

Tenth Liblice Conference on the Statistical Mechanics of Liquids

MOLECULAR PHYSICS LECTURE:

Weeks J. D. Solvation thermodynamics and structure in simple liquid mixtures and aqueous solutions

INVITED KEYNOTE TALKS:

- Archer A. Liquid drops on a surface: using density functional theory to calculate the binding potential and drop profiles, and comparing, with results from mesoscopic modelling
- Frenkel S. Molecular Simulations: The Good, the Bad and the Ugly
- Likos Ch. Self-assembly of soft colloids beyond the pair potential approximation
- Michealides A. Cold water and ice: Insights from computer simulations
- Santiso E. Molecular modeling of crystal nucleation from the melt and from solution
- Shell S. Coarse-grained models of liquid state physics designed by the relative entropy
- Scortino F. Colloidal models with water-like behaviors: The liquid-liquid critical point and the re-entrant spinodal Speedy scenario
- Siepmann I. Development of transferable force fields for phase and sorption equilibria
- Vega C. Salts in water. Solubility, models and nucleation
- Stark H. Emergent collective dynamics of spherical microswimmers
- Wu J. Z. Classical and quantum billiards in liquid-state theory

COMPLETE LIST OF ORAL CONTRIBUTIONS

- | | |
|--|--|
| D. Toneian, R. Blaak, G. Kahl, C. N. Likos | In- and Out-of-Equilibrium Properties of Magnetic Star Polymers |
| S. Consta | Toward the understanding of the stability of non-covalent complexes of macromolecules in droplets and bulk solution |
| M. Klíma, J. Kolafa | Direct molecular dynamics simulation of nucleation during supersonic expansion of gas to vacuum |
| F. Uhlík | Hybrid Monte Carlo Simulations of Polymers |
| M. Předota, D. Biriukov, M. Machesky, D. Wesolowski | Molecular simulations of electrokinetic phenomena |
| M. Bley, M. Duvail, P. Guilbaud, J.-F. Dufreche | Molecular Simulation of Phase Diagrams from the Osmotic Equilibrium Method: Vapor Pressure and Activities in Complex Solutions |
| C. Nieto-Draghi, B. Rousseau | Modeling aqueous electrolyte solution by coarse grained simulations |
| L. Fu, S. Merabia, L. Joly | Understanding the effect of wetting on thermo-osmosis using molecular dynamics |
| P. Jedlovsky, M. Sega, L. Nyulászi, G. Horvai | Geometry in liquid structures |
| D. Boda, D. Fertig, E. Máda, Z. Ható, M. Valiskó, T. Kristóf, D. Gillespie | Simulating ion transport through nanopores: from molecular models to device functions |
| L. Wu, H. Sun | Phase Behaviour and Dynamics of Thermotropic Cholesteric Liquid Crystals |
| A. Patrykiejew | Wetting of non-selective and selective walls by highly non-additive symmetric mixtures |
| L. Baran, M. Borówko, W. Rżysko, S. Stefan | Self-assembly of adsorbed Janus particles forming monolayers and adsorbed in slit-like pores: molecular dynamic studies. |
| V. Ryzhov, Y. Fomin, E. Tsiok | Melting scenarios and unusual crystal structures in two-dimensional core-softened systems |
| M. Vasin | Description of glass transition as topological phase transition in frustrated system |

Z. Benková, L. Rišpanová, P. Cifra	Semiflexible macromolecules confined in an array of cylindrical nanoposts
F. Merzel, F. Avbelj	Why do water molecules around small hydrophobic solutes form stronger hydrogen bonds?
C. A. Cerdeirina, D. González-Salgado, H. E. Stanley	An Ising Model Approach to Understanding Water's Unusual Thermodynamics
E. Noya	Design of patchy colloid models that assemble into complex ordered structures
P. Llombart, D. N. Sibley, E. G. Noya, A. J. Archer, L. G. MacDowell	Water droplets on ice
Y. Kalyuzhnyi	Explicit-water theory for the salt-specific effects and Hofmeister series in protein solutions
K. Trachenko	New understanding of collective modes and thermodynamics of the liquid state
M. Sweatman	Giant SALR clusters: reproduction and adsorption at interfaces
A. Milne	Polarisation and the Hydration Free Energy of Water
J. Higham, S.-Y. Chou, F. Grater, R. Henchman	Entropy of Liquids Computed from Force-Torque Covariance and Contacts
M. Tortora, J. Doye	The origins of phase chirality in lyotropic cholesteric liquid crystals
C. Williams, P. Carbone, F. Siperstein	Understanding the Structure and Ion Selectivity of Graphene Oxide Membranes using Molecular Simulation
S. Ravipati, A. Haslam, A. Galindo, G. Jackson	Coarse-grained fluid-solid potentials for heterogeneous surfaces using free-energy-averaged mapping
P. Yatsyshin, A. O. Parry, C. Rascon, M. A. Duran-Olivencia, S. Kalliadas	Phase transitions on fluid interfaces and bulk. Equilibrium and dynamic studies using classical density functional theory
V. P. Sokhan, F. S. Cipcigan, J. Crain, G. J. Martyna	Quantum Drude oscillator: electronic coarse-graining route to predictive modelling
D. Corbett, A. Patti, A. Cuetos	Dynamic Monte Carlo simulations of out-of-equilibrium colloidal liquid crystals.
J. R. Elliott, S. V. Ramana, A. Schultz	Inference of an Infinite Order Thermodynamic Perturbation Theory
A. Panagiotopoulos, H. Jiang, J. Young	Free energies, solubilities, and nucleation rates of aqueous electrolyte solutions
B. Laird, H. Hansen-Goos, R. L. Davidchack	Curvature dependence of interfacial free energy: Deviations from morphometric thermodynamics
V. Varshavskiy, D. Ford, P. Monson	On the mechanical stability of the body-centered cubic phase and the emergence of a metastable cl16 phase in classical hard sphere solids
W. Lin, A. Goyal, S. Moustafa, A. Schultz, D. Kofke	Mapped averages: Reformulation of statistical mechanical ensemble averages using coordinate mapping
P. Debenedetti	Computational investigation of the relationship between folding and chirality in model polypeptides
R. Manichetti	Computational high-throughput screening of drug permeation through biological membranes
M. Jorge	Multiscale Model for the Synthesis of Bioinspired Porous Silica Materials
P. Malani	Adsorption of Ions at Solid-Liquid Interface: Role of Ion Hydration Structure and Energies
M. Lisal	Surface Structure and Surface Tension of Ionic Liquids as Seen from Molecular Dynamics and Rutherford Backscattering Spectroscopy

INFORMATION FOR AUTHORS:

- It is assumed that all oral presentations will be in the form of *.ppt(x) (PowerPoint) or *.pdf (Adobe Acrobat) files, stored either on a CD or a flash-disk.
- **NO USE OF PRIVATE NOTEBOOK COMPUTERS WILL BE ALLOWED (OR POSSIBLE).**
- The provided PC runs under WINDOWS-10 with MS Office 2016.
- Be sure that your CD or flash-disk works properly under Windows O/S.

PROGRAM STRUCTURE

SUNDAY							
14.00-19.30	registration						
20.00-20.10	Opening address						
20.10-21.10	J. D. WEEKS						
21.10-23.00	SOCIAL MIXER						
MONDAY	June 18	TUESDAY	June 19	WEDNESDAY	June 20	THURSDAY	June 21
	SESSION I		SESSION IV		SESSION VI		SESSION IX
chair	<i>W. R. Smith</i>	chair	<i>P. Debenedetti</i>	chair	<i>M. Sweatman</i>	chair	<i>G. Kahl</i>
8.30-9.10	F. SCORTINO	8.30-9.10	C. VEGA	8.30-9.10	A. MICHEALIDIS	8.30-9.10	Ch.. LIKOS
9.10-9.30	Corbett	9.10-9.30	Panagiotopoulos	9.10-9.30	MacDowell	9.10-9.30	Rzysko
9.30-9.50	Vasin	9.30-9.50	Kalyuzhnyi	9.30-9.50	Marzel	9.30-9.50	Cifra
9.50-10.10	Wu	9.50-10.10	Milne	9.50-10.10	Malani	9.50-10.10	Lisal
10.10-10.30	Remembrance	10.10-10.30	Cerdeirina	10.10-10.30	Horvai	10.10-10.30	Jorge
10.30-11.00	coffee	10.30-11.00	Coffee	10.30-11.00	coffee	10.30-11.00	coffee
	SESSION II		SESSION V		SESSION VII		SESSION X
chair	<i>Ch. Likos</i>	chair	<i>A. Panagiotopoulos</i>	chair	<i>I. Siepmann</i>	chair	<i>E. Santiso</i>
11.00-11.40	H. STARK	11.00-11.40	E. SANTISO	11.00-11.40	D. FRENKEL	11.00-11.40	S. SHELL
11.40-12.00	Tonelan	11.40-12.00	Sweatmann	11.40-12.00	Kolafa	11.40-12.00	Debenedetti
12.00-12.20	Boda	12.00-12.20	Laird	12.00-12.20	Kofke	12.00-12.20	Monson
12.20-12.40	Predota	12.20-12.40	Elliott	12.20-12.40	Bley	12.20-12.40	Manichetti
12.40-13.00	Ryzhov	12.40-13.00	Fu	12.40-13.00	Uhlik	12.40-13.00	Henchman
13.00	lunch	13.00	Lunch	13.00	lunch	13.00	lunch
		13.45	CONFERENCE				
			EXCURSIONS:				
							SESSION XI
						chair	<i>C. Vega</i>
18.00	dinner			18.00	dinner	15.00-15.40	A. J. ARCHER
		19.30	Dinner			15.40-16.00	Patrykiewicz
	SESSION III				SESSION VIII	16.00-16.20	Yatsyshin
chair	<i>J. Gross</i>			chair	<i>J. R. Elliott</i>	16.20-16.40	Nezbeda
19.30-20.10	I. SIEPMANN	20.30-22.30	POSTER SESSION	19.30-20.10	J. Z. WU	16.40-17.00	closing remarks
20.10-20.30	Nieto-Draghi			20.10-20.30	Consta		
20.30-20.50	Noya			20.30-20.50	Dove		
20.50-21.10	Ravipati			20.50-21.10	Williams	19.00-24.00	BANQUET
21.10-21.30	Sokhan			21.10-21.30	Trachenko		

LIST OF POSTERS (in the alphabetical order with only the corresponding author listed)

- | | | | |
|----|----------|------------|--|
| 1 | Beránek | Pavel | Effect of blockiness and monomer sequence on self-assembly of gradient copolymer melt |
| 2 | Boda | Dezső | Intercalation properties of kaolinite from molecular simulations |
| 3 | Borowko | Malgorzata | Mono-tethered nanoparticles at solid surfaces |
| 4 | Brazhkin | Vadim | Dynamical crossover in supercritical fluids: theoretical background and experimental evidences |
| 5 | Ciach | Alina | Combined density functional and Brazovskii theories for systems with spontaneous inhomogeneities |
| 6 | Ciach | Alina | Simple theory for oscillatory charge profile in ionic liquids near a charged wall |
| 7 | Dreher | Thibaud | Computing the solid/liquid surface tension for anisotropic systems using atomistic simulations |
| 8 | Eller | Johannes | Molecular transport in confined media utilizing dynamic density functional theory |
| 9 | Fábián | Balázs | Ammonia Clathrate Hydrate As Seen from Grand Canonical Monte Carlo Simulations |
| 10 | Fábián | Balázs | Single Particle Dynamics at the Intrinsic Surface of Various Liquids |
| 11 | Fertig | David | Modeling a nanofluidic transistor: controlling ionic currents by changing the charge pattern on the wall of the nanopore |

12	Figueroa-Gerstenmaier	Susana	Olefin/paraffin separation using a membrane of syndiotactic polystyrene membrane
13	Fomin	Yury	Anomalously high heat capacity of core-softened liquids
14	Gebhardt	Julia	Prediction of activity coefficients for solvent mixtures from molecular dynamics simulations
15	Gotlib	Igor	Molecular dynamics simulation of solutions of cross-associating chains: inactive spacers' effect on thermodynamics and kinetics of association
16	Haji-Akbari	Amir	Jumpy FFS: A Generalized Forward-Flux Sampling Algorithm for Studying Aggregation Phenomena
17	Hantal	Gyorgy	Chemistry and water dynamics at the surface of hydrated magnetite
18	Hantal	Gyorgy	Dissolution mechanism of simple sugars in water and ionic liquids
19	Huerta Hernández	Adrián Arturo	Caging of hard disk fluid confined to quasi 1D
20	Jasiok	Bernadeta	A Fluctuation Equation of State for Prediction of High-Pressure Speed of Sound
21	Jedlovsky	Pal	Investigation of problems related to the lateral pressure profile
22	Jirsák	Jan	Binding of ibuprofen enantiomers to β -cyclodextrin: calculation of potentials of mean force along dissociation of inclusion complexes using umbrella sampling
24	Kahl	Gerhard	Novel hybrid crystal-liquid phase formed by heterogeneously decorated colloidal particles
25	Kahl	Gerhard	The polymorphic plethora of Wigner bilayer systems
26	Kalyuzhnyi	Yurij	Controlling the viscosities of antibody solutions through control of their binding sites
28	Kopanichuk	Iliia	Electrical properties of reverse AOT micelles with and without salts by molecular dynamics simulations
29	Lemarchand	Claire	Test of the "radical-like polymerization" scheme in molecular dynamics on the structural and dynamical properties of polymers
30	Lindeboom	Tom	Coarse-grained SAFT force fields for the study of biologically relevant systems
31	Llombart Gonzalez	Pablo	Adsorbed aggregates on gold nanoparticles determine their size.
32	Mádai	Eszter	Monte Carlo simulation of a model nanopore sensor: device behavior emerging from ion competition
33	Malani	Ateeque	Multiscale Simulation Studies of CO ₂ Separation and CH ₄ Storage in Two Dimensional (2D) Covalent Organic Framework (2D-COF) Nanoporous Materials
34	Millot	Claude	Structural and Dynamical Properties of Water at High Pressure. Molecular Dynamics Simulations with the BK3 Model
35	Moučka	Filip	Ion-ion interaction models for NaCl yielding accurate density, chemical potential, and good mechanical properties of the crystalline phase
36	Nieto-Draghi	Carlos	Calculation partition coefficients of complex molecules by combining DPD with a Monte Carlo method
37	Parez	Stanislav	Granular Mechanics
38	Pękalski	Jakub	Self-assembly of nanoparticles on a surface of a microdroplet
39	Prokacheva	Varvara	The core-shell structure of comb-like polyelectrolytes
40	Předota	Milan	Adsorption of oxalic acid on rutile surfaces
41	Předota	Milan	Application of Electronic continuum correction for modelling of solid-liquid interactions using scaled charges
42	Punnathanam	Sudeep	Study of crystal nucleation from solution and solvent induced polymorphism of Orcinol
43	Radhakrishnan	Ravi	Incorporation of Hydrodynamic Interactions in Dynamical Density Functional Theory for

Suspensions in Flow and Confinement

44	Rajasekaran	M.	Interfacial water dynamics on graphene oxide surface
45	Rehner	Philipp	Curvature dependence of interfacial properties with non-local density functional theory and PC-SAFT
46	Rispanova	Lucia	Behavior of a block copolymer composed of flexible and semiflexible blocks confined in an array of nanoposts
48	Rzysko	Wojciech	Self-assembly of nanodisks with tethered diblock copolymers on surfaces
49	Santiso	Erik E.	Molecular modeling of crystal nucleation from the melt and from solution
50	Singh	Jayant	Nucleation of Aqueous Salt Solutions on Solid Surfaces
51	Sizova	Anastasia	Molecular simulations of CO ₂ /CH ₄ and CO ₂ /N ₂ mixed hydrates
52	Skutnik	Robert	Defect topologies in chiral blue phases confined to spherical cavities
53	Sliwinska-Bartkowiak	Malgorzata	Structure of ice confined in nanopores; X-ray (WAXS) and neutron diffraction (ND) studies
54	Stierle	Rolf	Interface Analysis of Droplet Coalescence via Dynamic Density Functional Theory
55	Svoboda	Martin	Modelling Aqueous Dissolution of Sodium Chloride in Clays at Thermodynamic Conditions of Hydraulic Fracturing by Molecular Dynamics
56	Škvára	Jiří	Separation of racemic mixtures: Molecular dynamic study
57	Trokhymchuk	Andrij	Excluded volume and its temperature dependence
58	Trokhymchuk	Andrij	Statistical mechanics of aggregation in anisotropic solvents: kinetic energy of aggregates and universal power-law behavior far from criticality.
59	Trokhymchuk	Andrij	Statistical field theory of liquids: Novel expression for the grand partition function of a system with short and long-range interactions
60	Tsiok	Elena	New melting scenario of Hertzian disks system induced by random pinning
61	Valiskó	Mónika	How can we turn a selective nanopore into a rectifying one (and vice versa) by changing the surface charge pattern?
62	Vanin	Aleksandr	Structure and electrostatic interaction of droplet-like micelles of nonionic surfactants in solutions
63	Veesam	Shivanand Kumar	Improving the robustness of the van der Waals and Platteeuw theory for gas hydrates
64	Vyalov	Ivan	3D-RISM Integral Equations for Electrochemical Applications
65	Williams	Christopher	Atomic characterisation of the electrolyte/graphene interface
66	Yang	Yang	Tension, Bending Modulus and Dielectric Polarization of Water Surfaces Near Electrodes

INFORMATION FOR AUTHORS:

- Poster dimensions: A0 [841 times 1189 mm], portrait orientation.
- Authors should mount their poster on Monday before the beginning of the evening session.
- When mounting your poster(s), please respect the ordering and the number(s) assigned to your poster(s).
- **Use of any adhesive material is strictly prohibited; pins will be provided by the organizers.**
- Remove your poster on Thursday afternoon (before the banquet).

Monte Carlo simulation of a model nanopore sensor: device behavior emerging from ion competition

Eszter Mádai, Mónika Valiskó, Dezső Boda

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Artificial nanopores are microscopic-length channels with a nanoscopic radius, therefore, they can be used as nanoscale devices. Rapidly improving experimental techniques make a wide range of sensing applications possible, thus, a chemically modified nanopore can be used as a sensor. The shrinking dimensions of these nanosystems, however, underly the importance of computational techniques in order to get insight into the molecular mechanism behind ion transport in nanopores. In this work, a study about a nanosensor made of a nanopore is presented [1]. An analyte ion is contained by the electrolyte moving through the pore driven by an electric field. The selective attraction and binding of the analyte molecule to the wall of the nanopore (via a square-well potential) make this ion more effective to compete for space with the main current-carrying ion inside the nanopore. This competition depends on the concentration of the analyte ion, therefore, the degree of the current reduction also depends on the analyte concentration. By measuring the current reduction and establishing calibration curves the concentration of the analyte can be determined.

In this work we use the NP+LEMC method [2,3] to determine the current through the pore. The Local Equilibrium Monte Carlo (LEMC) method provides the chemical potential and the concentration profile, from which the ionic flux can be calculated via the Nernst-Planck (NP) equation. The Primitive Model of electrolytes is used, where ions are charged hard spheres in an implicit solvent. This model reproduces the behavior of the device correctly compared to all-atom molecular dynamics simulations [4]. We examine a general model with well-defined, tunable parameters. We study the effect of these parameters on the response function of the device. We show that the model of this nanopore sensor coupled to the applied computational method, an analyte ion present at very low concentrations can be detected based on this competition principle.

1. Mádai et al. Simulation of a model nanopore sensor: ion competition underlies device behavior. *J. Chem. Phys.* **147**, 244702, 2017.
2. Boda and Gillespie. Steady state electrodiffusion from the Nernst-Planck equation coupled to Local Equilibrium Monte Carlo simulations. *J. Chem. Theory Comp.*, **8**, 824, 2012.
3. Boda. Monte Carlo simulation of electrolyte solutions in biology: in and out of equilibrium. *Ann. Rep. Comp. Chem.*, **10**, 127, 2014.
4. Ható et al. Multiscale modeling of a rectifying bipolar nanopore: explicit-water versus implicit-water simulations. *Phys. Chem. Chem. Phys.* **19**, 17816, 2017.

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msMS modeling and simulation of complex Molecular Systems research group

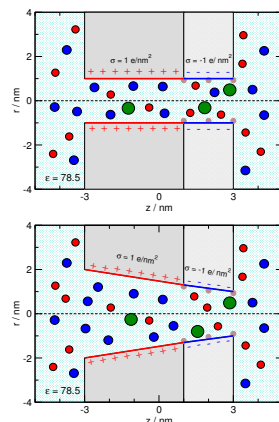


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Introduction

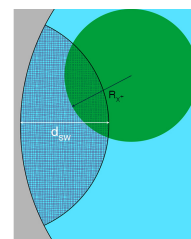
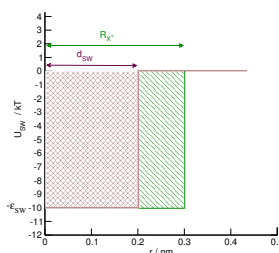
The alkali and different metal ions play a key role in today's raw material policy. Therefore, in the case of recycling of wastage, new methods for detection are needed. One possible solution are sensors fabricated of nanopores with the basic operational concept of detecting the presence of these ions qualitatively and quantitatively. By placing binding sites on the nanopore's wall which are selective for one of these ions (analyte, X^+ or X^{2+}), the binding of the analyte creates a change in the current flowing through the nanopore, thus, the presence of the analyte can be detected through this current-modulation. We present a modeling study which examines the effects of experimentally controllable parameters on the device behavior. Through these parameters (voltage and background electrolyte concentration) current- voltage and calibration curves can be obtained to determine the concentration of the analyte.

Model



Schematics of the cylindrical and conical nanopore with two regions of surface charge and the binding sites.

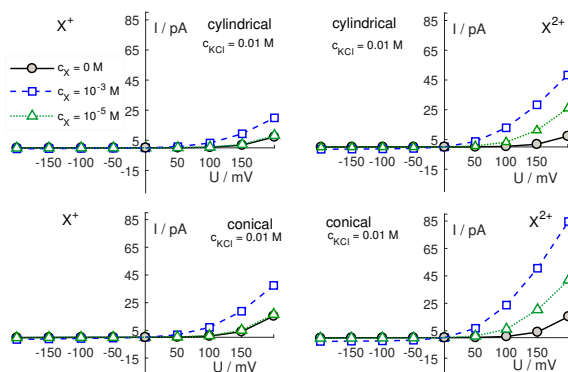
- **Ions:** Charged hard spheres (Primitive Model of electrolytes)
- **Solvent:** implicit water. Ions are immersed in a dielectric continuum of dielectric constant $\epsilon = 78.5$.
- **Binding sites:** Square-well potential. The short-range potential attracts X with ϵ_{SW} energy once the closest point of the X ion's surface is closer to the site than the distance parameter d_{SW} :



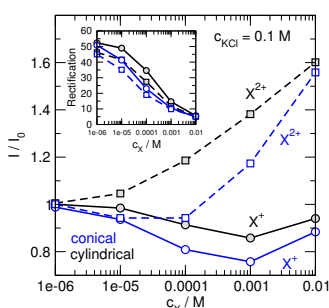
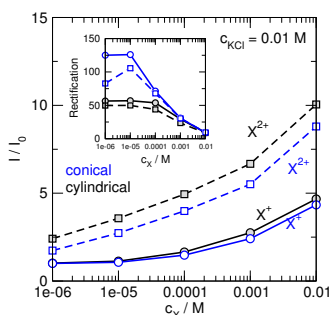
Results

Current-voltage (I-V) curves

- The main charge carrier is Cl^- due to the left positive zone of the pore.
- The presence of various analyte concentrations modulates the shape of the I-V curves differently,
- Unknown analyte concentration is determinable from the shape of the I-V curve
- The pore rectifies due to charge asymmetry.
- The mechanism of X detection is that more X attracts more Cl^- into the pore thus.



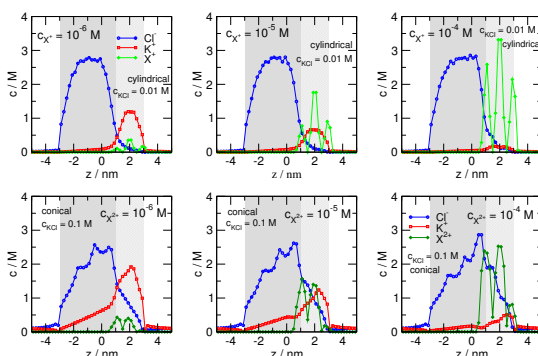
Calibration curves and rectification



- On lower c_{KCl} increasing c_X attracts more Cl^- and repulses more K^+ , the shape of the calibration curve is monotonic
- Competitive effect: higher c_{KCl} gives higher I_{K^+} while increasing c_X extrudes K^+ from the pore, creating an extremum in the calibration curve

Concentration profiles

- As c_X increases, X ions attract more Cl^- ions into the pore.
- At $c_X = 0.01$ M, K^+ ions are excluded from the left hand side, so K^+ current is absent.
- At $c_X = 0.1$ M, K^+ ions are present, but this (K^+ leakage vanishes with as more X ion appears in the pore. This causes the maximum in the I/I_0 curve.



Method

Nernst-Planck equation

$$\mathbf{j}_i(\mathbf{r}) = -\frac{1}{kT} D_i(\mathbf{r}) c_i(\mathbf{r}) \nabla \mu_i(\mathbf{r})$$

$\mathbf{j}_i$ is the flux density of ionic species, k is the Boltzmann's constant, T is temperature, $c_i(\mathbf{r})$ is the concentration profile, $\mu_i(\mathbf{r})$ is the electrochemical potential profile.

The relation between $c_i(\mathbf{r})$ and $\mu_i(\mathbf{r})$ is established with Local Equilibrium Monte Carlo (LEMC) simulation. The computation domain of the NP system is divided into volume elements with different μ_i values.

NP + LEMC method

$$\mu_i[n] \xrightarrow{LEMC} c_i[n] \rightarrow \mu_i[n+1]$$

The whole system is solved in an iterative scheme until conservation of mass ($\nabla \cdot \mathbf{j}_i(\mathbf{r}) = 0$) is satisfied.

Conclusion

This modeling study presents a option for recognition of ions with different valences. Through the examination of the effects of experimentally controllable parameters, deductions for molecular mechanisms inside the pore can be made.

1. Through the usage of an asymmetric charge pattern on the nanopore's wall, the analyte and the surface charge together modulate the current of the main charge carrier ion (Cl^-).
2. Higher c_{KCl} leads to a leakage of K^+ ions through the pore which creates an extremum in the calibration curve, thus lower c_{KCl} is preferable.

This model sensor is able to detect the analyte ions in low concentrations. Using NP+LEMC methodology it is possible to handle finite size of ions and ionic correlations at the same time with reasonable computational time.

References

1. E. Mádai et al., *J. Chem. Phys.*, 147(24):244702, 2017.
2. D. Boda et al., *J. Chem. Theor. Comput.* 8(3):824-829, 2012.
3. D. Boda., *Ann. Rep. Comp. Chem.*, 10, 127, 2014.
4. Z. Ható et al., *Phys. Chem. Chem. Phys.* 19(27):17816, 2017.

Acknowledgements

This work was supported by the Hungarian National Research, Development and Innovation Office (NKFIH K124353) and Project No.GINOP-2.3.2-15-2016-00053. Supported by the UNKP-17-4 New National Excellence Program of the Ministry of Human Capacities (M. V.)

How can we turn a selective nanopore into a rectifying one (and vice versa) by changing the surface charge pattern?

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The transport characteristics in nanofluidic devices can be regulated with surface charge patterns and geometrical asymmetry. Nanopores with negative surface charge are cation selective while a junction between the positively and negatively charged zones of the pore walls becomes the basis of rectification of bipolar nanopores. Unipolar pores consisting of a neutral and uniformly charged zone are ion selective but also rectify due to the asymmetry. The behavior of selectivity and rectification can be tuned via changing the surface charge pattern.

Here we present computer simulation results for uni-, bi- and nonpolar nanopores on two modeling levels. In an all-atom model, we use explicit water to simulate ion transport directly with the Molecular Dynamics (MD) technique. In a reduced model, we use an implicit water model and apply the Local Equilibrium Monte Carlo method together with the Nernst-Planck transport equation (NP+LEMC) [1,2]. The two modeling levels are connected by the diffusion coefficient of ions inside the pore fitted to the results of the MD simulation.

We show that the implicit water electrolyte is able to reproduce the basic behavior of nanopores with different conduction properties because it can reproduce the behavior of the concentration profiles along the nanopore [3]. Both models show that the physical basis of rectification and selectivity is the formation of the depletion zones of the proper ions.

1. Boda and Gillespie. Steady state electrodiffusion from the Nernst-Planck equation coupled to Local Equilibrium Monte Carlo simulations. *J. Chem. Theory Comp.*, **8**, 824, 2012.
2. Boda. Monte Carlo simulation of electrolyte solutions in biology: in and out of equilibrium. *Ann. Rep. Comp. Chem.*, **10**, 127, 2014.
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How can we turn a selective nanopore into a rectifying one (and vice versa) by changing the surface charge pattern?

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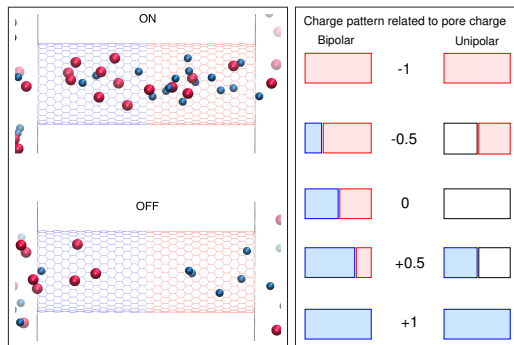
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Introduction

The transport characteristics in nanofluidic devices can be controlled via manipulating surface charge pattern on the pore's wall. Nanopores with negative surface charge, for example, are cation selective, while pores with charge asymmetry rectify. Bipolar nanopores contain both negative and positive zones, while unipolar pores consist of neutral and charged zones. We present computer simulation results on three different modeling levels.

Model and Methods



Nernst-Planck equation

$$\mathbf{j}_i(\mathbf{r}) = -\frac{1}{kT} D_i(\mathbf{r}) c_i(\mathbf{r}) \nabla \mu_i(\mathbf{r})$$

$c_i(\mathbf{r})$ vs. $\mu_i(\mathbf{r})$ relation is established in NP+LEMC and PNP differently (particle simulation vs. mean field theory).

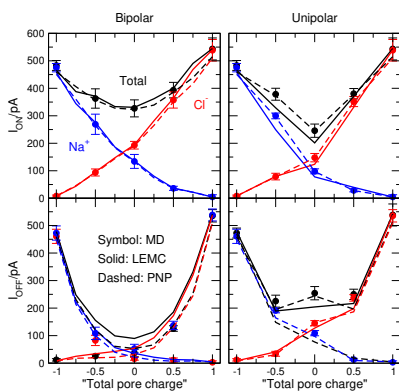
MD simulates ion transport directly.

Link between the models: diffusion coefficient profile (fitted D_i^{pore} , exp. D_i^{bulk})

	All-atom model	Reduced model	Continuum theory
Method	Molecular Dynamics (MD)	Nernst-Planck + Local Equilibrium Monte Carlo (LEMC)	Poisson-Nernst-Planck (PNP)
Ions	LJ + point charge	HS + point charge	Point charge in mean field
Water	SPC	Dielectric continuum	Dielectric continuum
Diffusion coefficient in the pore	Natural outcome	Input parameter fitted to MD	Input parameter fitted to MD
Computation time	Weeks	Hours	Minutes

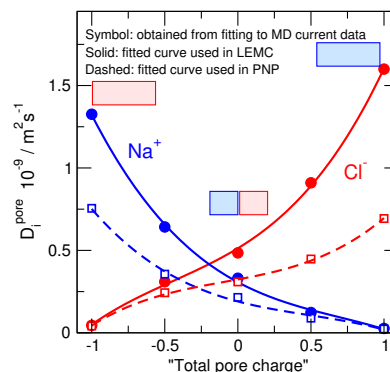
Results

Ionic currents



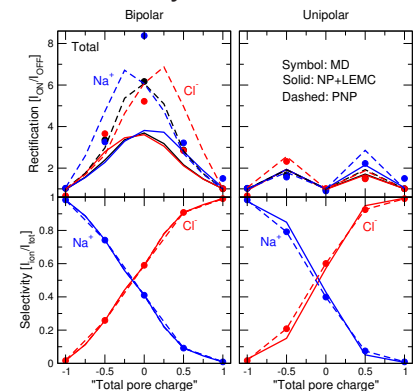
Currents show a minimum for zero pore charge when both ions have depletion zones. This current is smaller in the OFF state (rectification). For +1 and -1 pore charges the pores are selective and currents are maximal.

Diffusion coefficients

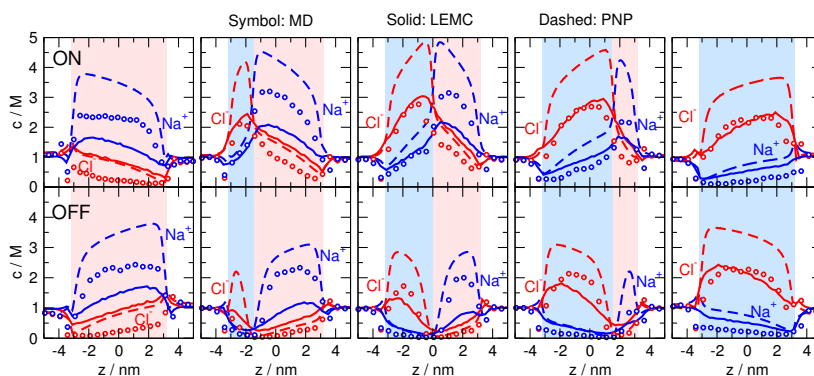


Diffusion coefficients in the pore (D_i^{pore}) are fitted to MD current data in selected states (bipolar in ON state). D_i^{pore} values obtained through fitting are used in other states (unipolar in both states, bipolar in OFF state).

Selectivity vs. rectification



Selectivity is maximal when the pore is uniformly charged (+1 or -1). Rectification is maximal for maximal charge asymmetry (zero pore charge for bipolar pore, -0.5 and 0.5 for unipolar pore).



Concentration profiles

- Axial concentration profiles show peaks for counterions and depletion zones for coions in a zone of a given charge.
- In selective pores, peaks of counterions determine current.
- In rectifying pores, depletion zones govern the rectification behavior: voltages of different signs influence the depletion zones differently.
- Qualitative agreement between NP+LEMC vs. MD (implicit vs. explicit water) curves is good. Quantitative disagreement is balanced by D_i^{pore} (see above).
- PNP overestimates concentrations, but qualitative behavior is still appropriate. The difference can be balanced with fitted D_i^{pore} values different from those fitted in NP+LEMC (see above).

Conclusion

We are interested in the question why the reduced models can reproduce device behavior despite the fact that important molecular details are ignored and/or approximated. We show that the implicit water electrolyte is able to reproduce the basic behavior of nanopores with different conduction properties because it can reproduce the behavior of the concentration profiles along the nanopore. All the applied models show that the physical basis of rectification vs. selectivity is the formation of the depletion zones vs. peaks of the respective ions. Our results show that reduced models work if they contain those degrees of freedom that are relevant for device function.

References

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- Z. Ható, M. Valiskó, T. Kristóf, D. Gillespie, D. Boda. Multiscale modeling of a rectifying bipolar nanopore: explicit-water versus implicit-water simulations. *Phys. Chem. Chem. Phys.* 19(27):17816, 2017.

Acknowledgements

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Modeling a nanofluidic transistor: controlling ionic currents by changing the charge pattern on the wall of the nanopore

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Nanofluidic devices containing artificial nanopores can be used as diodes, transistors, sensors [1], or switches. Through integrating these devices into nanofluidic circuits it is possible to regulate ionic currents. In order to gain insight and to understand the mechanism of ion transport through nanofluidic devices in the presence of an applied electric field, a model should be developed that explains this complex phenomenon in a simplified way. In this work, a model transistor made of a nanopore is presented. The inside surface of the nanopore is divided into three regions, where different surface charges can be applied. To simulate the transport, the Nernst-Planck transport equation is used combined with the Local Equilibrium Monte Carlo Method (NP+LEMC), which provides electrochemical potential and concentration profiles [2,3]. The model uses the Primitive Model for electrolytes, where ions are charged hard spheres in an implicit solvent. This model reproduces the behavior of the device correctly compared to all-atom molecular dynamics simulations [4].

The purpose of this work is to construct a general model with well-defined parameters and to see their effect on the device's response function. Every applied parameter in this reduced model plays an important role in the competition of different ions carrying the current. The effect of the nanopore's geometry was also examined; two different geometries were used: cylindrical and biconical nanopores. The behavior of the device (changing the surface charge pattern) can be tuned experimentally by changing the pH of the electrolyte. In our model, pH influences the surface charge through protonation and deprotonation of chemical groups on the pore wall. Therefore, a pH-sensitive device can be built. If a charge pattern that produces depletion zones for every ionic species produces, the total current is inhibited so the device can be used a switch.

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3. Boda. Monte Carlo simulation of electrolyte solutions in biology: in and out of equilibrium. *Ann. Rep. Comp. Chem.*, **10**, 127, 2014.
4. Ható et al. Multiscale modeling of a rectifying bipolar nanopore: explicit-water versus implicit-water simulations. *Phys. Chem. Chem. Phys.* **19**, 17816, 2017.

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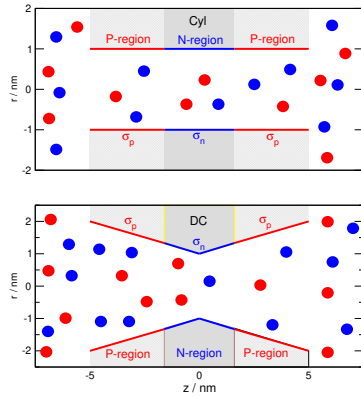


Introduction

The purpose of this work was to create a model of a nanofluidic transistor which is able to mimic the effects of pH on nanopore conductance. The pH of the electrolyte is an experimentally controllable parameter through which the charge pattern can be tuned: pH effects the ratio of the protonated/deprotonated forms of the functional groups anchored to the surface of the nanopore (for example, amino and carboxyl groups). Thus, the behaviour of the bipolar transistor is changed, as it becomes ion selective in acidic/basic environments. Here, we present the results of a particle simulation method (Local Equilibrium Monte Carlo), where the surface charge can be related to pH.

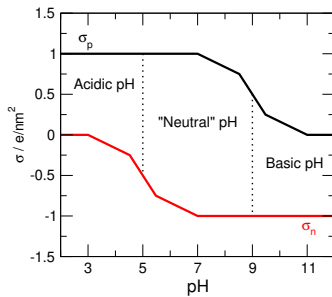
Model

A model of a nanopore with a length of 10 nm combined with the Restricted Primitive Model of electrolytes was used. Two types of geometries were constructed: cylindrical (Cyl) and double conical (DC).



- Maximum value of surface charge is $|\sigma| = 1 \text{ e/nm}^2$.
- σ depends on pH and on the pK_a value of the functional groups in the corresponding region.
- σ_p comes from basic functional groups, σ_n from acidic functional groups.
- $\text{pK}_a^{\text{COOH} \rightarrow \text{COO}^-} = 5$, $\text{pK}_a^{\text{NH}_3^+ \rightarrow \text{NH}_2} = 9$

Surface charge can be adjusted by changing pH. However, pH is not in the model directly. σ is derived from the molar fraction of the charged functional group (Φ), which depends on pH. σ values reach their maximum/minimum at $\text{pK}_a = \pm 2$.



Method

Nernst-Planck equation is used to compute the ionic flux:

$$\mathbf{j}_i(\mathbf{r}) = -\frac{1}{kT} D_i(\mathbf{r}) c_i(\mathbf{r}) \nabla \mu_i(\mathbf{r}),$$

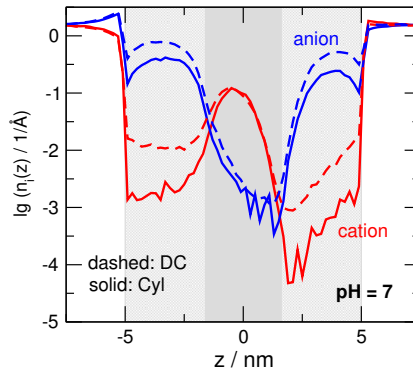
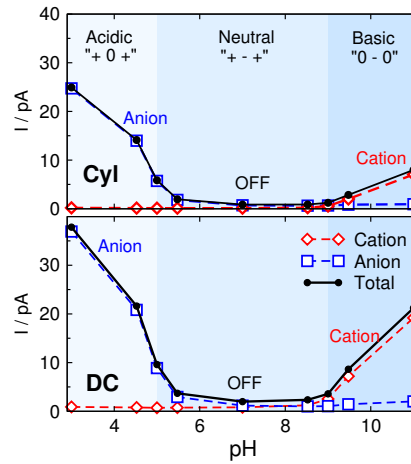
where $\mathbf{j}_i$ is the flux density of ionic species i , k is the Boltzmann's constant, T is temperature, $c_i(\mathbf{r})$ is the concentration profile, $\mu_i(\mathbf{r})$ is the electrochemical potential profile.

The relation between $c_i(\mathbf{r})$ and $\mu_i(\mathbf{r})$ is provided by Local Equilibrium Monte Carlo (LEMC) simulation.

$$\mu_i[n] \rightarrow c_i[n] \rightarrow \mu_i[n+1]$$

The whole system is solved in an iterative way until the conservation of mass ($\nabla \cdot \mathbf{j}_i = 0$) is satisfied.

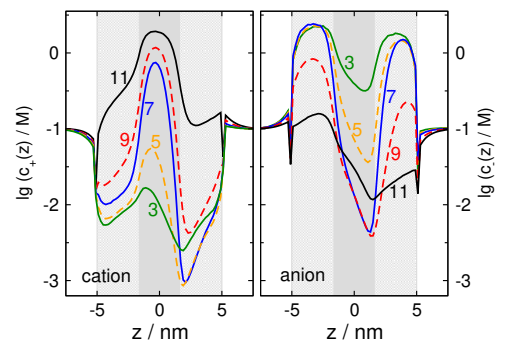
Results



- pH=3:** "+0+" – small cation concentration, large anion concentration (ON state)
- pH=5:** decreasing σ_n – increasing cation concentration, decreasing anion concentration in the n zone
- pH=7:** "+-+" – depletion zones are present for both ions (OFF state)
- pH=9:** decreasing σ_p – increasing cation concentration, decreasing anion concentration in the p zone
- pH=11:** "0-0" – large cation concentration, small anion concentration (ON state)

- pH defines the charge pattern on the pore's wall.
- Low pH (acidic):** $\sigma_p > 0$, $\sigma_n = 0$, "+0+", main charge carrier: anions
- High pH (basic):** $\sigma_p = 0$, $\sigma_n < 0$, "0-0", main charge carrier: cations
- Intermediate pH ("neutral"):** $\sigma_p > 0$, $\sigma_n < 0$, "+-+", current is small, because there are depletion zones for both ions
- Currents are larger in the DC geometry, because there are more charge carriers available.
- Both channels provide small currents in a wide range of pH ($5 < \text{pH} < 9$) thus both can be used as pH-gated nanopores.

- Line densities: $n_i(z) = \langle N_i \rangle / \Delta z$
- Zero or minimal current is the result of depletion zones for both ionic species (in p zones for cations, in n zone for anions) at neutral pH.
- Cylindrical geometry provides a deeper depletion zone for cations in the p regions than double conical geometry.
- DC geometry allows larger concentration of anions in the p zones → larger anion current
- The effect of the inner N-region is the similar for the two geometries.



Conclusion

Only through manipulating pH and thus the surface charge pattern on the surface of the nanopore, a pH-sensitive and ion-selective device can be built, in which the pH can act as a switch for both the cation and the anion.

References

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