Challenges

Current developments

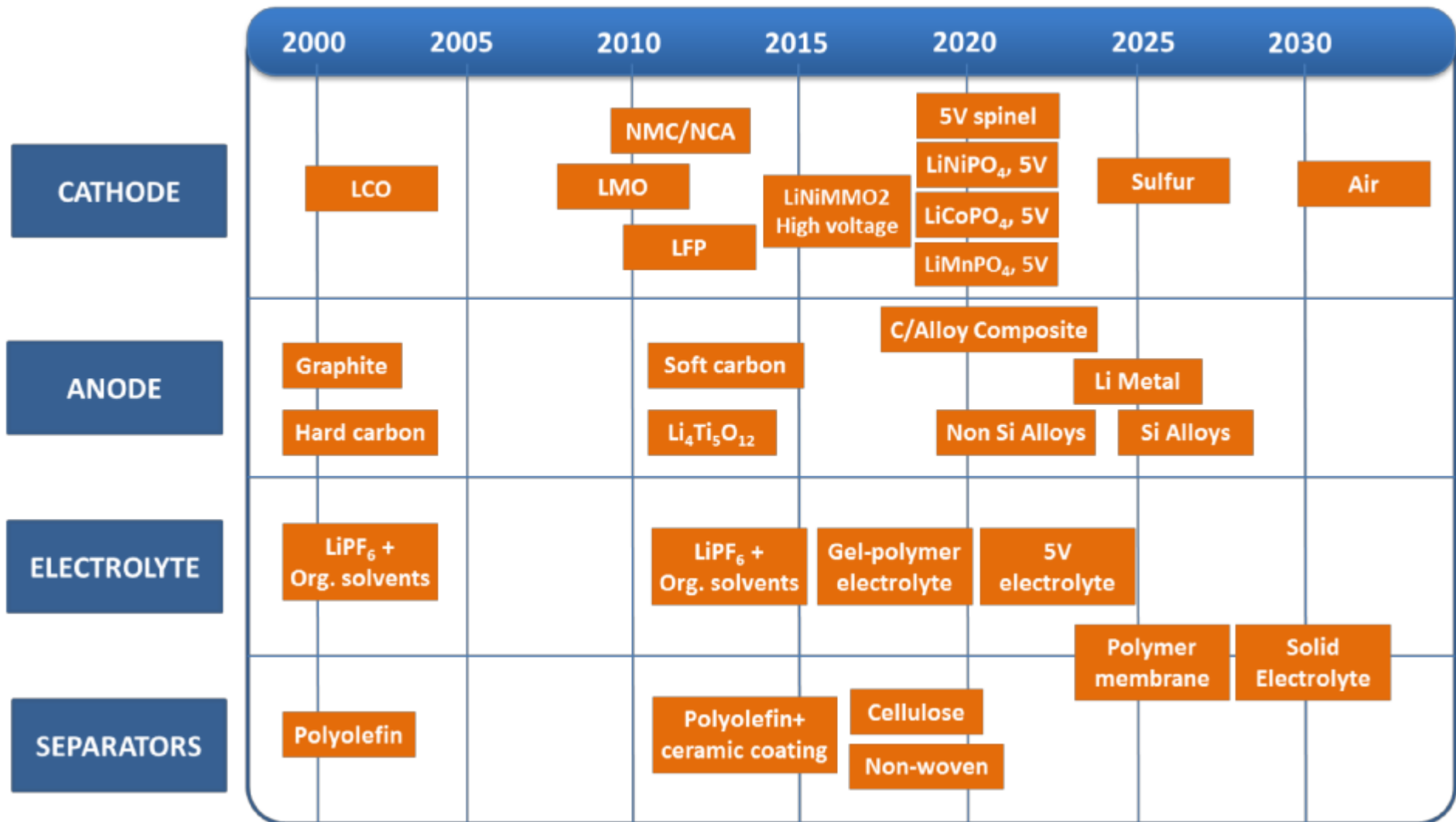
Energy sources, AVICCENNE



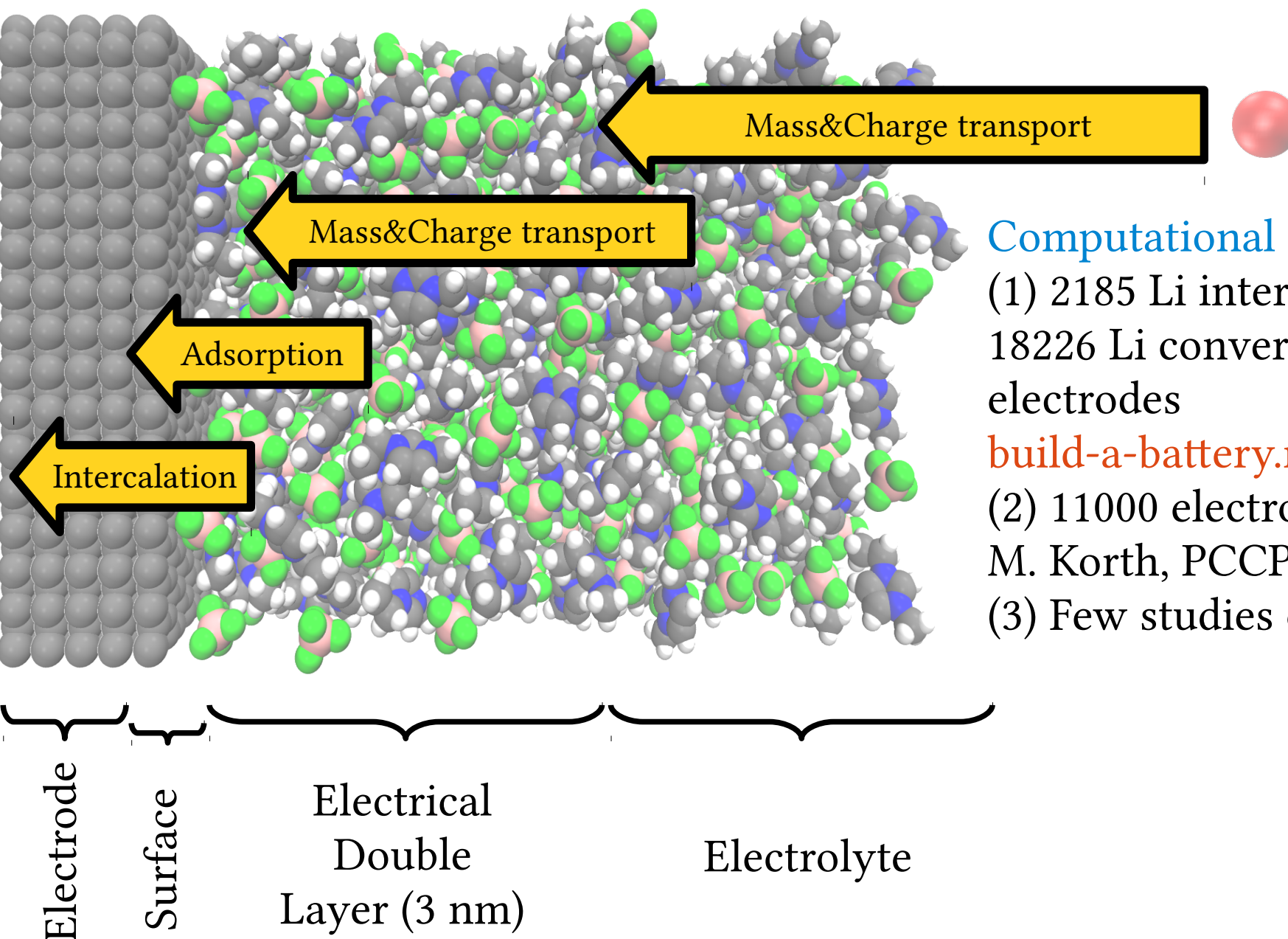
Computer power, top500.org



The battery market and materials trends



Ionic liquid–electrode interface



Computational screening:

(1) 2185 Li intercalation and 18226 Li conversion electrodes

build-a-battery.meteor.com

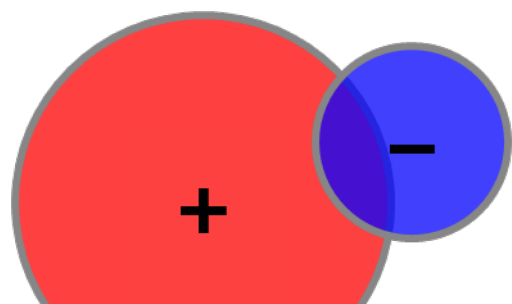
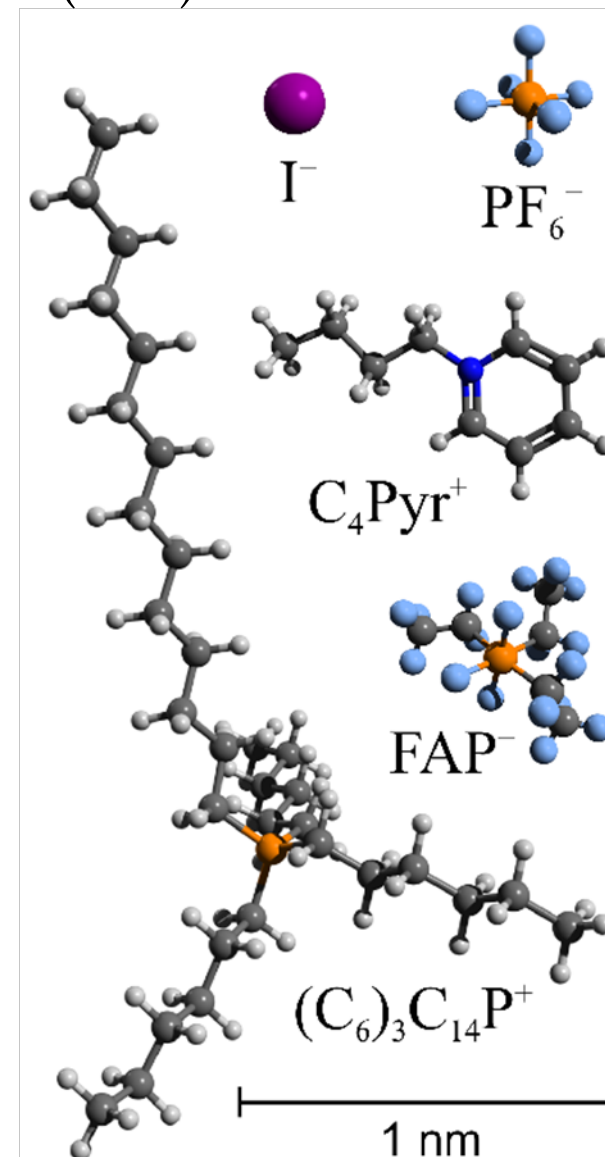
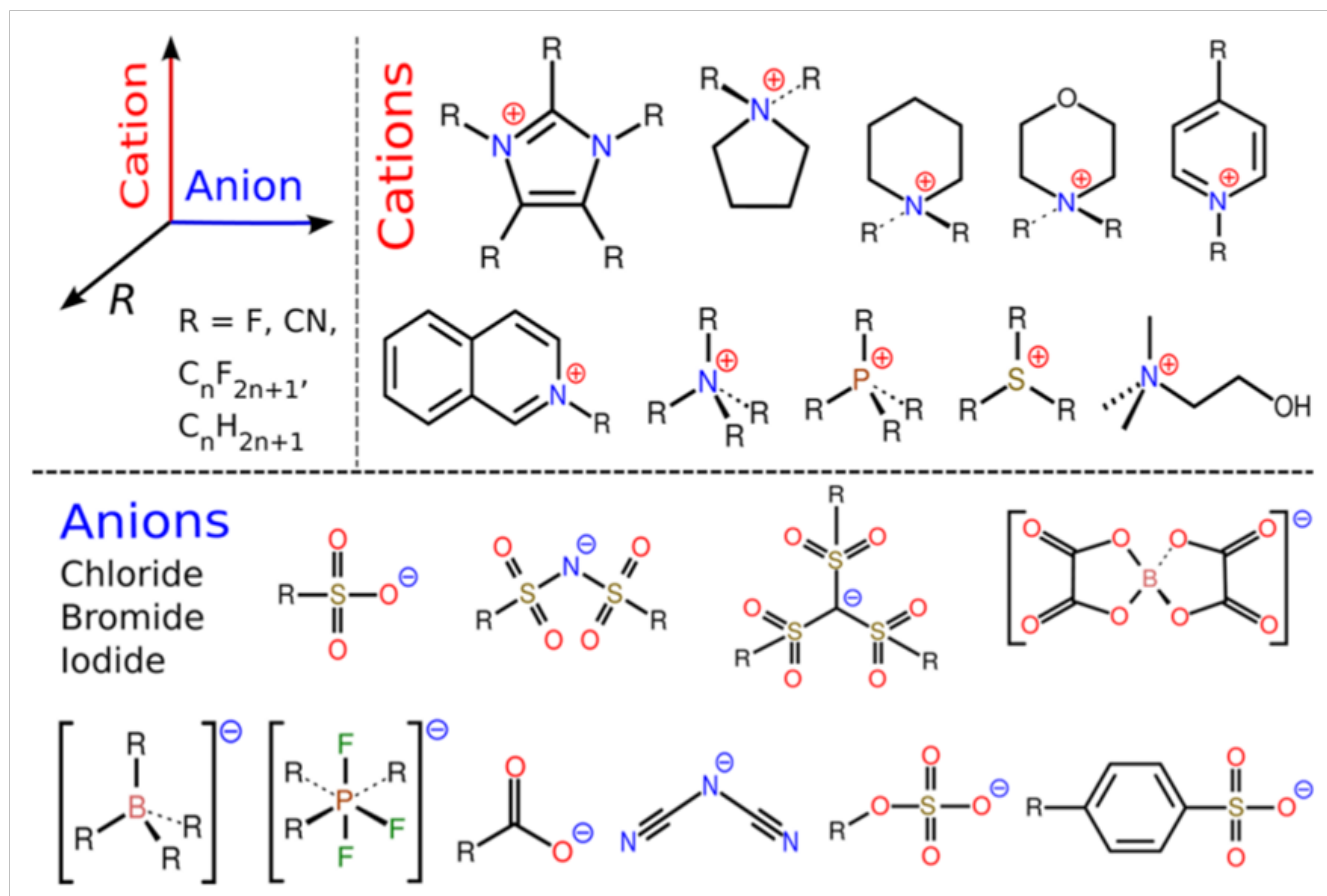
(2) 11000 electrolytes

M. Korth, PCCP 16 (2014).

(3) Few studies of interfaces

Chemical space of ionic liquids

M.V. Fedorov, A.A. Kornyshev, Chem. Rev. 114 (2014) 2978.



Atomistic model →

← Coarse grained model

Matrix of electrolyte compositions

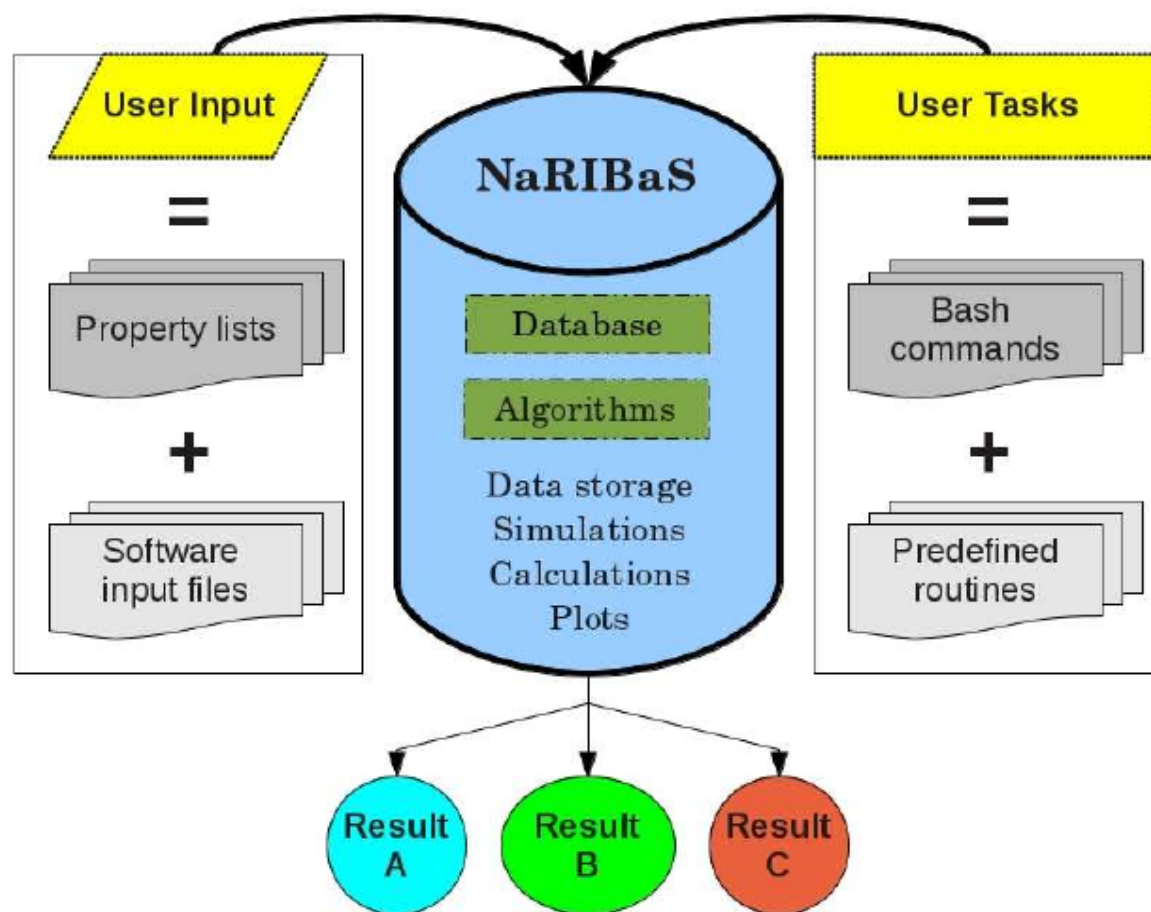
$$\begin{array}{c}
 [\text{BF}_4]^- \\
 [\text{DCA}]^- \\
 [\text{FSI}]^- \\
 [\text{TFSI}]^-
 \end{array}
 \begin{array}{c}
 [\text{BMIm}]^+ \quad [\text{BMPyr}]^+ \quad [\text{BPy}]^+ \\
 \left(\begin{array}{ccc}
 c_{11} & c_{12} & c_{13} \\
 c_{21} & c_{22} & c_{23} \\
 c_{31} & c_{32} & c_{33} \\
 c_{41} & c_{42} & c_{43}
 \end{array} \right)
 \end{array}
 \times
 \begin{array}{c}
 \text{F}^- \\
 \text{Cl}^- \\
 \text{Br}^- \\
 \text{I}^-
 \end{array}
 \begin{array}{c}
 \text{Li}^+ \quad \text{Na}^+ \quad \text{K}^+ \\
 \left(\begin{array}{ccc}
 h_{11} & h_{12} & h_{13} \\
 h_{21} & h_{22} & h_{23} \\
 h_{31} & h_{32} & h_{33} \\
 h_{41} & h_{42} & h_{43}
 \end{array} \right)
 \end{array}
 +$$

Variables:
 Electrode material
 Surface charge
 Temperature & Pressure

NaRIBaS: A scripting framework for computational modelling of Nanomaterials & Room Temperature Ionic Liquids in Bulk and Slab

NaRIBaS workflow:

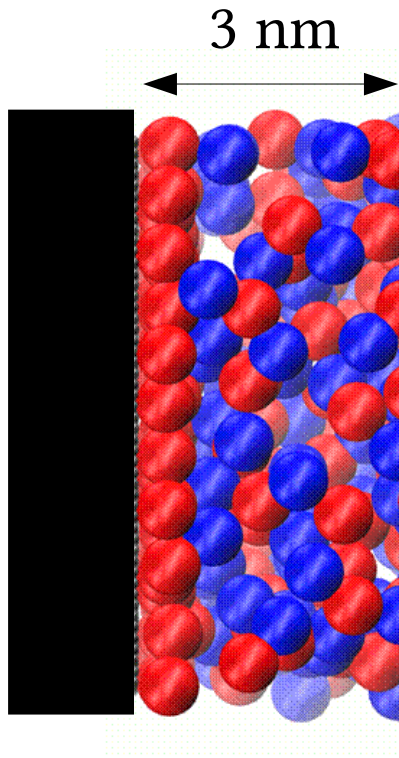
1. System preparation
2. Equilibration
10 ns
3. Production run
 $2 \text{ ns} \times n \text{ replica}$
4. Data management
5. Analysis



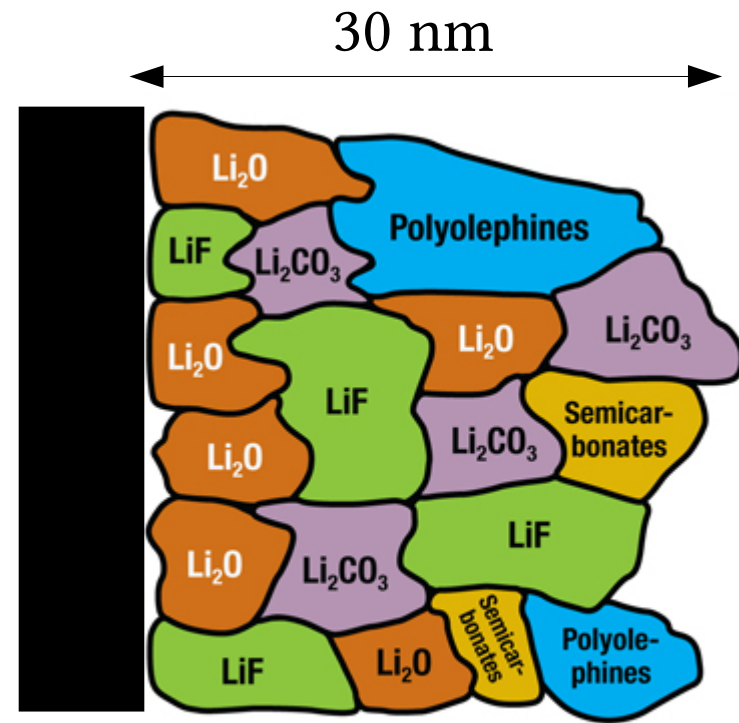
sourceforge.net/projects/naribas

Figure 1: General composition of NaRIBaS scripting framework.

A naive view on the interface

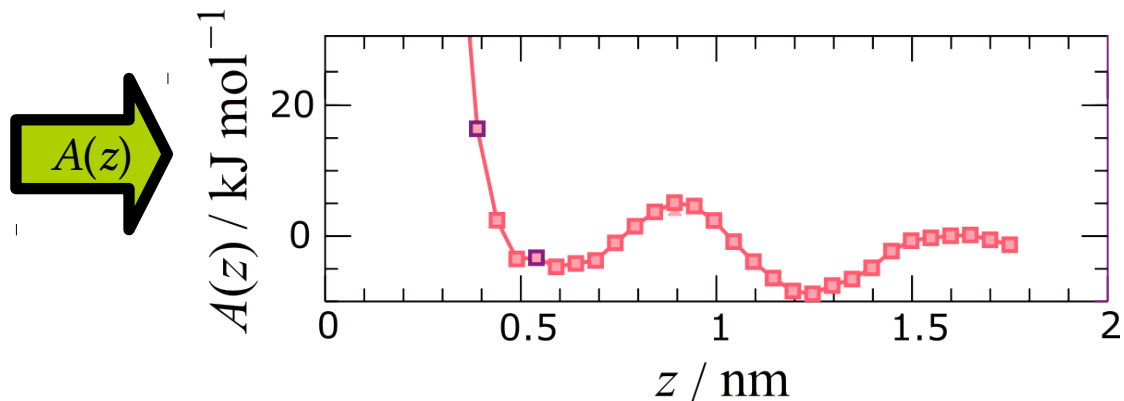
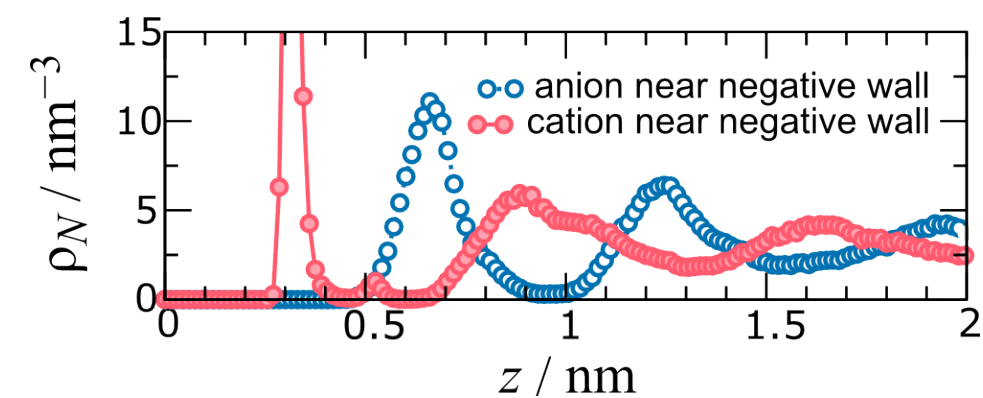
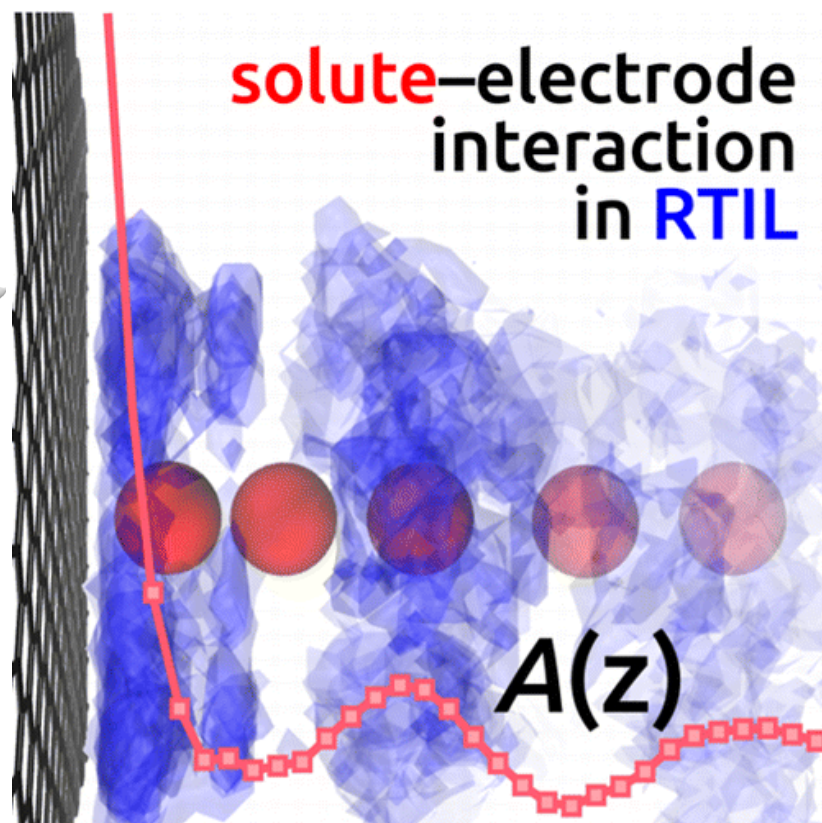
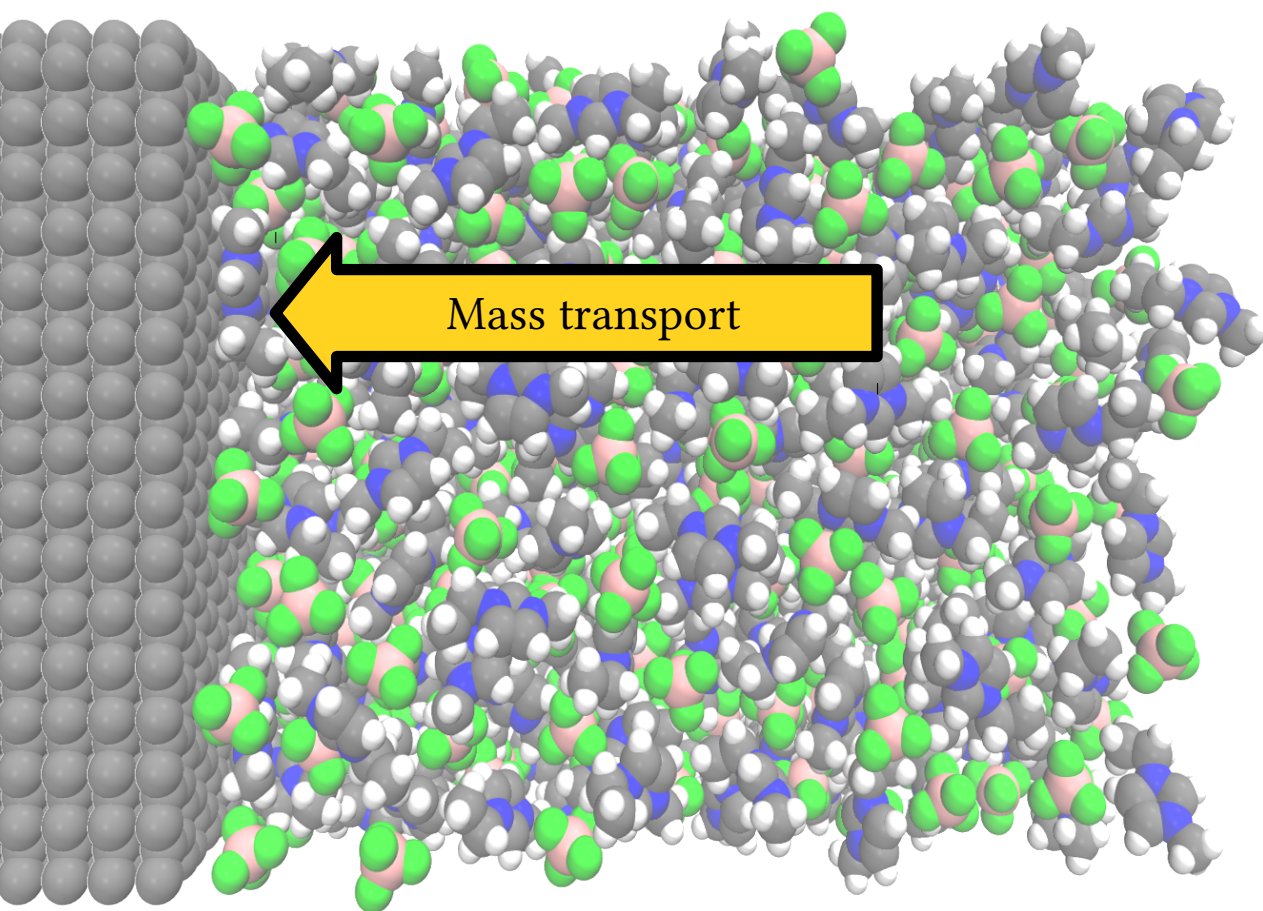


Model interface



Realistic interface

Mass transport and Free energy profiles



Mass transport and Free energy profiles

- Probability method

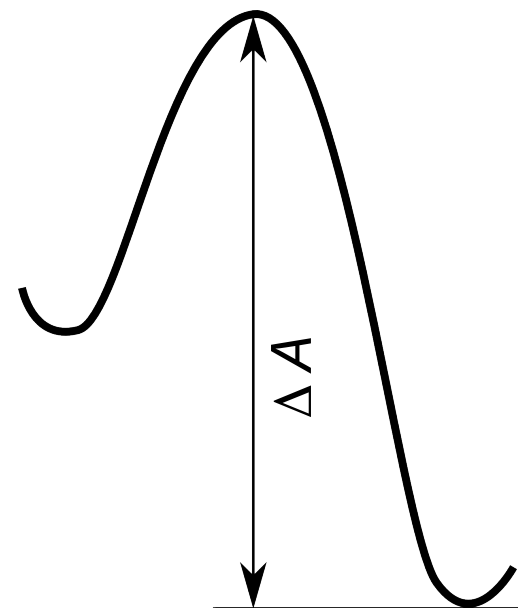
$$\rho(z) = \rho_{bulk} e^{-\beta A(z)} \Rightarrow$$

$$A(z) = -k_B T \ln \frac{\rho(z)}{\rho_{bulk}}$$

- Potential of mean force method

$$\langle F(z) \rangle = -\frac{dA(z)}{dz} \Leftrightarrow$$

$$A(z) = -\int_0^z \langle F(z') \rangle dz'$$

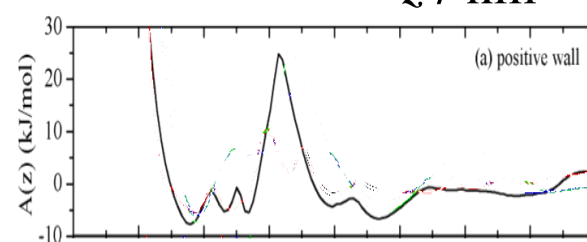
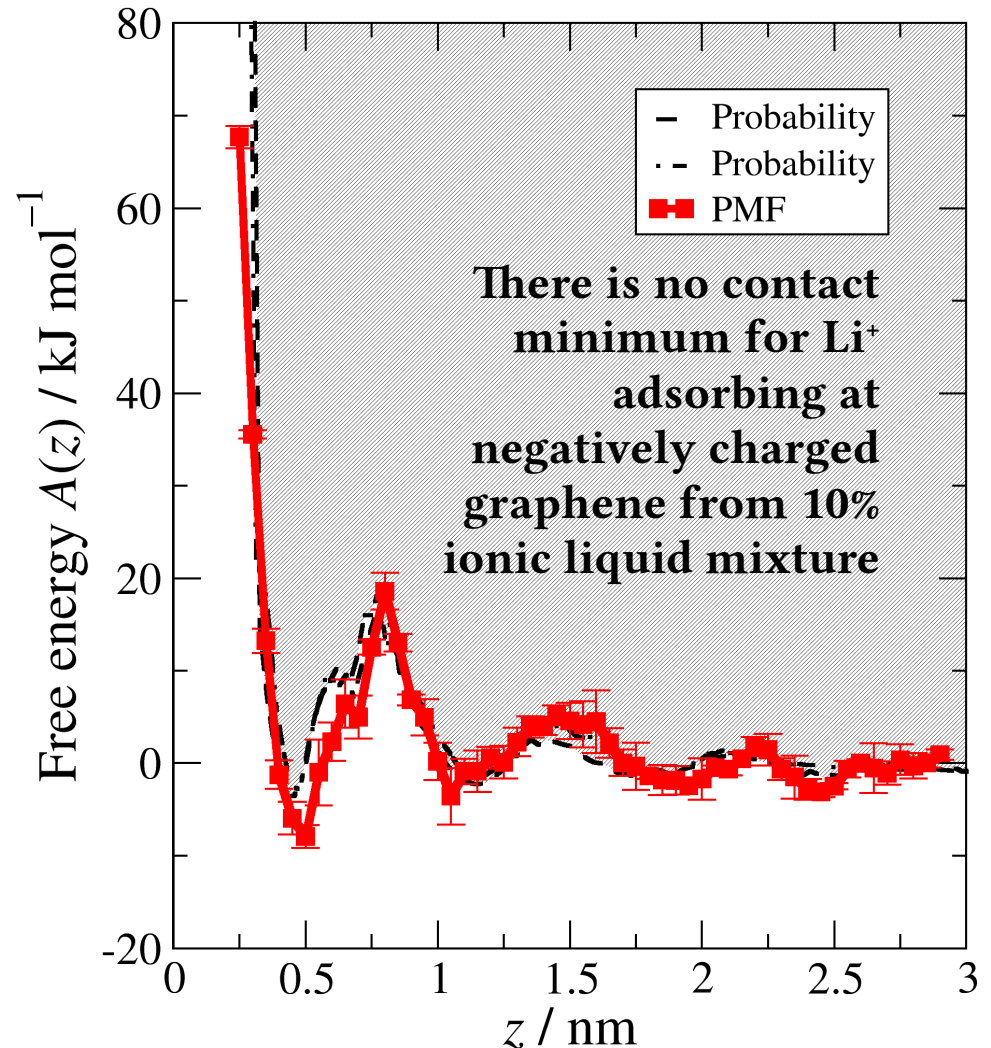
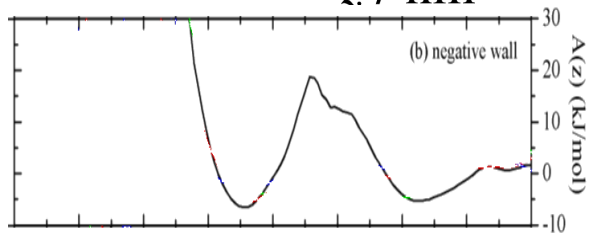
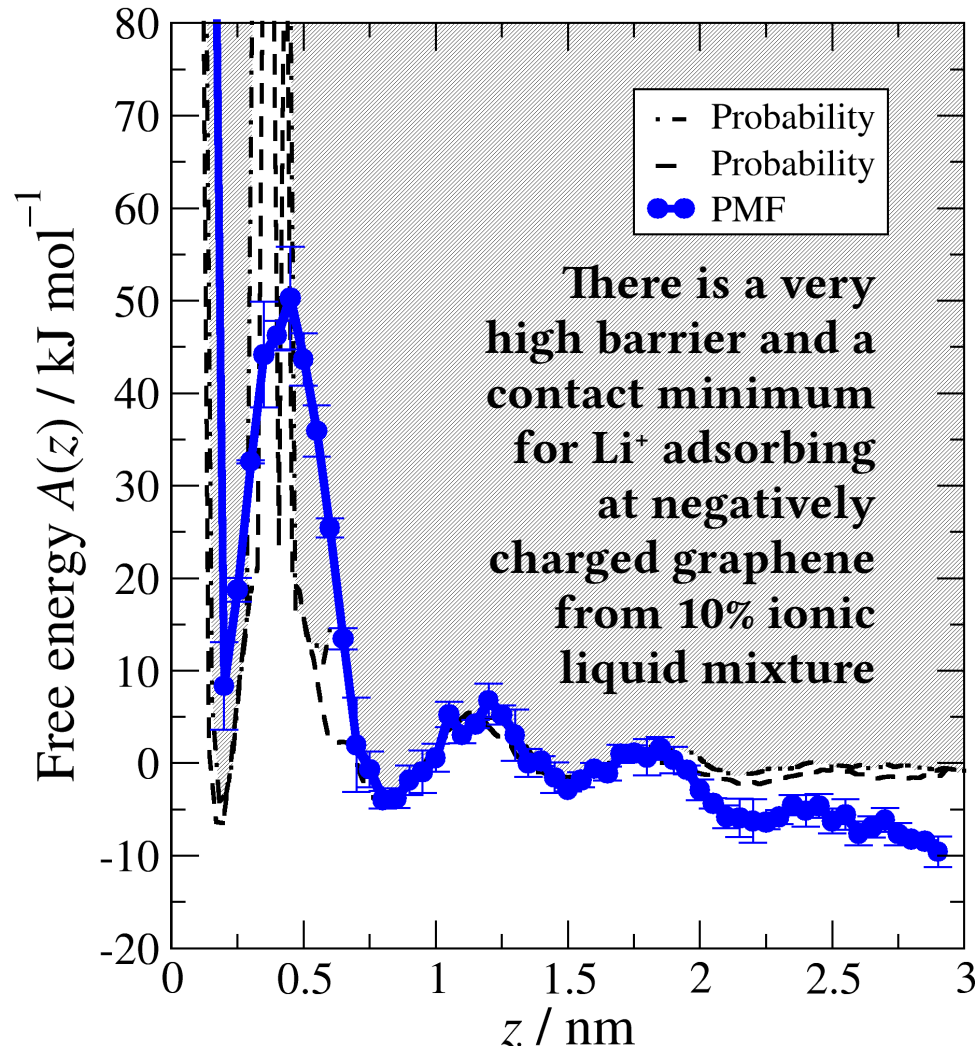


$$k = B \exp(-\Delta A / RT)$$

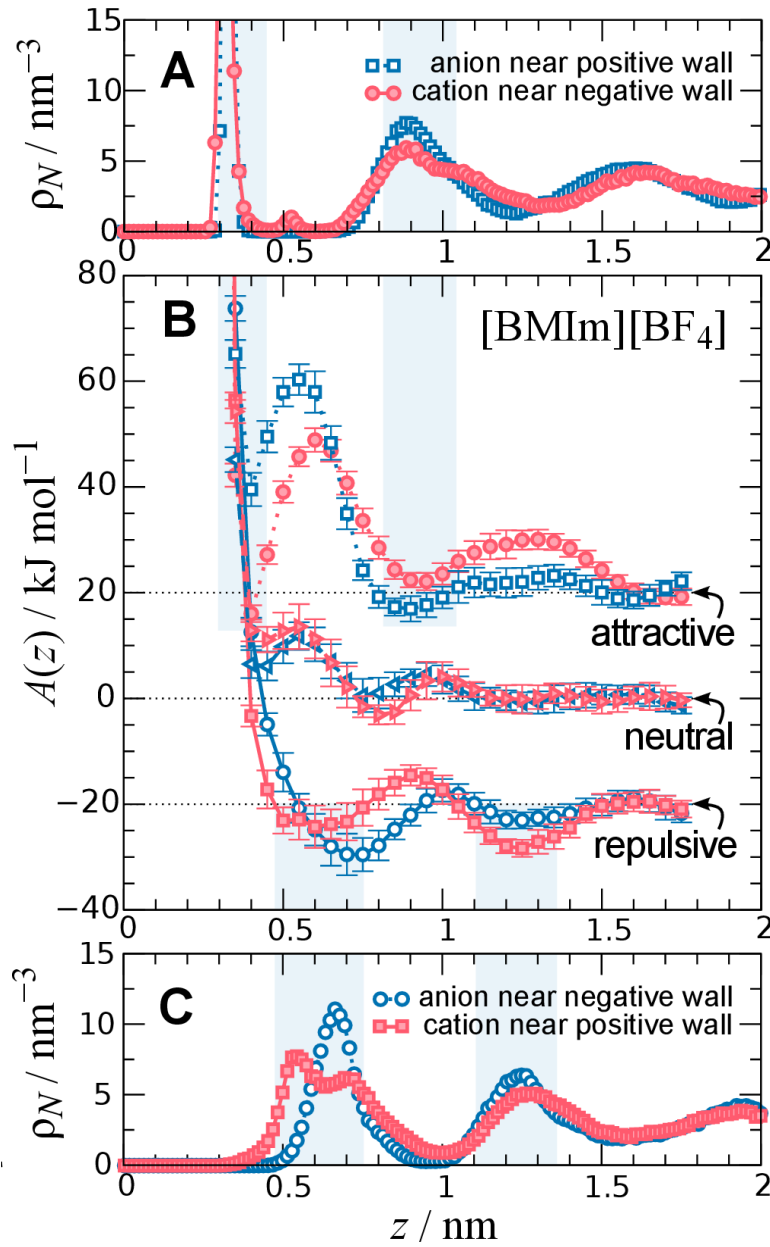
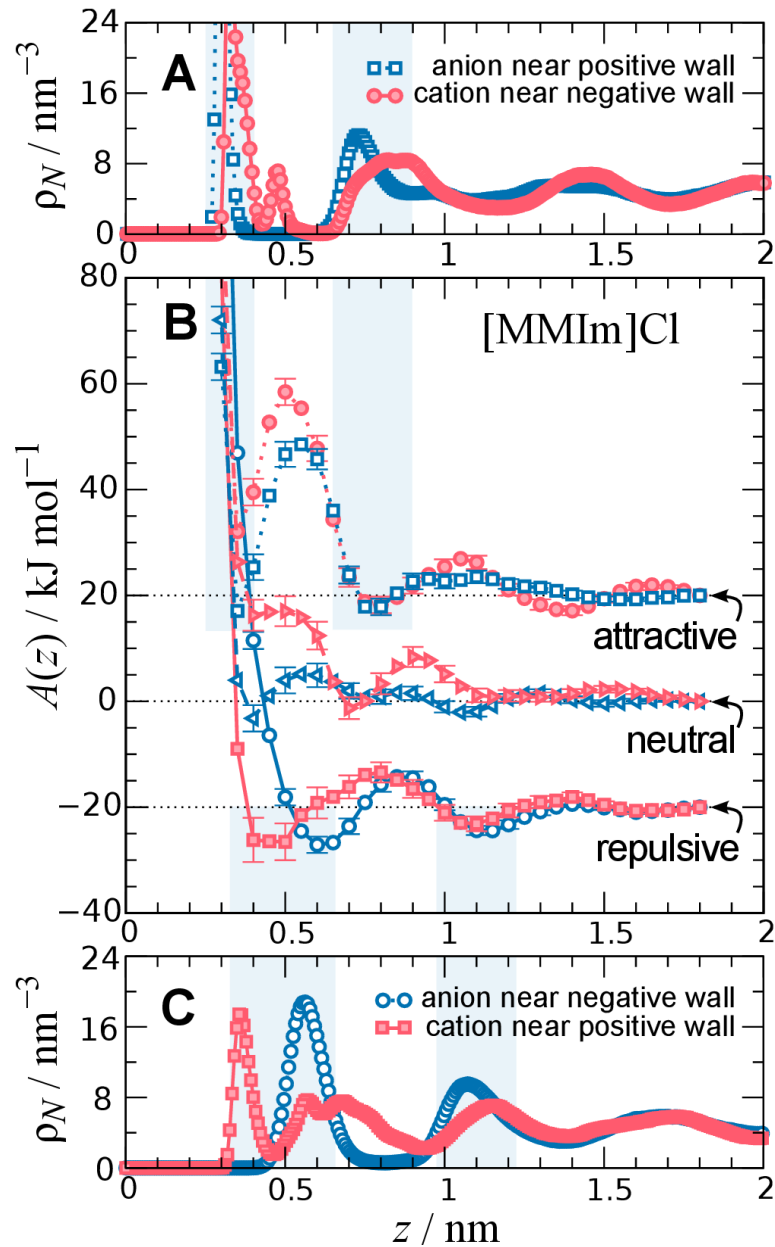
Li^+ ion approaching *negative* (left) and *positive* (right) graphene walls

$$\sigma = \mp 1 \text{ e nm}^{-2}, c_{\text{mol}} = 10\%$$

dashed line – $A(z) = -RT \ln(c/c_0)$; solid line – from the pulling results



Charged probe in [MIM]Cl and [BMIM]BF₄

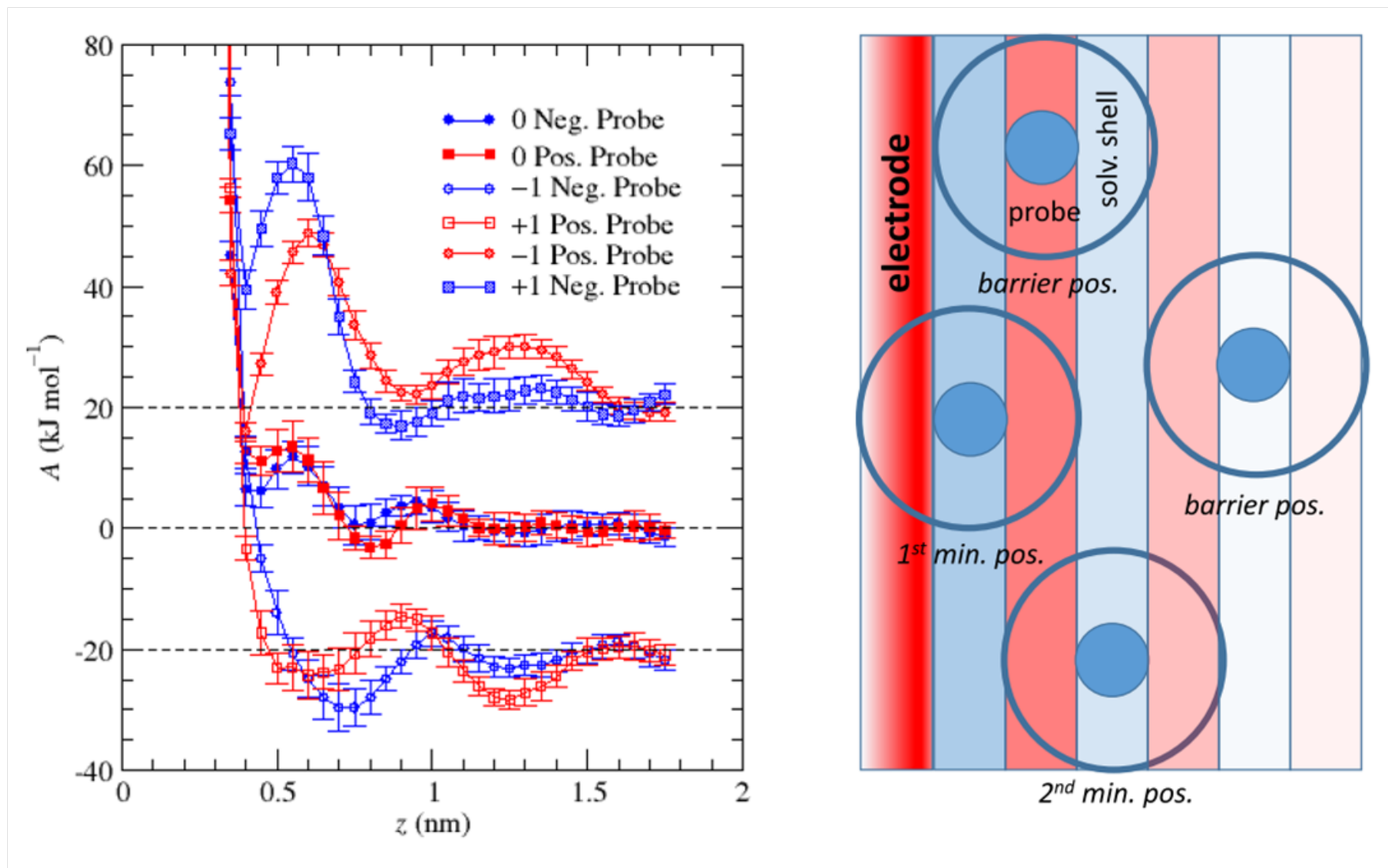


Probe charge	Surface charge
$\begin{pmatrix} +1 \\ 0 \\ -1 \end{pmatrix}$	$\begin{pmatrix} +1 \\ 0 \\ -1 \end{pmatrix}$

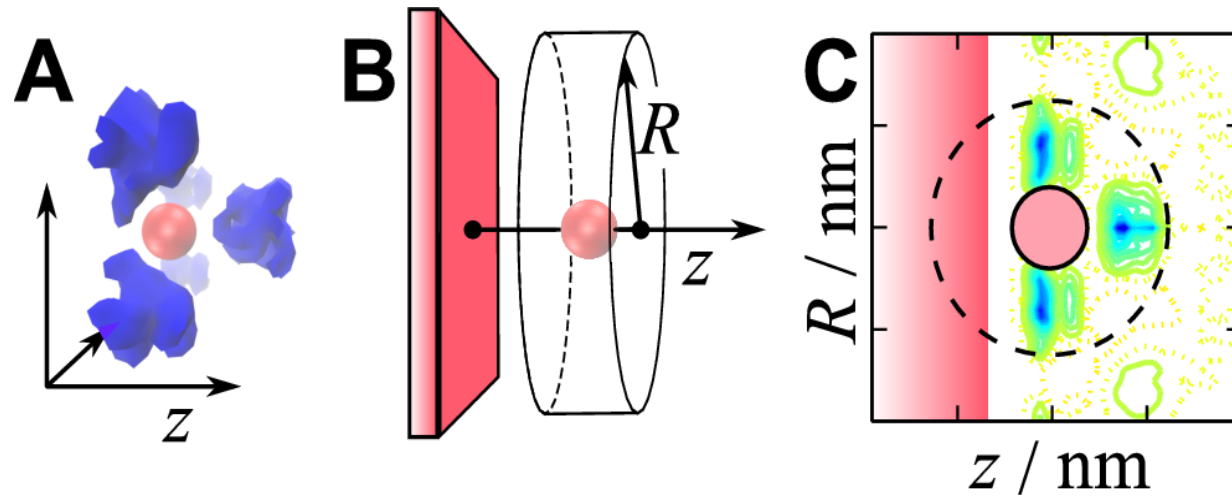
$\times$

	$[A]^-$	$[C]^+$
anode	$-$	$+$
cathode	$+$	$-$

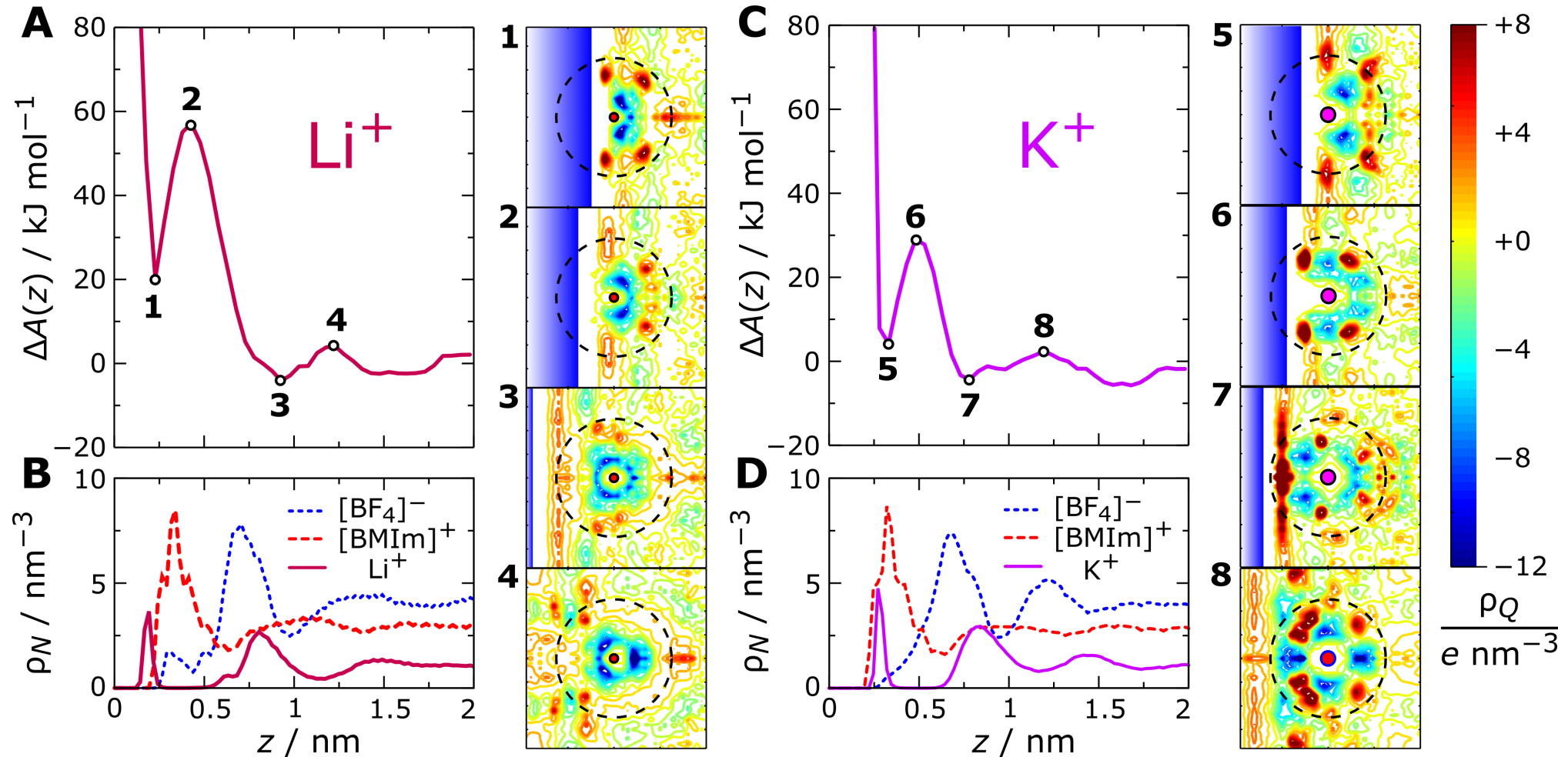
Solvation layers and the solvation shell



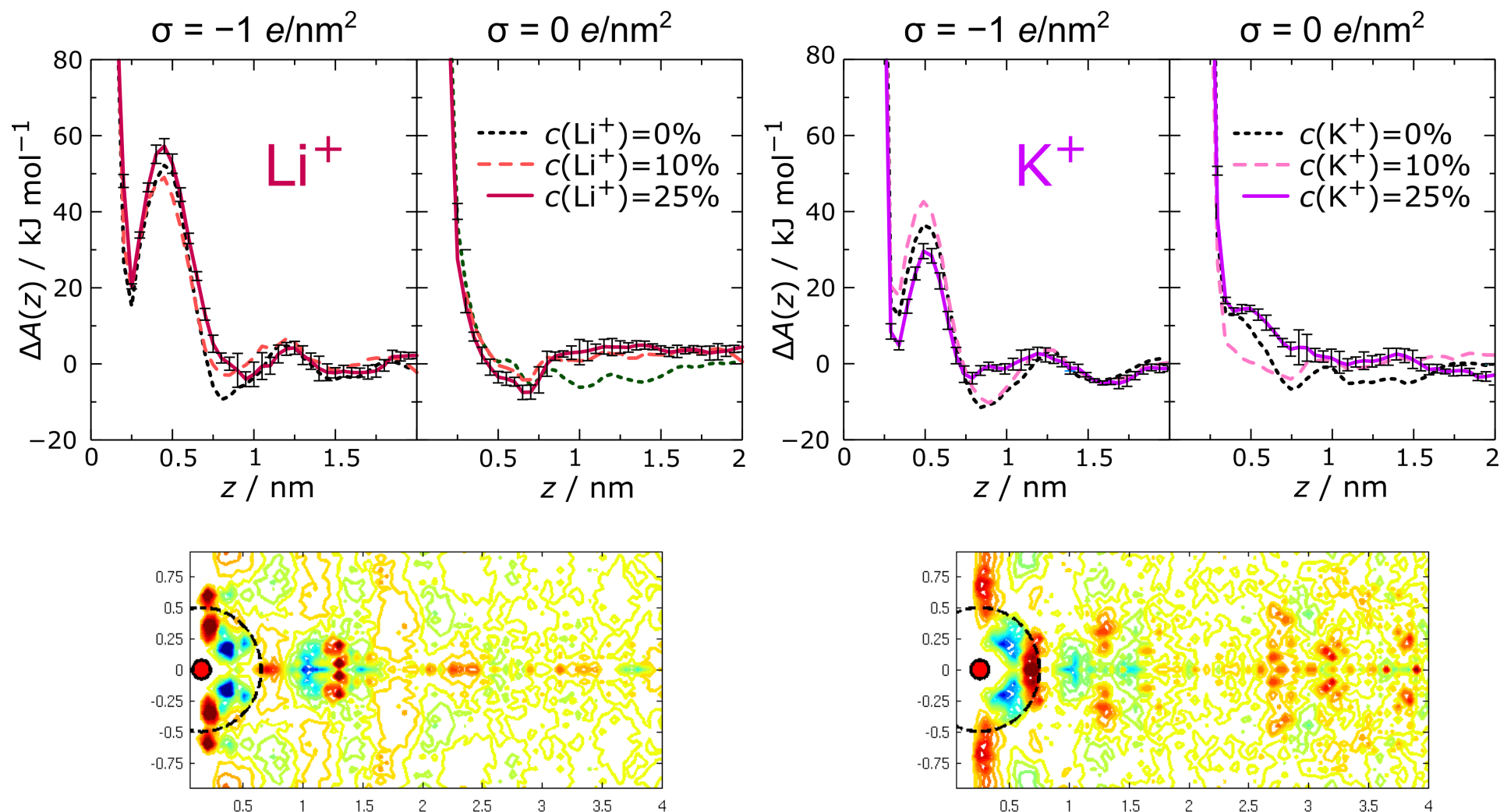
Cylindrically averaged charge density



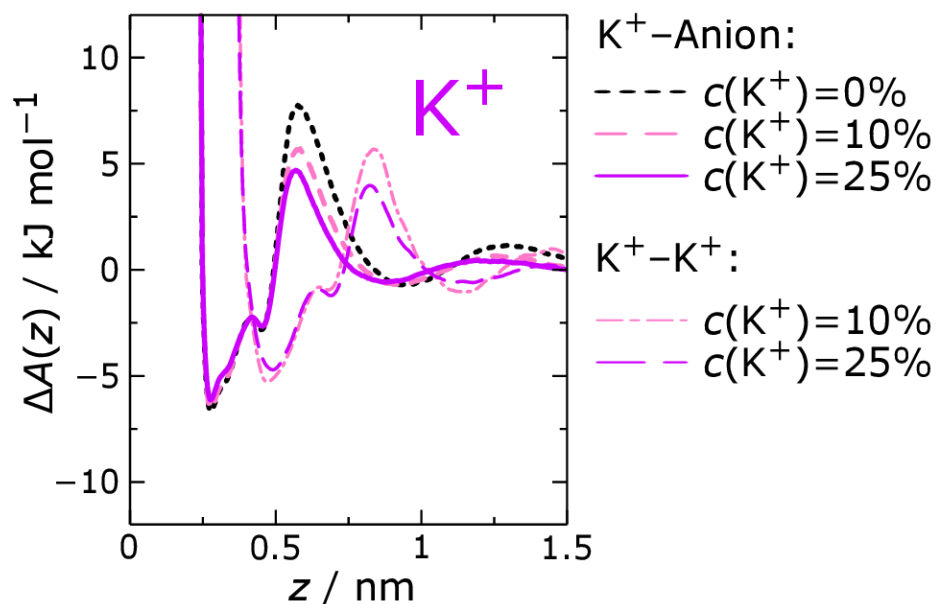
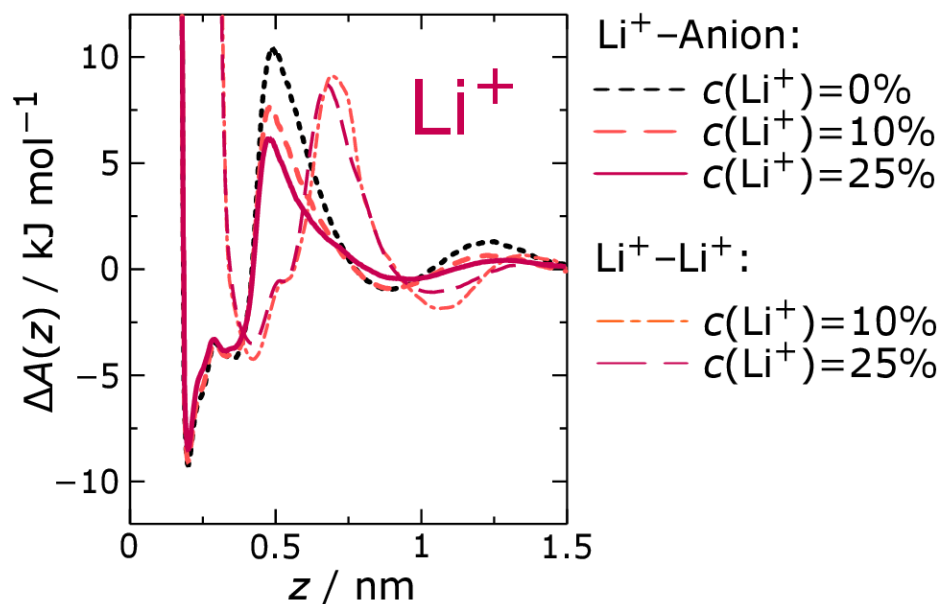
Li⁺ and K⁺ at Graphite | BMImBF₄ interface



Li⁺ and K⁺ at Graphite | BMImBF₄ interface



Li⁺ and K⁺ at Graphite | BMImBF₄ interface



metal-ion-anion binding
anion size
electrolyte density

J.B. Haskins, et al., J. Phys.
Chem. B 118 (2014) 11295.

Conclusions

- ♦ The interfacial mass-transport of a probe ion (Li^+ , K^+) is related to the free energy profiles from translation of the ion in direction perpendicular to the surface.
- ♦ The structure of solvation layers at the electrodes determines the positions of the minima and maxima on the free energy profiles.
- ♦ At those positions where these solvation structures enhance each other, the free energy profile is lower, whereas at those positions where they distort each other, the free energy is higher.
- ♦ Barrier for K^+ is lower than for Li^+ in $\text{BMImBF}_4 + \text{MeBF}_4$ mixtures.
- ♦ The method presented can be applied for ionic liquids screening.

Some preliminary results

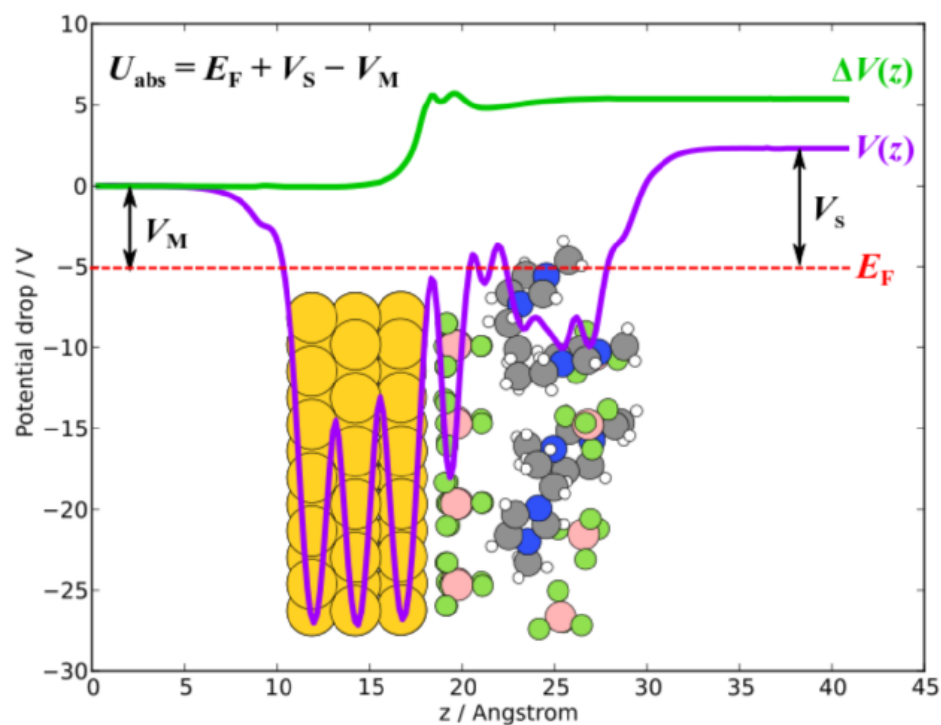
Unpublished results

Challenges

Potential scale

Polarisable force fields

Constant potential simulations



References

- V. Ivaništšev, M.V. Fedorov, R.M. Lynden-Bell, J. Phys. Chem. C 118 (2014) 5841.
- A.I. Frolov, K. Kirchner, T. Kirchner, M.V. Fedorov, Faraday Discuss. 154 (2012) 235.
- T. Méndez-Morales, J. Carrete, M. Pérez-Rodríguez, Ó. Cabeza, L.J. Gallego, R.M. Lynden-Bell, L.M. Varela, Phys. Chem. Chem. Phys. 16 (2014) 13271.

See also

- S.K. Reed, P.A. Madden, A. Papadopoulos, J. Chem. Phys. 128 (2008) 124701.
- V. Nikitina, S.A. Kislenko, R.R. Nazmutdinov, M.D. Bronshtein, G.A. Tsirlina, J. Phys. Chem. C 118 (2014) 6151.
- V. Ivaništšev, S. O'Connor, M.V. Fedorov, Electrochem. Commun. 48 (2014) 61.

Acknowledgements



Ruth M. Lynden-Bell



Luis Miguel Varela Cabo



Maxim V. Fedorov

Trinidad Méndez-Morales
Isabel Lage Lage-Estebanez
Kathleen & Tom Kirchner
Sean O'Conner

Thank you for your attention!

zotero.org/groups/ionic_liquids

- ♦ Comprehensive collection of articles on ionic liquids in bulk and at interfaces
- ♦ Based on the Prof. M.V. Fedorov's group bibtex-collection
- ♦ Zotero Group Library (1174 items+pds)
- ♦ Address: zotero.org/groups/ionic_liquids
- ♦ Public type, but closed membership
- ♦ Zotero free and open-source reference management software to manage bibliography
- ♦ Web browser integration, syncing, generation of citations

Zotero

<http://libguides.mit.edu/references>

Zotero 0\$/120\$

Mendeley 0\$/50x\$

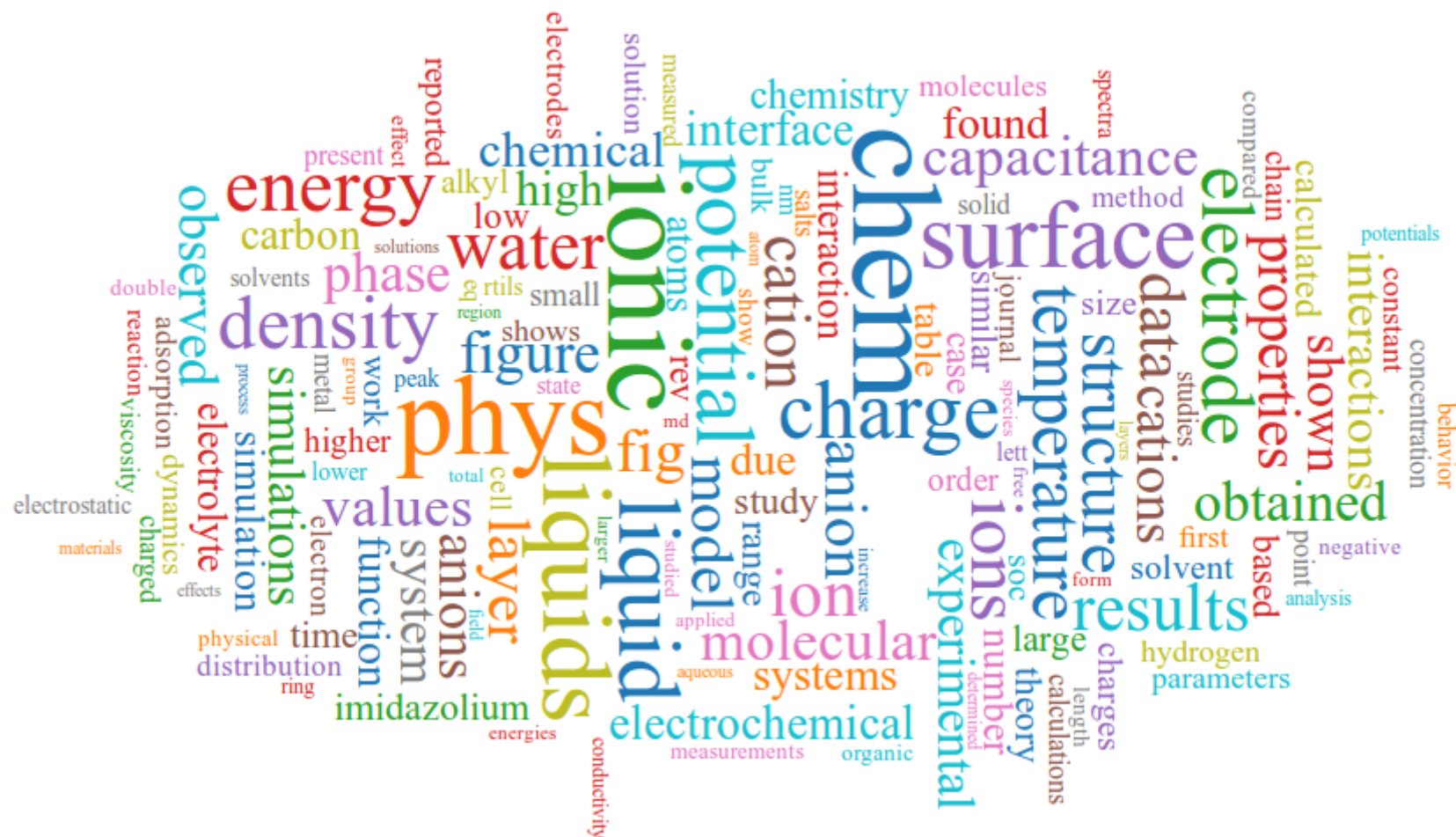
EndNote 150\$/150x\$

The screenshot displays the Zotero desktop application. On the left is a sidebar with a file explorer showing 'My Library' and 'Group Libraries'. The main pane shows a list of references with columns for Title, Creator, Year, and Date Added. The reference 'Extending the fast multipole method to charges inside or outside a dielectric sphere' by Cai et al. (2007) is selected. On the right, a detailed view of this item is shown, including its title, author, abstract, publication information, and various identifiers like DOI and URL.

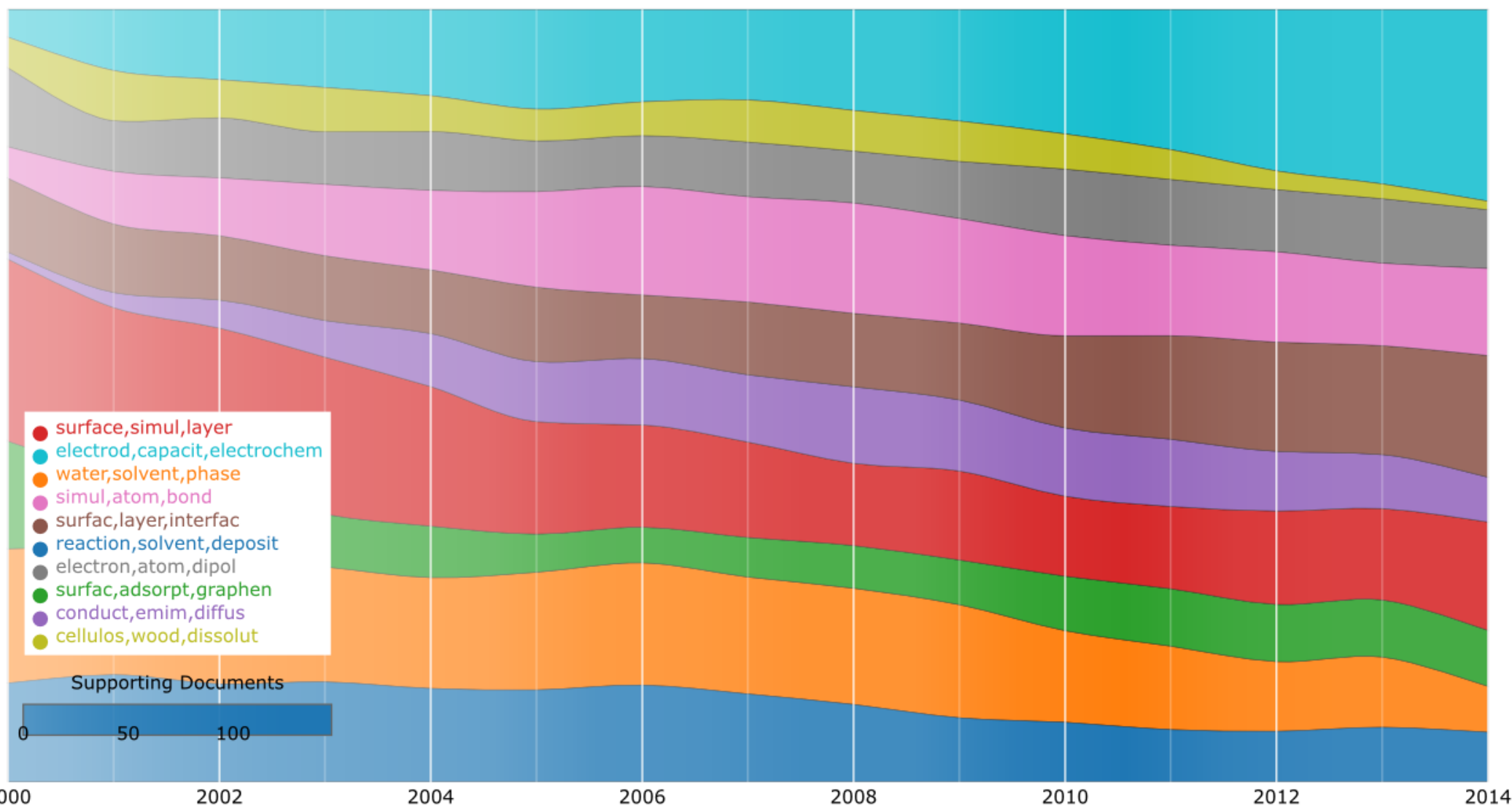
Title	Creator	Year	Date Added
Electrostatically embedded many-body method for dipole moments, ...	Leverentz et al.	2012	2/12/13 14:12:21
Multibody Effects in Ion Binding and Selectivity	Varma and Rempe	2010	2/8/13 02:03:27
Capacitance of the Double Layer Formed at the Metal/Ionic-Conducto...	Skinner et al.	2010	2/8/13 02:03:27
Average local ionization energy: A review	Politzer et al.	2010	2/8/13 02:03:27
Calcium Binding and Head Group Dipole Angle in Phosphatidylserine-...	Vernier et al.	2009	2/8/13 02:03:27
Ion adsorption at a metallic electrode: an ab initio based simulation s...	Pounds et al.	2009	2/8/13 02:03:27
Dipole polarizabilities of trimetallic nitride endohedral fullerenes M3...	He et al.	2009	2/8/13 02:03:27
Alkyl Radicals as Hydrogen Bond Acceptors: Computational Evidence	Hammerum	2009	2/8/13 02:03:27
Transferable Force Field for Alcohols and Polyalcohols	Ferrando et al.	2009	2/8/13 02:03:27
Notes on "Ewald summation of electrostatic multipole interactions u...	Laino and Hutter	2008	2/8/13 02:03:27
Localization and nucleotide specificity of Blastocystis succinyl-CoA sy...	Hamblin et al.	2008	2/8/13 02:03:27
Multiple free energies from a single simulation: Extending enveloping...	Christ and van Guns...	2008	2/8/13 02:03:27
Multilevel fast-multipole algorithm for solving combined field integra...	Song and Chew	2007	3/19/13 05:14:03
Electrostatic properties of ideal and non-ideal polar organic monolay...	Natan et al.	2007	2/8/13 02:03:27
Adsorption and self-assembly of aromatic carboxylic acids on Au/ele...	Han et al.	2007	2/8/13 02:03:27
Denaturation of hen egg white lysozyme in electromagnetic fields: A ...	English and Mooney	2007	2/8/13 02:03:27
Extending the fast multipole method to charges inside or outside a di...	Cai et al.	2007	3/19/13 05:13:37
First principles reaction modeling of the electrochemical interface: C...	Taylor et al.	2006	2/8/13 02:03:27
Using DL_POLY to study the sensitivity of liquid structure to potential...	Lynden-Bell and You...	2006	2/8/13 02:03:27
Calculation of ionic surface excess concentrations in the diffuse doub...	Mulder et al.	2005	2/8/13 02:03:27
Coherent coupling of molecular excitons to electronic polarizations o...	Wiederrecht et al.	2004	2/8/13 02:03:27
A New Parallel Kernel-Independent Fast Multipole Method	Ying et al.	2003	2/8/13 02:24:41
On the effective interaction between an ion and a hydrophobic particl...	Karlstrom	2003	2/8/13 02:03:27
Ewald summation of electrostatic multipole interactions up to the qu...	Aguado and Madden	2003	3/6/13 03:59:17
Car-Parrinello molecular dynamics simulation of the hydrated calciu...	Bako et al.	2002	2/8/13 02:03:27
Examining methods for calculations of binding free energies: LRA, LIE...	Sham et al.	2000	2/8/13 02:03:27
Computer simulations of sodium dodecyl sulfate at liquid/liquid and l...	Dominguez and Ber...	2000	2/8/13 02:03:27
Fast Multipole Methods for Electromagnetic Circuit Computations	Rohklin	1998	3/19/13 05:13:45
A combined calorimetric and semiempirical quantum chemical appro...	Reinwald and Zimm...	1998	2/8/13 02:03:27
Large scale simulation of macromolecules in solution: Combining the ...	Figueirido et al.	1997	2/8/13 01:57:22

Item Type: Journal Article
Title: Extending the fast multipole method to charges inside or outside a dielectric sphere
Author: Cai, Wei
Author: Deng, Shaoz...
Author: Jacobs, Donald
Abstract:
Publication: Journal of Computational Physics
Volume: 223
Issue: 2
Pages: 846-864
Date: 5/2007
Series:
Series Title:
Series Text:
Journal Abbr:
Language:
DOI: 10.1016/j.jcp.2006.10.019
ISSN: 00219991
Short Title:
URL: http://linkinghub.elsevi...
Accessed: 19/03/2013 05:13:37
Archive:
Loc. in Archive:

World cloud



Topic modeling by 3 words (2000–2014)



Research center ranking by number of publications

