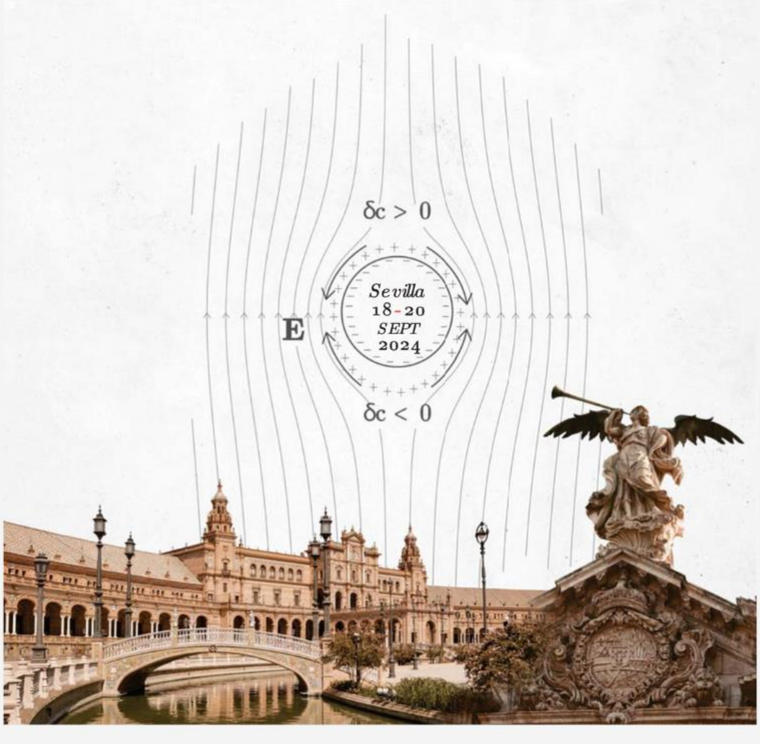
15TH INTERNATIONAL SYMPOSIUM ON ELECTROKINETICS
MEETING OF THE INTERNATIONAL ELECTROKINETICS SOCIETY

ELKIN2024

Conference Program
and
Book of Abstracts

Escuela Técnica Superior de
INGENIERÍA SEVILLA
www.elkin2024.org

September,18-20. Seville (Spain).



ELKIN 2024

IES International Electrokinetics Society

Universidad de Sevilla

Escuela Técnica Superior de
INGENIERÍA DE SEVILLA

Welcome to ELKIN2024

Dear colleagues,

It is our great pleasure to welcome you to the 15th International Symposium on Electrokinetics, ELKIN2024. We are very grateful to have you join us for what promises to be an exciting and enriching meeting.

ELKIN is a world-renowned forum featuring advances in theoretical and applied electrokinetics. The first ELKIN symposium took place in Granada, Spain, in 1993. Since then, ELKIN conferences have been held in different countries inside and outside Europe, where the two latest symposia were hosted by MIT in 2019 and Tel-Aviv University in 2022. The 15th International Symposium on Electrokinetics will take place in Seville, Spain, from 18 to 20 September 2024.

ELKIN symposia are organized by the International Electrokinetics Society (IES), which promotes interdisciplinary research in the field of Electrokinetics. ELKIN is the general meeting of the IES and is held biannually at locations around the globe. The IES has recently established two awards: *Stanislav Dukhin Medal in Electrokinetics*, for lifetime achievement, and the *Johannes Lyklema Early Career Award* in Electrokinetics. In ELKIN2024, awards will be announced for the first time during an ELKIN conference, and awardees will deliver corresponding named lectures.

In addition to our comprehensive scientific program, we have organized two special sessions in memory of two extraordinary scientists, Vladimir N. Shilov and Dennies C. Prieve. These sessions will honor their remarkable legacies and contributions to the field of Electrokinetics.

We also hope you will take time to enjoy our social events, which are designed to foster networking and camaraderie in a relaxed and enjoyable atmosphere. We look forward to sharing these moments with you.

Finally, we would like to thank the International Electrokinetics Society, the Universidad de Sevilla, and the Escuela Técnica Superior de Ingeniería for their support to this event.

Sevilla, September 2024.

The Local Organizing Committee:

Antonio Ramos

Pablo García-Sánchez

Pedro A. Vázquez

Contents

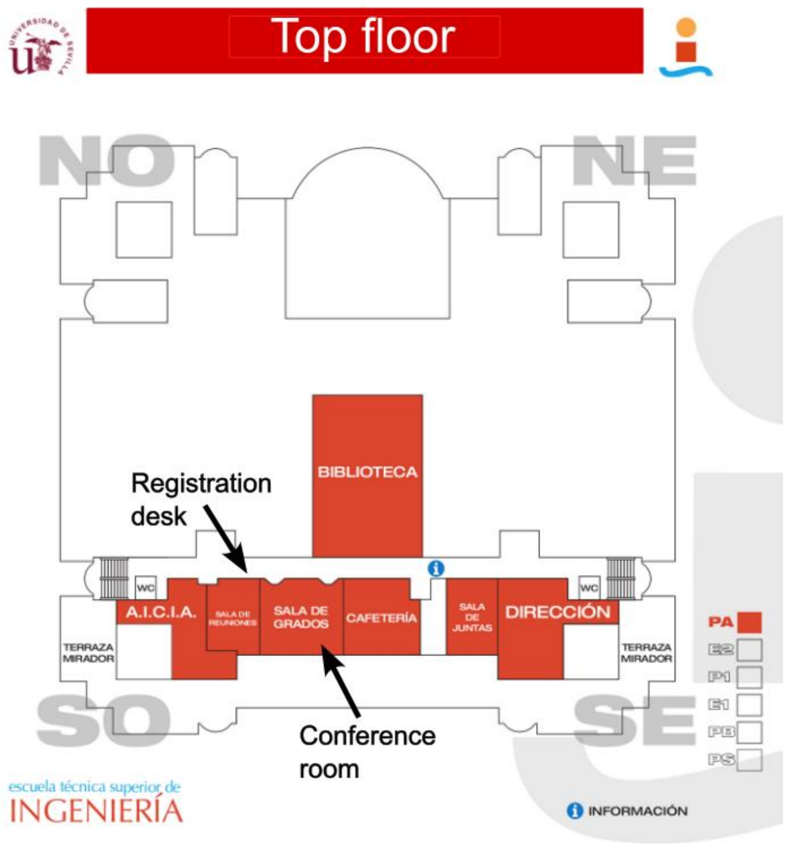
Conference Venue

The venue for ELKIN2024 will be the **Escuela Técnica Superior de Ingeniería (ETSI)** in Seville, Spain. The ETSI is part of the largest innovation space in Seville, the Cartuja Science and Technology Park (PCT Cartuja), with more than 500 companies and startups, university and research centers.

ETSI – **Escuela Técnica Superior de Ingeniería**.

Address: Camino de los Descubrimientos, 41092, Sevilla.

Conference Venue Map



Scientific Program

	Wednesday, September 18		Thursday, September 19		Friday, September 20
8:30	Registration	8:30	Registration	8:30	Registration
9:00	**Conference Opening**	9:00	**Micro and Nano fluidics. Active Colloids**	9:00	**Bioelectrokinetics and Biomedical I**
9:10	**Fundamentals Electrokinetics I**	10:45	Coffee break	10:25	Coffee Break
11:00	Coffee break	11:15	**Desalination, Selective Ion Separations, Batteries. I**	10:45	**Bioelectrokinetics and Biomedical II**
11:30	**Fundamentals of Electrokinetics II**	12:30	**Poster Soundbites**	12:00	**Desalination, Selective Ion Separations, Batteries. II**
12:30	**Poster Soundbites**	13:00	Lunch and poster session	13:00	Lunch and poster session
13:00	Lunch and poster session	14:30	**Aggregation and Assembly. Separation**	14:30	**Nanobubbles**
14:30	**IES Awards Announcements and Lyklema Lecture**	15:45	Coffee break	15:45	Coffee break
15:15	**Electrophoresis, Diffusiophoresis. Soft colloids I**	16:15	**Fundamentals of Electrokinetics III**	16:15	**Desalination, Selective Ion Separations, Batteries. III**
15:55	Coffee break	17:00	**Dukhin lecture**	18:00	**Closing of the conference**
16:15	**Electrophoresis, Diffusiophoresis. Soft colloids II**	17:50	End of second day		
17:40	End of first day				

Social Events Program

Date	Activity	Time and meeting point
Tuesday, September 17	**Welcome reception at the Rectorate building of *Universidad de Sevilla***	19:00 Rectorate building patio Calle San Fernando, 21. 41004. Seville.
Wednesday, September 18	**City center guided tour**	19:30 The meeting point will be announced during the conference
Thursday, September 19	**Boat trip**	19:30 Pier by *Torre del Oro*
Thursday, September 19	**Conference banquet**	20:30 Restaurante *Muelle 21**

* The boat trip ends at the *Muelle 21* restaurant (Avda. Santiago Montoto s/n).

Torre del Oro Pier

Main entrance to the Rectorate building of Universidad de Sevilla

Wednesday, September 18

9:00	Conference opening
9:10	**Fundamentals of Electrokinetics I. Special session in Memory of V. N. Shilov** - Chair A. Delgado
9:15	Invited talk - Nonequilibrium Electroosmotic Instability and Morphological Instability in Electrodeposition (B. Zaltzman)
9:45	Mechanism of Electrokinetic Length Selection in Electrodeposition (I. Rubinstein)
10:00	The Electrolyte Accumulation by a Porous Conductor Placed in an External Electric Field: The Small Perturbation Analysis (E. Zholkovskiy)
10:15	Cell Model for Arbitrary Surface Charge and Volume Fraction of Particles. Coagulation In Dilute and Concentrate Disperse Systems (N. Mishchuk)
10:30	Impedance Spectra of Soft Ionics (R. Hill)
10:45	Memory Effects in Electro-Optical Dynamic Response of Aqueous Suspensions (M. Jiménez)
11:00	Coffee break
	Fundamentals of Electrokinetics II - Chair A. Yaroschuchk
11:30	Invited talk - Electrokinetics of Electrolyte Solution Confined in a Nanotube (Y. Uematsu)
12:00	Dielectric Behaviour of Suspensions of Insulating, Conducting, and Heterogeneous Particles. The Different Manifestations of Concentration Polarization (A. Delgado)
12:15	Preconcentrations of Third Species near Ion-Selective Microgranule (G. Ganchenko)
12:30	**Poster Soundbites**
	Poster soundbite presenters: B. Shih, T. Tsou, A. Balaji-Wright, A. Hillman, D. Markiewitz, M. Liseanskaia,Y. Yan, Z. Zhang.

13:00	Lunch and poster session
14:30	**IES Awards Announcements** and Honorary Award Lecture**: Johannes Lyklema Early Career Award - Ankur Gupta.**
15:15	**Electrophoresis, Diffusiophoresis. Soft Colloids I. Special Session in Memory of D. C. Prieve -** Chair M. Bazant
15:25	Invited talk - Diffusiophoresis in Zwitterion Gradients: Theory and Experiment (T. Squires)
15:55	Coffee break
	Electrophoresis, Diffusiophoresis. Soft Colloids II. Special Session in Memory of D. C. Prieve - Chair M. Bazant
16:15	Keynote - The Dynamics of Single Elementary Charging Events at Nanoparticles in Water (Y. Ussembayev)
16:40	Ionic Self-Phoresis Maps onto Correlation–Induced Self-Phoresis (A. Domínguez)
16:55	Charging, De-Charging and Re-Charging of Dielectric Surfaces in Contact with Aqueous Electrolytes - The Influence of CO_2 (T. Palberg)
17:10	Invited talk - Electrokinetics of Soft Particles. Modelling, Experimental Investigation and Applications (S. Ahualli)

Thursday, September 19

	Micro and Nano-fluidics. Active Colloids - Chair S.J. Kim
9:00	Invited talk - Electrospray: from its Basics to its Electrokinetics (A. Gañán-Calvo)
9:30	Asymmetric Currents in Asymmetric Nanofluidic Systems (Y. Green)
9:45	Elucidating Particle-Wall Interactions through Bulk Mobility Measurements of Electric Field Driven Active Colloids (A. Boymelgreen)
10:00	Nanofluidic Transport in Channels with Defined Electronic Wall Properties (A. Noy)
10:15	Dipolophoresis of Travelling-Wave for Hydrophobic Conducting Colloids in Hydrogels (T. Miloh)
10:30	Coffee break
	Desalination, Selective Ion Separations, Batteries. I - Chair J. Santiago
11:15	Invited talk - Imparting Selectivity in Electrodialysis and Electrodeposition Platforms for Value-Added Ion Recovery (X. Su)
11:45	A Nanoporous Capacitive Electrochemical Ratchet for Continuous Ion Separations Desalination (G. Segev)
12:00	Blow-Spun Thin Fibers Prepared from Perfluorinated Sulfonic Acid Ionomers for Fuel Cell Applications (H. Matsumoto)
12:15	Submillimeter Bundled Microtubular Flow Battery Cells with Ultrahigh Volumetric Power Density (N. Liu)
12:30	**Poster Soundbites**
	Poster soundbite presenters: O. Lavi, F. Henrique, T. Kamsma, R. Fernández-Mateo, R. Hill, A. Cazorla, M. Sosa, J. Lirio, X. Yang.
13:00	Lunch and poster session

	Aggregation and Assembly. Separation - Chair P. García-Sánchez
14:30	Invited talk - Optoelectronically Driven Trajectory Reconfiguration and Directed Self-Assembly of Electrically Powered Self-Propelling Active Particles (G. Yossifon)
15:00	Low-Frequency Electrokinetics in a Periodic Pillar Array for Particle Separation (V. Calero)
15:15	Invited talk - Recycling of Lithium-Ion Batteries Using Dielectrophoresis (G. Pesch)
15:45	Coffe break
	Fundamentals of Electrokinetics III – Chair A. Ramos
16:15	Invited talk - Unified Quantum Theory of Electrochemical Kinetics Based on Coupled Ion-Electron Transfer (M. Bazant)
16:45	Using nanofluidic channels for neuromorphic circuits: Hysteresis, impedance, and synaptical behaviour (J. Bisquert)
17:00	Honorary Award Lecture**: Stanislav Dukhin Medal - Isaak Rubinstein.**

Friday, September 20

	Bioelectrokinetics and Biomedical I - Chair G. Yossifon
9:00	Invited talk - Electrokinetic Devices and Systems for Biomedical Diagnostics (H. Morgan)
9:30	Invited talk - Diffusiophoresis-Enhanced Turing Patterns: Continuum and Particle-Level Simulations (A. Gupta)
10:00	Keynote - Automatic On-Chip Aliquoting and Molecular Reaction Control Using Isotachophoresis (J. Santiago)
10:25	Coffee break
	Bioelectrokinetics and Biomedical II – Chair H. Morgan
10:45	Invited talk - Highly Multiplexed dCas9-Mediated Molecular Diagnosis by Nanoelectrokinetic Selective Preconcentration (S.J. Kim)
11:15	Electrokinetic Separation of DNA From an E-Coli Cell Lysis (T. Ladd)
11:30	Invited talk - Electro-Optical Sensing of Single Protein Biomarkers in Nanopores and Nanochannels: Towards Digital Proteomics (A. Meller)
	Desalination, Selective Ion Separations, Batteries II – Chair J. Dykstra
12:00	Invited talk – A Highly Selective and Energy Efficient Approach to Boron Removal Overcomes the Achilles Heel of Seawater Desalination (M. Elimelech)
12:30	Electroconvection and Water Splitting in Electrodialysis with Ion-Exchange Membranes (V. Nikonenko)
12:45	Tuning Device Configuration for Enhanced Performance of Electrical Double-Layer Capacitors (S. Kondrat)
13:00	Lunch and poster session

	Nanobubbles - Chair A. Abdel-Fattah and N. English
14:30	Molecular Simulations and Theoretical Models of the Stability and Mobility of Nanobubbles in Aqueous and Non-Aqueous Liquids (P. Kusalik)
14:45	Enhancing Kinetics of Physicochemical Wastewater Treatment Process by Nanobubbles Convective Aeration (C. Quintero)
15:00	Electrokinetic Characterisation of Electric-Field-Generated Nanobubbles (N. English)
15:15	Electrophoresis of Nanobubbles (V. Lobaskin)
15:30	Giant Carbon Geosequestration Potential with Supercritical CO_2 Nanobubbles in Brine (H. Chen)
15:45	Coffee break
	Desalination, Selective Ion Separations, Batteries III - Chair S. Ahualli
16:15	Invited talk – Electrokinetic Phenomena Strongly Affect the Removal of Organic Micropollutants in Membrane Separation Processes (J. Dykstra)
16:45	Modelling Polarization of and Salt Sorption by Floating Nanoporous Electrodes Using Homogeneous Approximation Desalination (A. Yaroshchuk)
17:00	Donnan Dialysis Under Non-Isothermal Conditions: How Temperature Gradients Could Accelerate/Manipulate Transport of Divalent Ionic Species Through Nanofluidic Channels? (A. Alizadeh)
17:15	A Network Model for Ionic Transport in Charged Porous Materials (F. Henrique)
17:30	Anomalous Electrokinetic Phenomena in Confinement (Y. Xie)

List of Invited Speakers

Hywel Morgan (University of Southampton, UK)

Alfonso Gañán-Calvo (Universidad de Sevilla, Spain)

Gilad Yossifon (Tel-Aviv University, Israel)

Amit Meller (Technion, Israel)

Silvia Ahualli (University of Granada, Spain)

Sung Jae Kim (Seoul National University, South Korea)

Boris Zaltzman (Ben-Gurion University of the Negev, Israel)

Menachem Elimelech (Yale University, USA)

Ankur Gupta (University of Colorado Boulder, USA)

Yuki Uematsu (Kyushu Institute of Technology, Japan)

Georg Pesch (University College Dublin, Ireland)

Xiao Su (University of Illinois Urbana-Champaign, USA)

Martin Z Bazant (MIT, USA)

Todd Squires (UC Santa Barbara, USA)

Jouke Dykstra (Wageningen University & Research, Netherlands)

Oral Presentations Abstracts

Nonequilibrium Electroosmotic Instability and Morphological Instability in Electrodeposition

Boris Zaltzman

Ben-Gurion University of the Negev, Beer Sheva, Israel

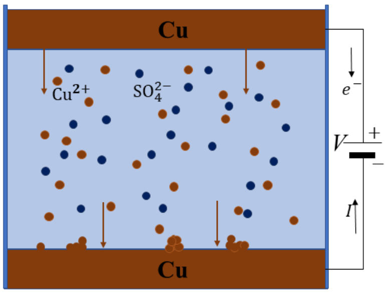
Keywords: Electrodeposition, Electroconvection, Dendrites, Instability

Cathodic electrodeposition is the background in which two instabilities unfold: Morphological Instability (MI) and Nonequilibrium Electroosmotic Instability (NEOI). Without a suitable regularization, both are singular for shortwave perturbations. For MI, the plane-parallel propagation of the electrodeposition front is unstable for all perturbation wavelengths, with the growth rate increasing indefinitely with the increase of the wave number. For NEOI, in terms of quasi-electroneutrality the voltage threshold is lowest for infinitesimal wavelength perturbations of quiescence. A self-consistent theory of both instabilities must provide some regularization mechanisms.

A commonly assumed regularization mechanism for MI is surface tension, which is not an easily measurable parameter, yielding a colloidal length scale (nanometers) for the fastest growing mode. This scale is much shorter than the one typically observed for dendrites emerging in electrodeposition. As for NEOI, it has been known for some time that it can be regularized by considering the finite width of the Electric Double Layer (EDL) and its adjacent Extended Space Charge (ESC). Recently, we reported that for MI, too, considering the finite width of the EDL, combined with the finite electrode reaction rate provides a regularizing mechanism alternative to surface tension and yielding a length scale of the order of microns. This length scale has been inferred for current densities below the limiting value. In the limiting current regime, the formation of the ESC and the onset of NEOI yields a major further increase of the characteristic length scale towards that typical of NEOI; it is accompanied by a drastic increase of the growth rate in MI.

In my talk I focus on the physical understanding of the mechanisms of the electrokinetic regularization of the short-wave catastrophe and address the following issues:

- The physical source of the short-wave catastrophe in NEOI and MI and its electrokinetic regularization.
- The physical origin of the length scale selection: the role of the finite width of the EDL and of the finite reaction rate.
- The physics behind the NEOI effect on MI.



Mechanism of Electrokinetic Length Selection in Electrodeposition

Isaak Rubinstein, Boris Zaltzman

Ben-Gurion University, Midreshet Ben-Gurion, Israel

Keywords: Electrodeposition, Morphological Instability, Electro-Convective Instability

Without suitable regularizations, both morphological and non-equilibrium electro-osmotic instabilities occurring in electrodeposition are singular for short wave perturbations in the following sense: in the former instability the infinitesimal wave-length perturbation growth the fastest, whereas in the latter instability, assuming quasi-electroneutrality of the electrolyte, the quiescent state is the least stable for infinitesimal wave-length perturbations. The regularization of non-equilibrium electro-osmotic instability requires considering the finite width of the electric double layer. It was recently shown that also in electrodeposition, considering the finite width of the electric double layer combined with the finite electrode reaction rate constant yields selection of a finite critical perturbation wavelength for instability, thus providing a regularization mechanism alternative to surface tension. In this presentation we discuss a simple two-layer diffusion model aimed at clarifying the physical mechanism of this regularization.

The Electrolyte Accumulation by a Porous Conductor Placed in an External Electric Field: The Small Perturbation Analysis

Emiliy Zholkovskiy, Mykola Bomdarenko, Volodymyr Kovalchuk

Institute of Bio-Colloid Chemistry of National Academy of Sciences of Ukraine, Kyiv, Ukraine

Keywords: Porous Conductor, Electrolyte Solution, Electric Field, Electrical Sorption

A stationary boundary value problem is formulated to address the spatial distributions of ions and electric field within a Z:Z binary electrolyte solution phase in the presence of ideally polarizable porous body and uniform external electric field imposed at infinity. The bulk equation set includes the steady-state continuity equations for electro-diffusional ion fluxes and the Poisson equation. The interfacial boundary conditions reflect the impermeability of the metal/solution interface for the ions and a constant interfacial electric potential. At infinity, the boundary conditions set the uniform electric field and a common ion concentration.

The formulated problem is rearranged to contain three unknown spatially dependent local functions: the “electrolyte concentration” (half of the ion concentration sum); the charge density and the electric potential. An expression is proposed for the dimensionless parameter referred to as the Henry coefficient, H: the ratio of the excess “salt concentration” averaged over the porous body bulk to the common ion concentration at infinity.

The approximate analytical solution of the formulated problem is obtained by using the small perturbation analysis for the model of long straight pores with arbitrary crosssection geometry. The obtained leading terms for the excess “electrolyte concentration” and thus the coefficient, H, turn out to be positive and proportional to the squared external field strength. The latter reveals the effect of electrolyte accumulation within the porous body. The predicted Henry coefficient is a product of its maximum value, Hmax, and a geometrical factor which depends on the ratio of the crosssection hydrodynamic radius to the Debye length, only.

The obtained, Hmax, expectedly coincides with H determined by using the homogeneous approach. It is a half of the normalized external field strength quadrate over the porosity. The normalizing strength is the thermal potential over the half of capillary length. For arbitrary crosssection geometry, the abovementioned geometrical factor is obtained with the help of a strictly defined scheme of averaging. The respective analytical expressions derived for the slit and circular crosssections give close results.

Cell Model for Arbitrary Surface Charge and Volume Fraction of Particles. Coagulation in Dilute and Concentrate Disperse Systems

Nataliya Mishchuk

A.V. Dumansky Institute of Colloid and Water Chemistry of NAS of Ukraine, Kyiv, Ukraine

Keywords: Analytical Solution, Collective Interaction, Energy Barrier, Poisson-Boltzmann Equation

The two-layer spherical cell model is proposed to describe the equilibrium electrical potential distribution between strongly charged particles in a monodisperse system [1]. The internal layer is described using the approximation of excluded co-ions, while the external layer uses the Debye approximation. The sum of the obtained expressions, with consideration of the fitting potential ψ^* at the boundary between the layers, allows for obtaining the general analytical solution of the Poisson-Boltzmann equation at any volume fraction of particles. Choosing an appropriate fitting parameter ψ^* ensures a difference between numerical and analytical solutions of less than a few percent for any surface potential, volume fraction of particles, and distance between them. Thus, the obtained solution in the proposed two-layer cell model can be used without any restrictions.

The dependence of the potential distribution and, correspondingly, the characteristics of disperse systems on the type of particle arrangement is analyzed. It is shown that the results of theoretical modeling of different processes in concentrated disperse systems strongly depend on the correct choice of the radius of the cell.

As an example of the strong influence of the choice of characteristic parameters of the cell model on the final result of calculations of energy barriers in concentrated disperse systems with hexagonal packing of particles is considered [2]. In addition to electrostatic repulsion, the energy of van der Waals attraction is taken into account. It is shown that, unlike a dilute dispersion, where only pair interaction plays a decisive role, in a concentrated dispersion, the interaction between two coagulating particles also depends on their interaction with the surrounding particles. In the first case, the reference point of the interaction energy is its zero value at infinity, and in the second, it is the interaction energy with the averaged ensemble of the nearest particles. The larger the volume fraction of particles, the higher the collective interaction energy and the lower the energy barrier between coagulating particles.

The results for two different choices of the cell radius are compared.

[1] Col. Surf. A. doi:10.1016/j.colsurfa.2014.05.072
[2] Adv. Colloid Interface Sci. doi:10.1016/j.cis.2004.09.006

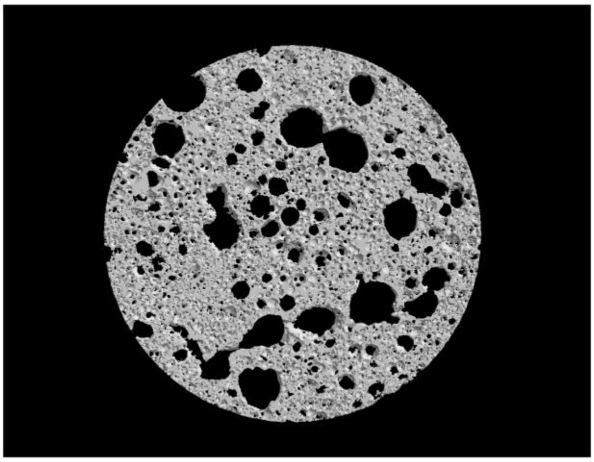
Impedance spectra of soft ionics

Reghan J. Hill

Chemical & Materials Engineering, McGill University, Montreal, Canada

Keywords: Impedance Spectroscopy, Soft Ionics, Polyelectrolyte Membranes, Poroelasticity

Impedance spectroscopy is widely applied for probing the charge and charge-mobility of soft ion-conducting media, such as synthetic membranes and biological tissue. The spectra exhibit a variety of distinctive signatures, but the physical basis of these is not well understood. This work explores a theoretical continuum model by which non-linear thermodynamics and linearized dynamics of a viscous electrolyte and compressible, elastic polyelectrolyte network are coupled under the forcing of an oscillatory electric field (Hill, J. Fluid. Mech., 2024). Here, the model is solved in a one-dimensional spatially periodic unit cell, reporting conductivity and dielectric permittivity spectra, including Nyquist representations. For heterogeneous anionic microstructures, hydrodynamic and elastic forces are demonstrated to produce a strongly diverging low-frequency dielectric permittivity, as first revealed by pioneering experiments conducted on Nafion membranes. For polyelectrolyte films bearing alternating layers of cationic and anionic charge, the model captures several distinctive features of experimentally reported impedance spectra, including those of fuel-cell membranes.



Memory Effects in Electro-Optical Dynamic Response of Aqueous Suspensions

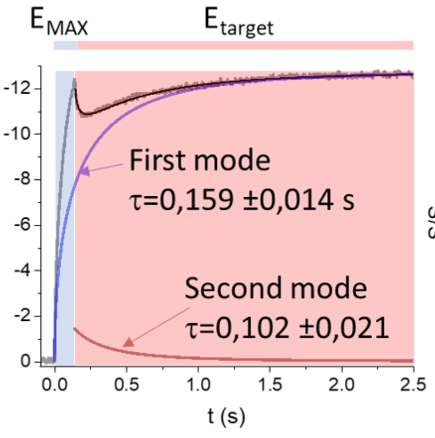
María L. Jiménez, Miguel Ibáñez, Raúl R Rica

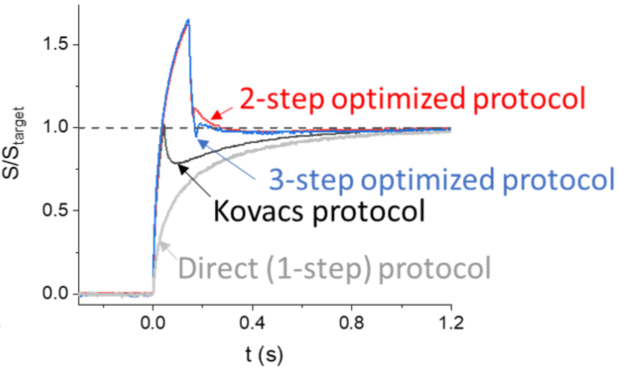
University of Granada, Granada, Spain

Keywords: Electric Birefringence, Kovacs, Non-Equilibrium Thermodynamics

When a system relaxes to a stationary state after a sudden change in a control parameter, the dynamics are determined by the distance to the equilibrium state. In principle, the relaxation could be assumed to occur throughout local equilibrium states that ensure ergodicity. However, when the system is initially far from the stationary state, the relaxation path strongly depends on the previous history and could be accelerated with more elaborated quenching protocols [1]. This is the case of the electro-optical response of non-spherical particles dispersed in water. Under the application of an electric field, the system evolves to a stationary state in which the partially oriented particles produce a birefringent response. The transient response is faster the larger the intensity of the electric field [2]. This serves as the basis for the appearance of Kovacs effect (KE) [3] when trying to accelerate the dynamics with a more elaborated protocol. KE and analogous crossover effects have been theoretically predicted in many models, but the experimental observations are scarce. Optimization protocols in the particle's alignment can be of practical interest in technological applications such as the realization of polarizers. Here, we present a combined experimental and theoretical study of memory effects in the optical birefringence induced by electro-oriented planar-shaped montmorillonite particles suspended in a water solution. We observe that the fastest response cannot be obtained by a two steps protocol.

[1] Ibáñez M. et al. Nature Physics. doi.org/10.1038/s41567-023-02269-z
[2] Arenas-Guerrero P. et al., Soft Matter, doi.org/10.1039/C6SM00512H
[3] Kovacs A.J. et al. Polymer Science B. doi.org/10.1002/pol.1979.180170701





Electrokinetics of Electrolyte Solution Confined in a Nanotube

Yuki Uematsu

Kyushu Institute of Technology, Iizuka, Japan

Keywords: Nanotube, Surface Conduction, Nonlinear Electrokinetics

I will talk about theoretical studies on electrokinetics of electrolyte solution confined in a nanotube.

In the first part, I report a theory of the ionic conduction of electrolyte solution through a nanotube with radius from several to several tens nanometers [1]. It was known that the ionic conductance is proportional to the salt concentration for a macroscopic channel. However, in a nanotube, the surface conduction dominates the bulk conduction in the low salinity. We constructed the theory of ionic conduction with the surface charge regulation on the nanotube surface. Then, we derived characteristic scaling law for the conductance with the exponent of 1/2 and 1/3 about the salt concentration.

In the second part, I present a theory for the nonlinear electrokinetics in a nanotube with sub-nanometer radius [2]. Recent experiments reported the streaming current depending quadratically on the pressure difference and linear with the gate voltage [3]. I constructed a theory to calculate such a nonlinear electrokinetic transport coefficient by perturbation method.

[1] Uematsu, Y. et al. J. Phys. Chem. B. doi.org/10.1021/acs.jpcb.8b01975
[2] Uematsu, Y. Phys. Fluids. doi.org/10.1063/5.0131481
[3] Bocquet, L. et al. Nature Materials. doi.org/10.1038/s41563-020-0726-4

Dielectric Behaviour of Suspensions of Insulating, Conducting, and Heterogeneous Particles. The Different Manifestations of Concentration Polarization

Ángel V. Delgado, Juan A. Lirio Piñar, Marina Lázaro, Silvia Ahualli

University of Granada, Granada, Spain

Keywords: Dielectric Dispersion, Conducting Particles, Heterogeneous Particles

It is well known that concentration polarization (CP) is the key phenomenon in determining the electrokinetic response of disperse systems when the particles are moderately charged. Its occurrence is linked to the different transport numbers of counter- and co-ions in the electric double layer (EDL). The analysis of the frequency dependence of the dielectric constant of the systems is the most powerful tool for the detection of CP, since a small change in the induced dipole moment of the particle (including its EDL) manifests itself as a huge relaxation of the electric permittivity [1]. The phenomenon has been widely studied for different kinds of dispersed particles, with a range of surface charges, ionic concentrations (down to salt-free) or particle geometry [2]. In most cases, the particles studied were non-conducting. The features of the dielectric dispersion of conducting colloids have been much less investigated, and in fact, as shown in Fig. 1, the phenomenon shows quite different features in both cases. The present contribution is intended to generalize these results to more complex dispersed systems, considering the frequency dispersion of the permittivity in conducting, porous and conducting, or with heterogeneous surface. The results confirm the considerable sensitivity of dielectric dispersion measurements (including the frequency range where the concentration polarization is significant, typically in the kHz interval) for the electrokinetic evaluation of the interfacial nanostructure.

Dedicated to the memory of professor V.N. Shilov, who so generously shared his enormous knowledge in electrokinetics.

Acknowledgements
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References
[1] Lyklema, J. et al. J. Electroanal. Chem. 143 (1983) 1-21. doi.org/10.1016/S0022-0728(83)80251-4
[2] Delgado, A.V. et al. Adv. Colloid Interface Sci. 299 (2022) 102539. doi.org/10.1016/j.cis.2021.102539

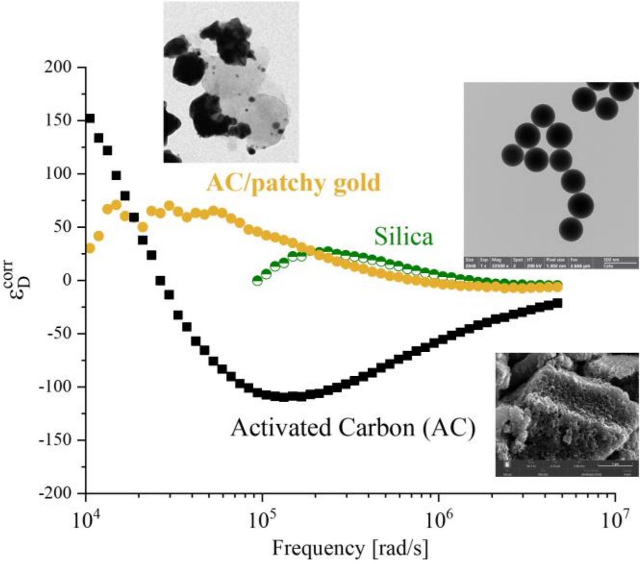

Fig. 1. Comparison between the dielectric dispersion of suspensions of insulating (silica) and conducting (activated carbon, AC; AC coated with gold patches) particles.

Preconcentrations of Third Species Near Ion-Selective Microgranule

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Keywords: Preconcentration, Ion-Selective Surface, Numerical Modelling

The process of preliminary concentration of analytes in micro-samples is an essential step in the development of microfluidic devices for medical diagnostics (μTAS systems). Several techniques for preconcentration are available, including using flat ion-selective surfaces [1] and ion-selective microparticles [2].

In the first approach, superconcentration has been observed, where a stable local increase in analyte concentration by millions of times can occur. In the second approach, the technique has the advantage of a simpler device geometry, but the concentration is only observed for a short period of time.

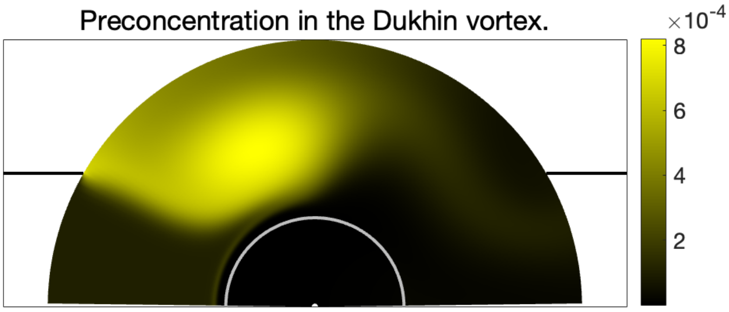
In our study, we conducted mathematical modeling of analyte and ion concentrations in a microsystem over a range of parameters similar to those presented in [2]. This microdevice can also function as a micropump and micromixer, as described in [3]. Numerical simulations have shown that under certain conditions, two types of concentration patterns can be observed. The first is the concentration in the Dukhin vortex region, which is consistent with mechanism [1]. The second is the concentration in the near wake region of the particle, which resembles the mechanism described in [2], but it is more stable and exists in a stationary state.

During the study, it was found that larger analyte ions tend to be concentrated in the Dukhin vortex, which requires an optimal ratio between the external electric field and the external pressure gradient. The maximum concentration of the analyte in the vortex region can only be an order of magnitude greater than the initial concentration. More charged ions tend to accumulate in the near wake region, where they can completely displace ions of the same charge. As a result, the concentration can be millions of times higher than the initial concentration of the analyte.
The work was supported by the Russian Science Foundation, project 22-79-10085.

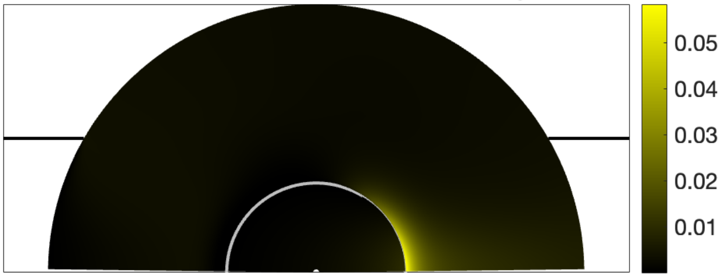
[1] W. Ouyang, X. Ye, Z. Li, and J. Han, Nanoscale 10, 15187 (2018). doi.org/10.1039/c8nr02170h
[2] S.-C. Wang, H.-H. Wei, H.-P. Chen, M.-H. Tsai, C.-C. Yu, and H.-C. Chang, Biomicrofluidics 2, 14102 (2008). doi.org/10.1063/1.2904640
[3] G. S. Ganchenko, M. S. Alekseev, and E. A. Demekhin, Microfluid Nanofluid 27, 32 (2023). doi.org/10.1007/s10404-023-02642-7

The third species dimensionless concentration density.

Preconcentration in the Dukhin vortex.



Preconcentration in the near-wake region.



Diffusiophoresis in Zwitterion gradients: theory and experiment

Electrophoresis, diffusiophoresis, and colloids. Soft colloids

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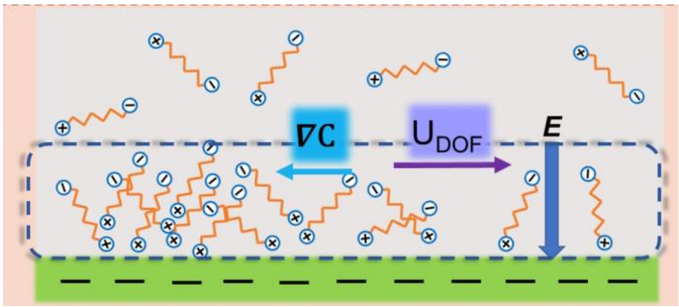
Keywords: Diffusiophoresis, Zwitterion, Microfluidics, Colloids

Diffusiophoresis (DP) has seen increasing attention for its ability to control and manipulate suspended objects using external solute gradients. It has been studied and employed in a wide variety of settings – examples include enhanced oil recovery, water filtration, drug delivery and film deposition. While most work has focused on DP under electrolyte gradients, here we present theoretical and experimental studies of particle diffusiophoresis under gradients of zwitterions, i.e. electrical dipoles. We develop a theory for zwitterion DP that predicts that colloids will always migrate up zwitterion concentration gradients, but with velocities that scale linearly with the concentration gradient, in contrast to the logarithmic gradient scaling of conventional electrolyte diffusiophoresis. Moreover, diffusiophoretic mobilities scale with the square of the zwitterion dipole moment – which depends on the distance between the charged ends of the molecule.

Experiments confirm the theory both qualitatively and essentially quantitatively. Using a microfluidic geometry we developed to impose steady state gradients, we make direct and repeatable DP velocity measurements for hours at a time, thereby obtaining excellent statistics. We performed experiments under gradients of three distinct zwitterions with varying intercharge distances: Glycine, 4-aminobutyric acid (4-ABA) and 6-aminohexanoic acid (6-AHA). In all cases, colloidal particles migrated up the steady-state gradients with constant velocities, validating the linear dependence of DP on the imposed zwitterionic gradient. Also, DP velocities increased with increasing intercharge distance, being highest for 6-AHA, followed by 4-ABA and Glycine, as predicted by the theory. Furthermore, the dielectric increments of each zwitterionic species interpreted from experimentally-measured DP mobilities agree well with literature values, further corroborating our theory. Our results elucidate a previously unexplored phenomenon that opens new avenues for DP to be employed.



The Dynamics of Single Elementary Charging Events at Nanoparticles in Water

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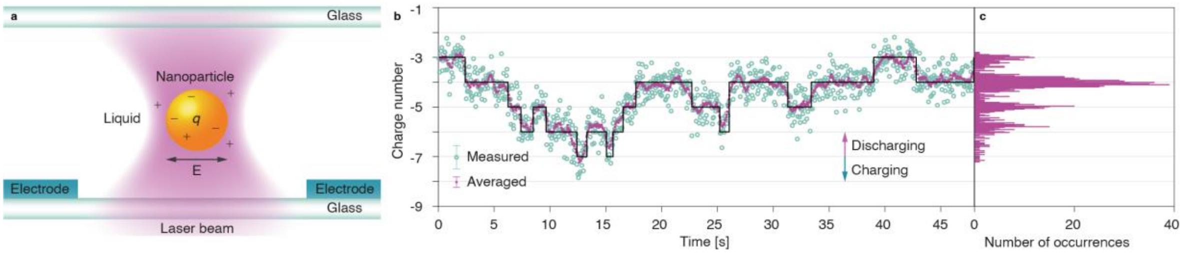
Keywords: Elementary Charge, Nanoparticles, Electrophoresis, Optical Trapping

The charge exchange between nanoparticles or molecules and their surrounding medium becomes prominent at the nanoscale, revealing the discrete nature of electrical charge. The ability to observe these interactions with high resolution at the level of a single elementary charge promises to enhance our understanding of diverse reactions, such as oxidation, ionization, and catalysis. However, this task is greatly hindered by the high concentration of ions in water-based solutions. In this work, we present the observation of single elementary charge fluctuations, occurring on nanoparticles suspended in water [1]. By analyzing the electrophoretic motion of optically trapped nanoparticles subjected to a high AC electric field (Fig. a), we detect distinct changes in electrical charge with single elementary charge resolution (Fig. b and c). Our measurements allow us to monitor individual charge binding and unbinding events occurring, on average, every 3 seconds. These findings pave the way for exploring the dynamics of a wide range of chemical and biological phenomena on the nanoscale at the level of elementary charges.

[1] Y. Ussembayev, F. Beunis, L. Oorlynck, M. Bahrami, F. Strubbe, and K. Neyts, “Single Elementary Charge Fluctuations on Nanoparticles in Aqueous Solution,” ACS Nano, Oct. 2023, doi: 10.1021/acsnano.3c08161.



Schematic illustration (a) of an optically trapped nanoparticle with a size of 100 nm and surface charge q, which oscillates under an external sinusoidal electric field E. The measured electrical charge as a function of time (b) and corresponding histograms for the averaged charge (c). All the data are adapted from ref. [1].

Ionic Self-Phoresis Maps onto Correlation–Induced Self-Phoresis

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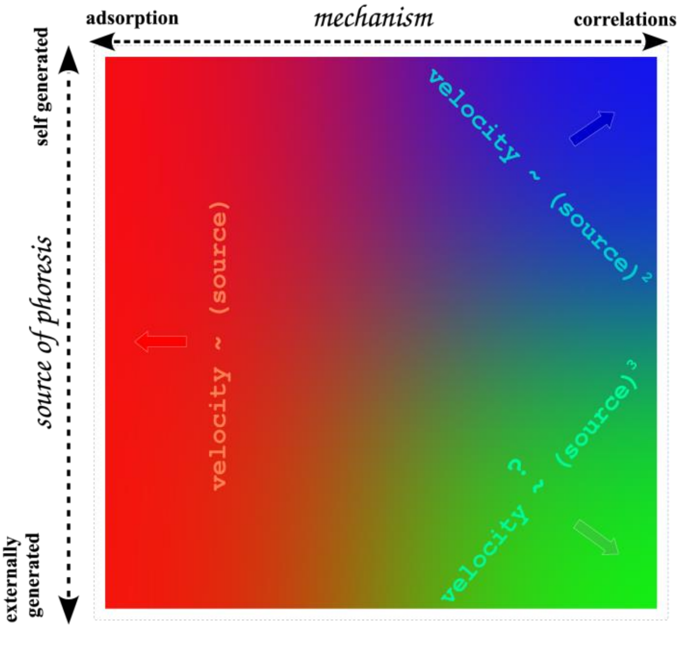
Keywords: Diffusiophoresis, Active Colloid, Electrolytes

The self-phoresis of a particle that releases pairs of ions into the electrolyte solution is addressed [1]. It is shown analytically that, in the linear regime, the mathematical description of this system maps onto that of the recently proposed mechanism of correlation–induced (self-)diffusiophoresis [2]. This connection provides a unifying perspective of the two phenomena, within which one recovers and extends recent predictions as particular instances of correlation–induced diffusiophoresis. Conversely, ion-phoretic particles are identified as candidates for experimental investigations into the rich variety of motility patterns predicted by the theoretical model of correlation-induced diffusiophoresis.

[1] Domínguez A., Popescu M.N., submitted,
https://doi.org/10.48550/arXiv.2404.16435
[2] Domínguez A. et al., Physical Review Letters,
doi.org/10.1103/PhysRevLett.125.268002



Phoretic diagram: source of phoresis (either external or self-induced gradients) vs. mechanism (either surface charge or correlations)

Charging, De-Charging and Re-Charging of Dielectric Surfaces in Contact with Aqueous Electrolytes - The Influence of CO2

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Keywords: Neutral CO2, Electrode Charging, Dielectric Surfaces, Electrokinetics

While the charging mechanisms of dielectric surfaces and the dependence of measurable charge numbers and potentials on the electrolyte- and particle-concentration have been extensively studied, the possible influence of CO2 on the charging behaviour remained largely unexplored. Initially motivated by inconsistent reports on the zetapotential of dielectric surfaces in contact with aqueous electrolytes, we performed electro-kinetic experiments under controlled CO2 concentrations [1,2,3]. We found that molecular CO2 lowers the zetapotential way beyond the expected effects of electrolyte-concentration induced screening and pH induced charge regulation (Figure 1a). This applied both to hydrophobic polymer- and hydrophilic silica-surfaces and may at elevated CO2-concentrations even lead to complete de-charging [2]. Molecular dynamics simulations related these observations to the formation of a diffusive monolayer of CO2 adjacent to the surface. We proposed that this layer reduces the local dielectric constant, which in turn leads to an increased electrostatic interaction between dissociated surface groups. The corresponding Coulomb-penalty then results in an increase of the effective surface pk and a significantly lowered degree of dissociation. We termed this effect dielectric charge regulation [1]. Indeed, recent complementary conductivity experiments on initially deionized systems reveal a drastic reduction of bare charge numbers of particle with diameter $2a = 359$nm from $Z = 10x10^{3}$ under CO2-free conditions to $Z = 1.3x10^{3}$ after equilibration against ambient CO2. As a result, the number of immobilized protonic counter-ions dropped to zero and the exchange of protons for added other cations vanished. In electrophoresis, this relates to an empty Stern Layer, in charge renormalization theory this corresponds to the absence of counter-ion-condensation. Moreover, upon adding electrolytes to CO2-decharged but otherwise deionized surfaces these re-charge, if the added anion has a large polarizability (Figure 1b). Given the importance of charged surfaces in contact with aqueous electrolytes, we anticipate that our observations bear substantial theoretical challenges and important implications for applications ranging from desalination to biomembranes.

[1] P.V. et al., J. Am. Chem. Soc. 144, 21080–21087 (2022). DOI: 10.1021/jacs.2c06793
[2] P.V., T.P., J. Colloid Interface Sci. 656, 280-288 (2023). DOI: 10.1016/j.jcis.2023.10.056
[3] P.V., T.P., Soft Matter (Submitted 2024).

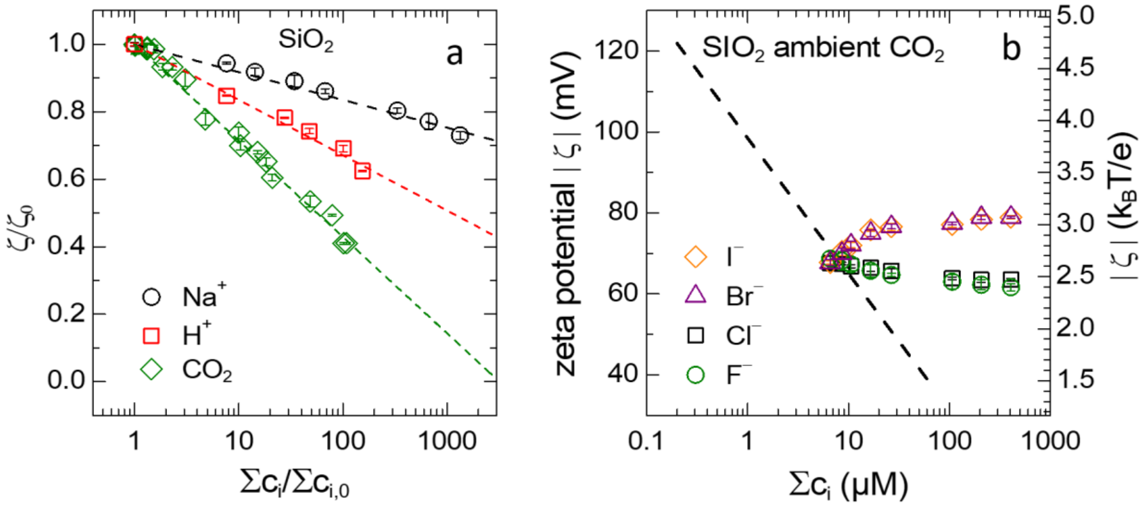

Fig. 1: Decharging and recharging of hydrophilic silica surfaces. a) Relative Zetapotentials in dependence on relative total electrolyte concentration. Shown is the addition of NaCl, HCl or molecular CO2 to deionized and CO2-free systems. b) Zetapotential versus total electrolyte concentration. Shown is the addition of NaF, NaCl, NaBr and NaI to deionized surfaces after equilibration against ambient air.

Electrokinetics of Soft Particles. Modelling, Experimental Investigation and Applications

Electrophoresis, diffusiophoresis, and colloids. Soft colloids

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Keywords: Soft Particles, Electrophoresis, Dielectric Relaxation, Capacitive Deionization

The term “soft” particle has become of general use for designating colloids carrying a polymer (often, polyelectrolyte) layer coating their surfaces. This structure largely determines their behaviour when subjected to external fields (ac or dc electric fields, pressure gradients, for instance), as well as particle-particle interactions. This is because the layer is deformable, permeable to the dispersion medium and ions, and in many cases highly charged. The phenomenology observed when a field is applied is far more complicated than it is with smooth interfaces. Thus, electrophoretic mobility can reach values in a wide range (from very high because of the layer volume charge to very low if the coating produces enhanced viscous drag on the liquid), and even become independent of ionic strength. But it is in the frequency dependence of both the (dynamic) mobility and the electric permittivity that the presence of the charged layer manifests most clearly [1,2], even in the complex systems in which several polymer layers are used by means of the layer-by-layer technique. The example in Fig. 1 allows to compare the frequency dependences of the relative permittivity of suspensions of bare and polyelectrolyte-coated particles. Note the intense effects observable and the sensitivity of both the dynamic mobility and the dielectric dispersion to the structure of the successive layers. The use of these techniques provides valuable and complementary information on the interfaces. The interest of electrokinetics goes beyond the fundamental aspects of surface characterization and offers new paths on more applied aspects. For instance, we have demonstrated that the application of a soft layer on carbon electrodes significantly enhances our capabilities in the desalination of solutions by capacitive methods and enables the harvesting of renewable energy by salinity exchange, taking advantage of the high capacitance of electric double layers.

Acknowledgements
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References

[1] Duval, J.F.L. et al. Langmuir 22 (2006) 3533-3546. doi.org/10.1021/la0528293
[2] Ahualli, S. et al. M. Ballauff, F.J. Arroyo, A.V. Delgado, M.L. Jimenez Langmuir 28 (2012) 16372-16381. doi.org/10.1021/la302483e

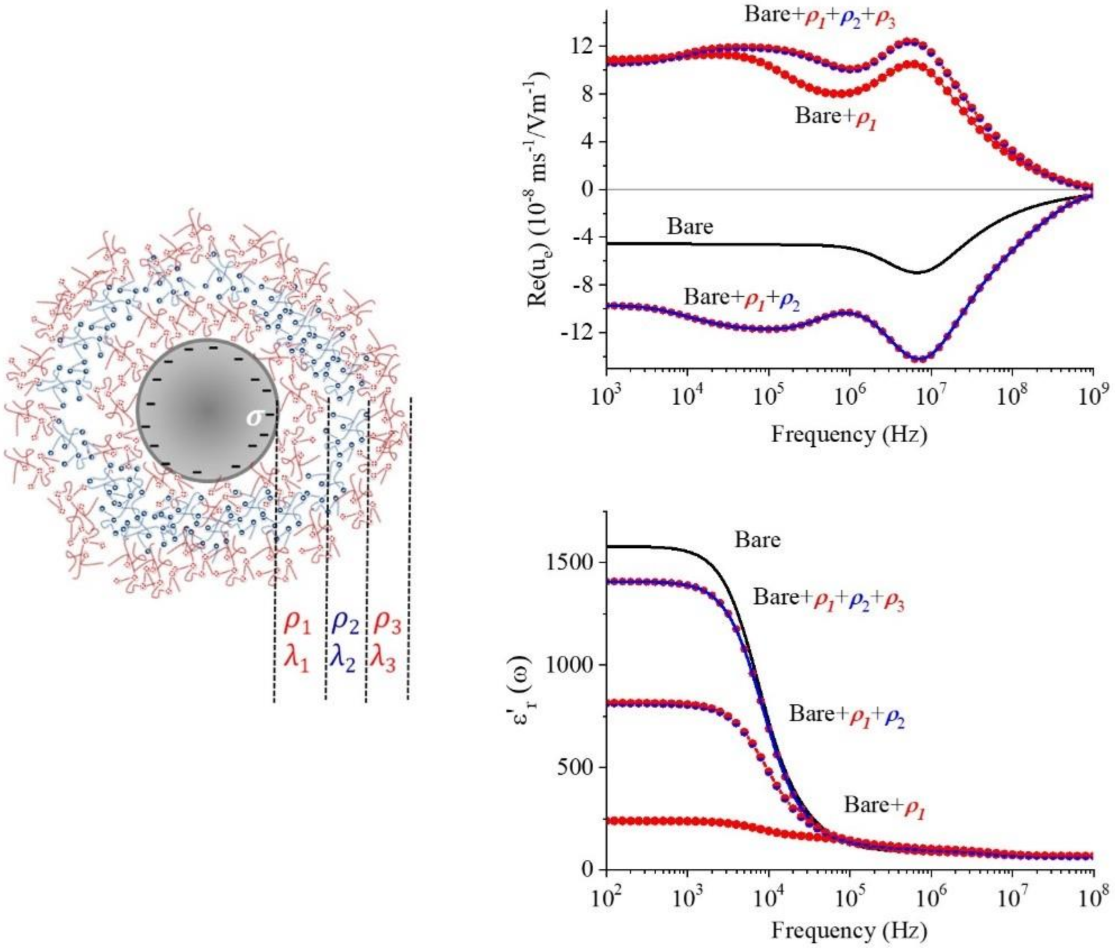

Fig. 1. Left: Schematic representation of a multi-layered soft particle (core surface charge density: sigma; layer volume charge density: rho_i; friction coefficient of the i-th layer: lambda_i). Right: Real part of the dynamic mobility (top) and dielectric dispersion (bottom) for suspensions of latex particles with the indicated surface charge density of coatings. rho_1, rho_3 >0; rho_2 < 0. Absolute values of charges are the same.

Electrospray: From its Basics to its Electrokinetics

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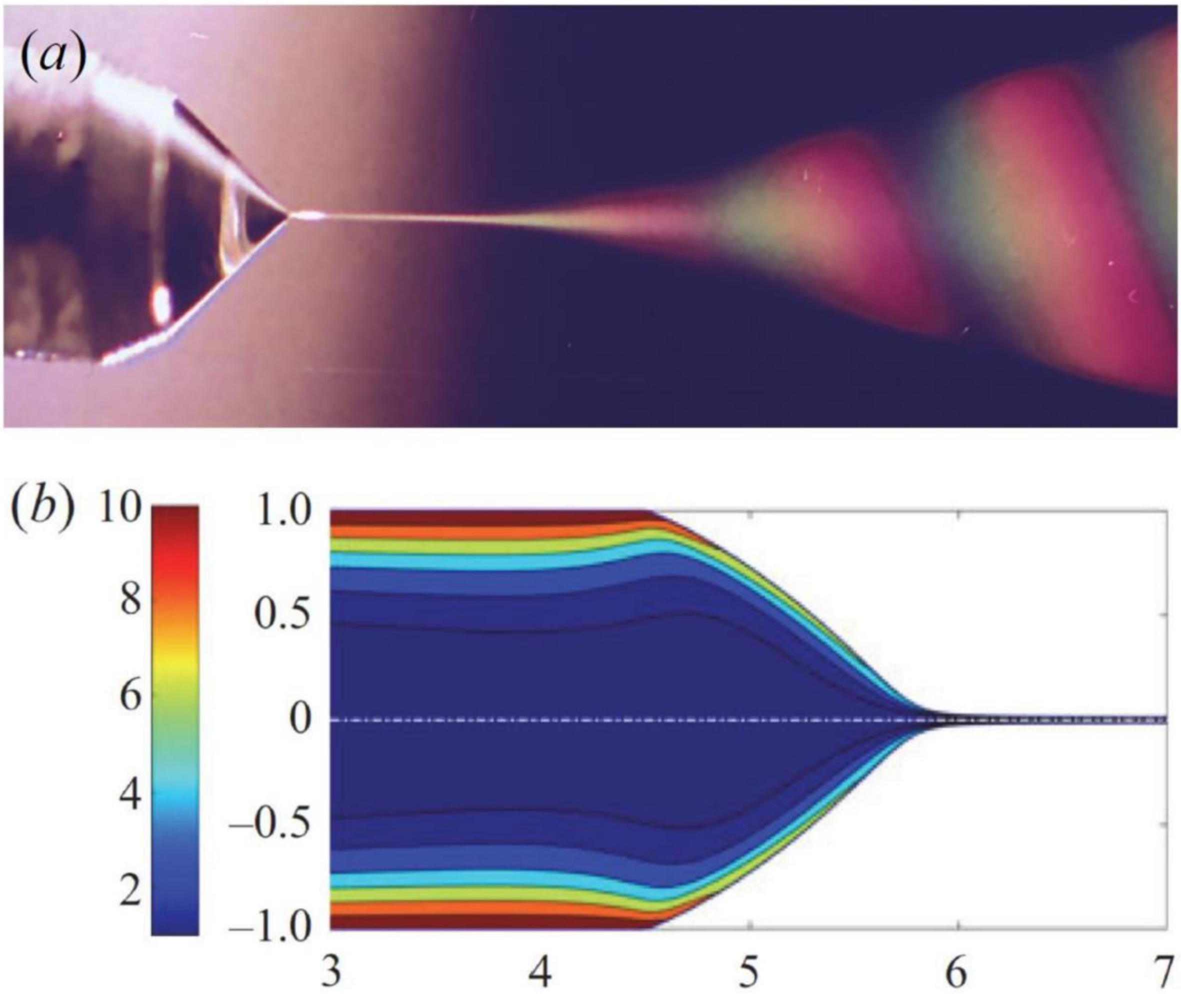
Keywords: Electrospray, Taylor Cone-Jet, Scaling Laws, Mass Spectrometry

Electrospray is a natural phenomenon fundamentally driven by the ability of ions and molecules in solution to form a highly charged layer at the surface of a liquid when subjected to a strong electric field. The formation of this surface layer is a basic electrokinetic process that is determined by the mobility of the ions in the solvent and the constant of dissociation of the chemical species involved in the generation of the ions. In normal operating conditions, the dissociation constant is typically fixed, along with the mobilities of the ions, which collectively define the electrical conductivity of the dissolution. This foundational electrokinetic parameter plays a critical role in electrospray operation, particularly in determining the charge relaxation time scale. In fact, the electrical permittivity of the dissolution, which is the resistance of the medium to the penetration of an electric field, and electrical conductivity regulate how rapidly charges will move and find the liquid-vapour interface boundaries and form surface layers compared with the hydrodynamic timescales. In specific operational ranges involving applied electric fields and mass balance (flow rate) in the system, the Taylor cone-jet emerges as a particularly elegant form of liquid structure for its universality, symmetry and simplicity. This phenomenon has opened unique avenues for analysis and identification of organic molecules that elementary mass spectrometry could not achieve. We analyze two distinct macroscopic scaling laws that emerge when the Taylor cone is either steady or in the process of formation, which may occur when the cone is unstable. A deeper insight into this phenomenon reveals that the electrochemistry may explain not only unexpected deviations from these basic scaling laws but also dependencies on factors such as the polarity of the applied electric field and the electrochemistry of substrates in contact with the liquid dissolution. Furthermore, we demonstrate how the electrokinetic processes occurring within the Taylor cone-jet can significantly influence the composition of the ejected liquid mass in comparison with the liquid bulk. This may result in the measurements taken being misrepresented in relation to the actual chemical composition of the dissolution.



a) Taylor cone-jet operating in low flow rate with the emission of monodisperse droplets (see Tyndal waves).
b) Normalized ionic species concentration. Figure from Lopez-Herrera et al. 2023, J. Fluid Mech. 964, A19.

Asymmetric Currents in Asymmetric Nanofluidic Systems

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Keywords: Electrokinetics, Electroosmotic Instability, Concentration-Polarization, Nanofluidics

At the heart of nanofluidic lays a symmetry-breaking phenomenon – permselectivity – which allows for the selective transport of ions based on their electrical charge. Permselectivity results from an interplay of electric double-layer overlap of two surfaces with their surface charge density. While it can be expected that the existence of a symmetry-breaking mechanism would result in an asymmetric response, in fact, the simplest response of a unipolar system is symmetric. However, introducing any additional asymmetry into the system (geometric, surface charge, concentration, etc.') leads to an asymmetric current-voltage response, which is further complicated when the effects of electroconvection are accounted for.

In this talk, I will delineate the current-voltage response dependency on geometry and surface charge in a bipolar nanochannel/membrane subject to an electroconvective instability (ECI) forming at the channel's interface. ECI has been established as the primary mechanism of overlimiting currents in ideally selective unipolar systems [1]. Still, little work has been conducted on how ECI varies the response of selective bipolar systems. Here, we extend our previous work on "symmetric" and "asymmetric" bipolar systems [2] by accounting for the effects of ECI, where the "a/symmetry" of the system depends on a ratio of the geometry and surface charge. For "asymmetric" bipolar systems, the current-voltage response is asymmetric, and, similar to unipolar systems, overlimiting currents are observed. In contrast, "symmetric" systems, that have an inner symmetry between the geometry and the surface charge, have the most asymmetric current-voltage response. Surprisingly, in these "symmetric" systems, the ECI appears and then decays such that steady-state over-limiting currents do not appear. Our theoretical and numerical findings can be used to elucidate the complicated behavior of ion transport in bipolar systems and to interpret experimental results better.

[1] Rubinstein, I. and Zaltzman, B., Phys. Rev. E. https://doi-org.bengurionu.idm.oclc.org/10.1103/PhysRevE.62.2238
[2] Abu-Rjal, R. and Green, Y., ACS Appl. Mater. Interfaces. https://doi-org.bengurionu.idm.oclc.org/10.1021/acsami.1c05643

Elucidating particle-wall interactions through bulk mobility measurements of electric field driven active colloids

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A marked conundrum exists in the literature of active colloid experiments: The fundamental theoretical models are derived for a single isolated particle in the bulk, with the most common particle configuration the metallodielectric Janus sphere. However, in reality, the heaviness of the metallic coating causes the particles to sediment such that all experimental measurements are made in proximity to the bottom substrate. The resultant particle-wall interactions can affect the mobility in a multitude of ways including the generation of localized gradients, onset of electrohydrodynamic flow and increased Stokes drag. Here, we discuss the challenges encountered in sending electrokinetically driven active colloids to the International Space Station where microgravity conditions will facilitate bulk mobility measurements. Key challenges were the need to mitigate the formation of bubbles from dissolved gas and adhesion of particles to the walls in chambers that must sit for up to 10 days before experiments are initiated. The experiments are currently scheduled to fly on NG-21 from Kennedy Space Center in August 24.

In parallel, we successfully obtain bulk mobility measurements here on earth through density matching. We demonstrate that electrokinetically driven active colloids constitute an advantageous platform for such experiments since the alignment of the metallodielectric interface with the electric field prevents out of plane motion and accumulation at the upper and lower surfaces/substrates. We quantify the reduction of mobility as a function of proximity to the channel walls across a broad range of frequencies -500Hz-1MHz; characteristic of both induced-charge electrophoresis and self-dielectrophoresis. It is show that surprisingly, wall effects may persist at length scales of multiple radii into the channel in contrast to current theoretical models. The results offer insight into the fundamental mechanisms of both ICEP and sDEP that are otherwise unobtainable in the standard experimental setups. It is anticipated that this approach opens a new direction for active colloid experiments and the validation of experimental models.

Nanofluidic transport in channels with defined electronic wall properties

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Keywords: Nanofluidics, Carbon Nanotube Porins, Layered 2D Materials, Diffusion-Osmosis

Strong confinement in nanofluidic channels induces profound changes on the transport of ions and molecules. Confinement often induces partial ion dehydration that not only creates channel entry energy barriers but also amplifies the ion interactions with the channel walls. These interactions are particularly important and interesting when the channel walls are polarizable or electrically conductive. We will present two systems where the electronic properties of the channel wall contribute to the ion dynamics. First, we will discuss water, proton and ion transport in metallic and semiconducting ultra-narrow carbon nanotube porins and show how nanotube polarizability contributes to transport efficiency in these channels. Second, we will present studies ion and neutral solute transport in electrically gated laminar MXene membranes, where we will show how complex ion dynamics at the walls of the MXene channels can lead to a self-pumping enhancement of transport efficiency.

Dipolophoresis Of Travelling-Wave For Hydrophobic Conducting Colloids In Hydrogels

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Keywords: Induced-Charge Electro-Osmosis, Gel Dielectrophoresis, Non-Uniform AC Fields And Travelling-Wave, Hydrophobic Navier Slipping Surfaces

The problem of polarized spherical colloids freely suspended in a Brinkman-hydrogel electrolyte is analytically studied, developing explicit expressions for the colloid's mobility, slip velocity and ICEO flow (stream-function) engendered around the colloid. Three typical length scales are identified; Brinkman, Navier-slip and Debye. These length scales are expressed through two parameters; the frictional dimensionless Darcy coefficient α (α→0 represents a 'clean' Stokes flow) and the Navier-Maxwell coefficient β (β→0 corresponds to a non-slipping surface). The ambient field amplitude is assumed as much smaller than the thermal scale (weak-field) and the inertia terms are neglected (small Peclet). Hence, the hydrodynamic and electrostatic problems are linear and partly decoupled. Spherical harmonics expansions and the method of multipoles are used to determine the dielectrophoretic (DEP) force. The interaction between the induced-charge distribution and the ambient field, results in an electroosmotic velocity field that yields an induced-charge electrophoretic (ICEP) force that can be expressed by using Teubner's integral formulation. The combination of the DEP and ICEP forces is coined as dipolophoresis (DIP), which determines the particle's mobility and the overall induced velocity field.

The case of a colloid subject to a non-uniform AC ambient electric forcing of 'sinusoidal' travelling-wave excitation is of particular interest and is studied in details, deriving new explicit expressions for the mobility, accounting for the excitation's frequency and wave number. The new formulation converges to a simple closed quadrupolar expression for the stationary colloid subject to a uniform excitation (zero wave number) of which the stream-function contours for two cases of α are depicted in Fig 1. It is seen that as α increases (i.e., as the medium's permeability decreases) the flow penetration away from the colloid decreases, while the flow field retains the characteristic of flowing from the plane perpendicular to the axisymmetry axis (x_1) to towards that axis. Further solutions for the vorticity field and surface skin friction will also be discussed.

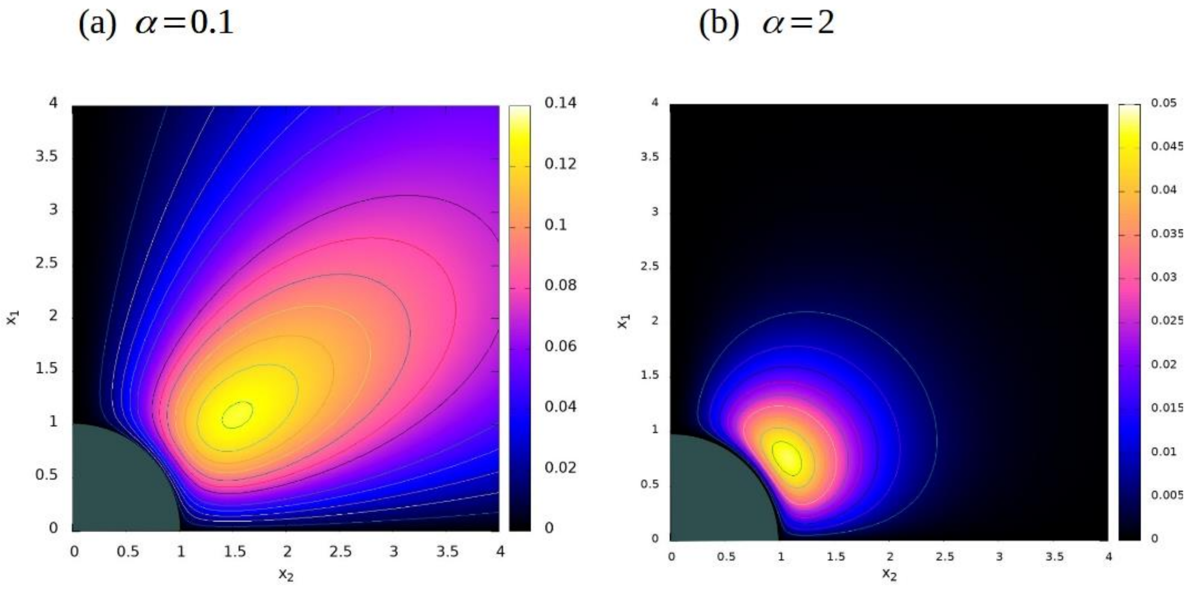

Figure 1: Contours of the Brinkman-Stokes ICEO stream function (multiplied by a) around a stationary hydrophobic spherical colloid subject to a uniform excitation. Only one quarter of the flow field’s plane is shown since the other quarters are mirror images.

Imparting Selectivity in Electrodialysis and Electrodeposition Platforms for Value-Added Ion Recovery

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Keywords: Electrodialysis, Electrokinetic Separations, Redox-Electrodialysis, Selective Ion Separations

The development of selective ion separations are essential for environmental remediation, chemical manufacturing, and critical element recovery. Electrokinetic mechanisms are at the core of emerging electrochemical separation technologies.[1] Here, we will discuss advances in imparting selectivity to redox-mediated electrodialysis (redox-ED) and electrodeposition platforms. First, we will present how ion-exchange membrane functionality in redox-ED can be tuned to control selectivity towards different ions, and how multicomponent separation can be achieved by tailored design.[2] The coupling of nanofiltration membranes with redox-polymers can lead to significant cost and energy savings,[3] and a perspective for translation of these technologies to practical biomolecule separations and downstream processing will be given. Second, we will discuss how electrokinetic effects can be leveraged for selective metal recovery. Through electrodeposition at functional surfaces, tuning of cobalt and nickel selectivity can be achieved for battery recycling applications.[4] We will also present current directions for amplifying the ion selectivity in electrodeposition through the use of charged porous media and leveraging electrokinetic phenomena. We believe that the combined understanding and integration of interfacial interactions with electrokinetic phenomena can lead to the development of next-generation electrochemical separations.

[1] M. A. Alkhadra, X. Su, M. E. Suss, H. Tian, E. N. Guyes, A. N. Shocron, K. M. Conforti, J. P. de Souza, N. Kim, M. Tedesco, K. Khoiruddin, I. G. Wenten, J. G. Santiago, T. A. Hatton, M. Z. Bazant, Chemical Reviews 2022, 122, 13547-13635.
[2] N. Kim, J. Lee, X. Su, Advanced Functional Materials 2023, 33, 2211645.
[3] N. Kim, J. Elbert, C. Kim, X. Su, ACS Energy Letters 2023, 8, 2097-2105.
[4] K. Kim, D. Raymond, R. Candeago, X. Su, Nat Commun 2021, 12, 6554.

A Nanoporous Capacitive Electrochemical Ratchet for Continuous Ion Separations

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Keywords: Ion Pumps, Ratchets, Selective Ion Separation

Directed ion transport in liquid electrolyte solutions underlies many phenomena in Nature and industry. While Nature has devised structures that drive continuous ion flow without Faradaic redox reactions, artificial analogs do not exist. In this contribution we report the demonstration of an ion pump that drives aqueous ions against a force using a capacitive ratchet mechanism that does not require redox reactions. Ratchet-based ion pumps were fabricated by coating the two surfaces of nano-porous alumina wafers with gold, thus forming nano-porous capacitor-like devices (figure 1a). The coated wafers were placed as membranes between two compartments of electrolyte and the ion pumping response to various capacitor voltages was studied (figure 1b). While the application of a constant bias resulted in no steady-state output, the introduction of an alternating input signal produced persistent voltages and ionic currents indicative of directional ion pumping (figure 1c). This occurs due to the non-linear double layer capacitances at the gold-electrolyte interfaces, whose repeated charging and discharging sustains a continuous ion flux. The generated ionic power was used in conjunction with an additional shunt pathway to demonstrate electrolyte demixing. Finite elements simulations show that surface charge on the pore walls is essential for obtaining the non-linear capacitance driving the ion transport. These ratchet-based ion pumps can potentially enable continuous desalination and selective ion separation using a modular, electrically powered device with no moving parts.

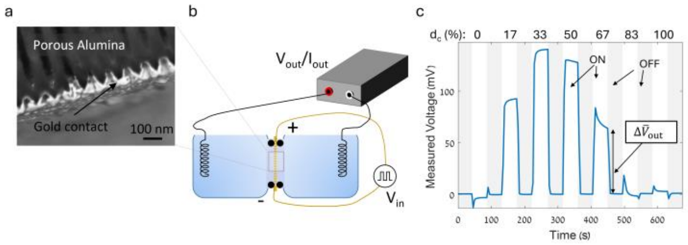

Figure 1: (a) A cross section SEM image of a gold coated porous alumina wafer. (b) The measurement setup- the wafer is placed between two compartments of electrolyte. An electric signal Vin is applied to the membrane contacts and the current or voltage is measured between two Ag/AgCl wires. (c) The voltage measured between two Ag/AgCl wires. The shaded areas are times in which the ratchet was OFF, and the bright regions are times in which the ratchet was ON. The signal is a rectangular wave with an amplitude of 1 V, and a frequency of 500 Hz. The duty cycle, dc, of each signal is indicated above the corresponding measurement.

Blow-Spun Thin Fibers Prepared From Perfluorinated Sulfonic Acid Ionomers For Fuel Cell Applications

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Keywords: Perfluorinated Sulfonic Acid Ionomer, Thin Fiber, Polymer Electrolyte Fuel Cell

Perfluorinated sulfonic acid (PFSA) ionomers, a random copolymer consisting of semicrystalline polytetrafluoroethylene (PTFE) backbone and pendant side chains terminated by sulfonic acid groups, are commonly used as polymer electrolyte membranes (PEMs) for polymer electrolyte fuel cells (PEFCs) because of their high proton conductivity and excellent chemical stability. In this study, PFSA thin fibers were prepared aerodynamically by blow spinning from PFSA dispersions, because inherent electrical charges of PFSA dispersions can prevent charging and/or cause instability of the polymer jet under a high electric field for the commonly used electrospinning [1]. Thereafter, all PFSA composite PEMs containing PFSA thin fibers were prepared, and their structures and FC performance were characterized. Herein, a representative PFSA ionomer with a short-side chain, Aquivion, was used for both the substrate and the matrix of the composite PEMs

To clarify the internal structures of the prepared PFSA thin fibers with an average diameter of 1.2 µm, small-angle X-ray scattering measurements were performed. Both the PTFE crystalline domains and ionic domains are oriented along the fiber axis direction for the as-spun fibers. Aquivion is water soluble and requires annealing treatment to insolubilize. This treatment slightly decreases the orientation of crystalline domains and greatly promotes the structural relaxation of ionic domains. All PFSA composite PEMs were prepared by casting an Aquivion aqueous dispersion on the hot-pressed PFSA thin fiber webs and successive annealing. The hot-pressed PFSA thin fiber webs functioned as the well-interconnected fiber framework, subsequently enhancing the proton transport and slightly improving the mechanical properties of the composite PEMs. In addition, the 15 wt % PFSA thin fiber composite PEM showed better FC performance than that of the pristine PFSA one for both the low-temperature high-humidity and high-temperature low-humidity conditions [2]. We believe that the preparation method of the PFSA thin fiber composite membranes presented here is easily scalable and all PFSA thin fiber composite electrolyte membranes can be applied to other electrochemical devices such as batteries and water electrolysis as well as PEFCs.

[1] Matsumoto, H. et al. Membranes. doi.org/10.3390/membranes11060389
[2] Matsumoto, H. et al. ACS Appl. Mater. Interfaces. oi.org/10.1021/acsami.3c17643

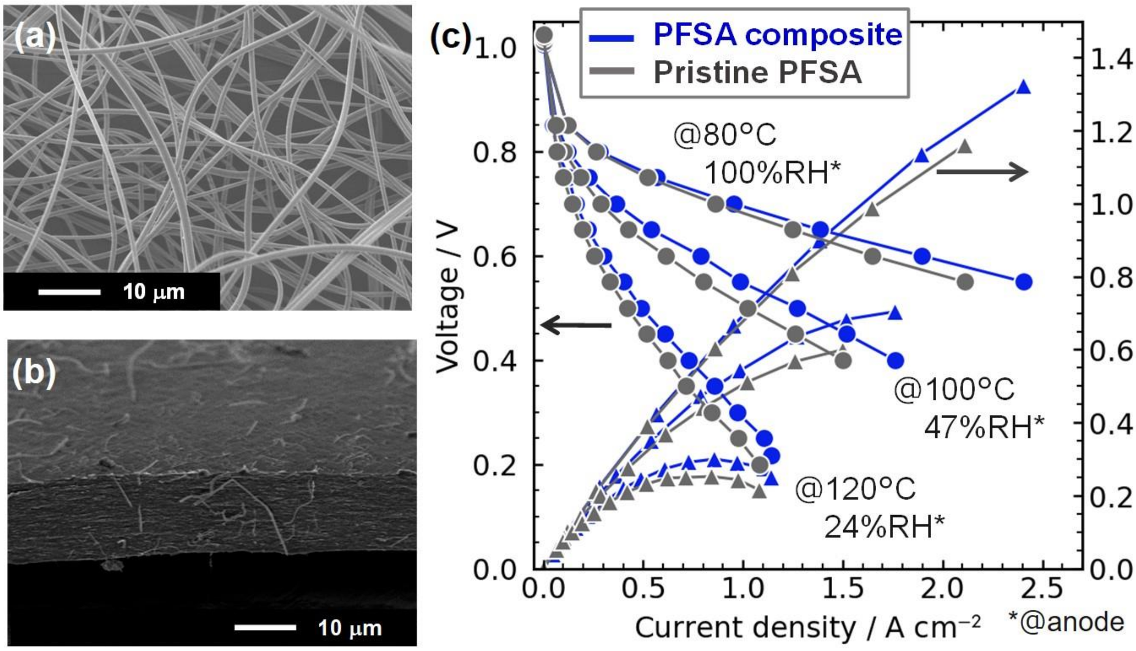

Figure 1. Typical electron micrographs of (a) blow-spun PFSA thin fibers and (b) all PFSA composite membranes. (c) Polarization curves of fuel cells using pristine and composite PFSA membranes.

Submillimeter Bundled Microtubular Flow Battery Cells With Ultrahigh Volumetric Power Density

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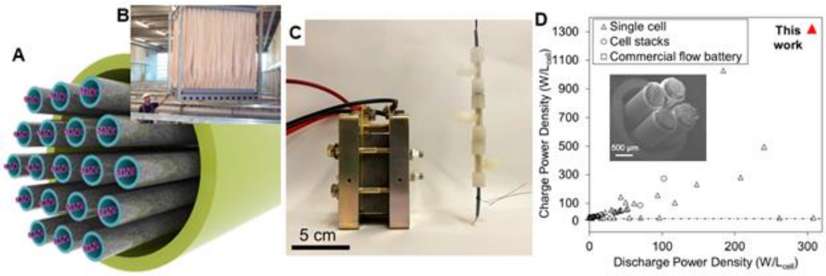
Keywords: Flow Battery; Hollow Fiber; Energy

Flow batteries are a promising energy storage solution. However, the footprint and capital cost need further reduction for flow batteries to be commercially viable. The flow cell, where electron exchange takes place, is a central component of flow batteries. Improving the volumetric power density of the flow cell (W/Lcell) can reduce the size and cost of flow batteries. While significant progress has been made on flow battery redox, electrode, and membrane materials to improve energy density and durability, conventional flow batteries based on the planar cell configuration exhibit a large cell size with multiple bulky accessories such as flow distributors, resulting in low volumetric power density. In this talk, I will introduce a submillimeter bundled microtubular (SBMT) flow battery cell configuration that significantly improves volumetric power density by reducing the membrane-to-membrane distance by almost 100 times and eliminating the bulky flow distributors completely. Using zinc–iodide chemistry as a demonstration, our SBMT cell shows peak charge and discharge power densities of 1,322 W/Lcell and 306.1 W/Lcell, respectively, compared with average charge and discharge power densities of <60 W/Lcell and 45 W/Lcell, respectively, of conventional planar flow battery cells. The battery cycled for more than 220 h corresponding to >2,500 cycles at off-peak conditions. Furthermore, the SBMT cell is compatible with zinc–bromide, quinone–bromide, and all-vanadium chemistries. The SBMT flow cell represents a device-level innovation to enhance the volumetric power of flow batteries and potentially reduce the size and cost of the cells and the entire flow battery.

Our publication: Y. Wu, F. Zhang, T. Wang, P. Huang, A. Filippas, H. Yang, Y. Huang, C. Wang, H. Liu, X. Xie, R.P. Lively, N. Liu, A submillimeter bundled microtubular flow battery cell with ultrahigh volumetric power density, Proc. Natl. Acad. Sci. U.S.A. 2023, 120 (2), e2213528120.



(A) Schematic of the submillimeter bundled microtubular (SBMT) flow battery showing the flowing paths of two liquid electrolytes. (B) An industrial scale microtubular module produced by SUEZ for water filtration application. (C) Photo of a compact and modular SBMT flow cell prototype side-by-side with a bulky and expensive conventional flow cell. (D) Superior power density (W/L) compared to past literature. Inset is a scanning electron microscopy image showing the architecture of SBMT flow cell.

Optoelectronically Driven Trajectory Reconfiguration And Directed Self-Assembly Of Electrically Powered Self-Propelling Active Particles

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Keywords: Active Particles, Optoelectronic Control, Electrokinetics, Directed Self-Assembly

Self-propelling active particles represent a dynamic and interdisciplinary research frontier with promising biomedical and environmental applications. However, their autonomous motion makes it challenging to control their trajectories. This study employs optically patterned electrodes on a photoconductive substrate, utilizing a digital micromirror device (DMD), to dynamically regulate the movement regions of self-propelling particles, specifically metallo-dielectric Janus particles (JPs). Unlike previous studies where passive micromotors were manipulated by a translocating optical pattern, this system uses the optically patterned electrode to delineate the area within which JPs move autonomously. Notably, JPs avoid crossing the edges of the optical region, allowing for the constraint of their movement area and dynamic shaping of their trajectories [1]. The DMD system enables the simultaneous manipulation of multiple JPs, facilitating the self-assembly of JPs into stable active structures, such as JP rings, with precise control over the number of participating JPs and passive particles [1]. The optoelectronic system's compatibility with closed-loop operation through real-time image analysis further allows the exploitation of these active particles as microrobots. This enables their operation in a programmable and parallelized manner, expanding their potential applications.

[1] S.S. Das, G. Yossifon, Optoelectronic Trajectory Reconfiguration and Directed Self-Assembly of Self-Propelling Electrically Powered Active Particles, arXiv: 2302.04784, Advanced Science, 2206183 (2023).

Low-Frequency Electrokinetics In A Periodic Pillar Array For Particle Separation

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Keywords: Concentration Polarisation Electroosmosis, Deterministic Lateral Displacement, Particle Separation

Deterministic Lateral Displacement (DLD) is a well-established microfluidic technique for high precision micro- and nano-particle sorting. DLD devices contain arrays of precisely arranged micropillars in a periodic lattice where each pillar row is laterally displaced a given distance from the previous. This arrangement leads to a passive particle sorting based on their size. Particles bigger than a critical diameter deviate following the angle defined by the posts while particles smaller zig-zag throughout the array in net straight trajectories.

DLD separation can be significantly enhanced by integrating AC electrokinetic forces inside the microchannels, thereby increasing the tunability of the technique and expanding its range of applicability. This allows for the induction of particle deviation down to one order of magnitude smaller than the critical size, depending on the electrokinetic behaviour.

At high frequencies of the AC electric field (>1kHz) the dominant force is Dielectrophoresis (DEP). This leads to easily controllable and highly predictable particle trajectories. On the contrary, at low frequencies the particle behaviour is much richer and more complex and a combination of different forces come into play at once. Here, we present a detailed numerical analysis of the most relevant mechanisms governing particle motion inside a DLD micropillar array when low frequency AC electric fields are applied. We describe how a combination of low frequency Electrophoresis (EP) and Concentration-Polarisation Electroosmosis (CPEO) driven wall-particle repulsion account for the behaviour observed experimentally. Our results match the experimental observations and show that as particles oscillate due to low frequency EP nearby the pillars, the wall particle repulsion induced by CPEO flows repel the particles away from these posts, neglecting the zig-zag patterns. This mechanism enables effective prediction of the conditions leading to electrically induced deviation of particles smaller than the critical size of DLD, opening up the possibility of streamlining the design of microfluidic periodic structures for isolating micro- and nano-particles.

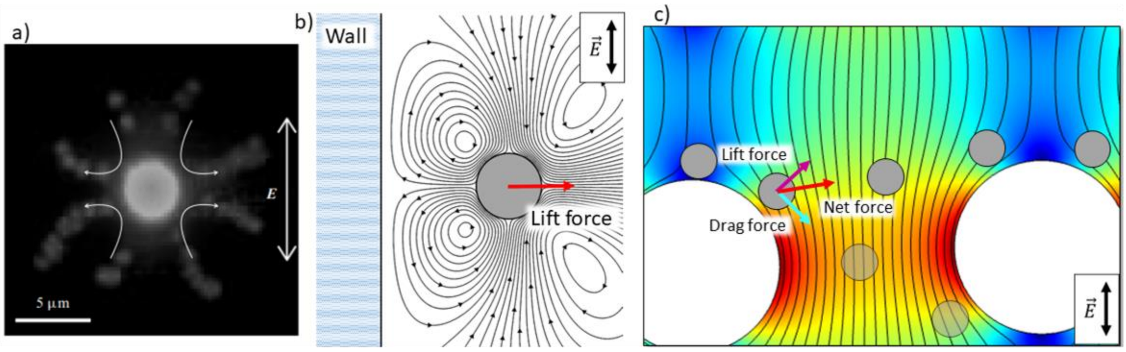

Figure1. Role of CPEO in the low frequency electrokinetic separation in DLD periodic arrays. (a) CPEO flows around a 3 µm diameter microsphere (f = 282Hz and E = 80kV/m) using 500 nm spheres as flow tracers. (b) Diagram of the particle repulsion from a flat wall induced by CPEO flows. (c) Deviation inside a DLD micropillar array induced by a lift force from the post wall – The colours represents the electric field magnitude.

Recycling Of Lithium-Ion Batteries Using Dielectrophoresis

Aggregation and assembly. Electrokinetic separation. Active colloids

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Keywords: Dielectrophoresis, Separation

Lithium-ion batteries (LIBs) offer a reliable energy storage solution and remain the most common rechargeable battery type on the market. They are particularly relevant in the electric vehicle (EV) sector. LIB batteries for EV application have a life span of roughly 10 years. Due to exponentially increasing EV sales, vast quantities of end-of-life batteries will accumulate in waste streams in the near future. Current recycling technologies are energy intensive and cannot recover all materials, especially graphite, responsible for ~ 50 % of the mass of each battery, is lost. The battery recycling industry is in need of cleaner, more efficient recycling methods.

Dielectrophoretic (DEP) is the movement of charged or uncharged particles in inhomogeneous electric field. It allows efficient and environmentally-friendly separation of microparticles based on their physical and chemical properties. Depending on their relative polarisability, particles will either move towards regions of high or low electric field, termed positive or negative DEP. DEP is mostly used in microfluidic separators for chemical or biomedical analysis. Recently, we have developed high-throughput separators that allow to address quantities several orders of magnitude larger than traditional DEP devices.

In this talk, we will use DEP to separate a mixture lithium-metal oxide and graphite particles. Such a separation would allow pre-treatment of black mass, an intermediate product during battery recycling. Successful black mass pre-treatment would increase recycling efficiency and decrease required input of chemicals and energy. Specifically, we are using DEP filtration, a method in which a porous insulating matrix is sandwiched between two electrodes, generating a highly inhomogeneous electric field in the filter. Positive DEP particles will become immobilised in the filter, whereas negative DEP particles will pass the filter unaffected. Lithium-metal oxide particles are semi-conducting and have a low polarisability, showing negative DEP. Conducting graphite particles have a high polarisability and show positive DEP. In this talk, we will show the separation of lithium iron phosphate (LFP) from graphite and demonstrate the applicability of the technology for a variety of cathode chemistries.

The results presented here will allow to establish a novel process that can make battery recycling cleaner and more efficient.

Unified quantum theory of electrochemical kinetics based on coupled ion-electron transfer

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Keywords: Butler-Volmer Equation, Coupled Ion-Electron Transfer, Faradaic Reactions

The Butler-Volmer equation is widely used to model Faradaic reaction rates in electrochemistry and electrokinetics, but it lacks a clear microscopic derivation. The theory of coupled ion–electron transfer (CIET) unifies quantum Marcus kinetics of electron transfer (ET) with classical Gurney-Butler kinetics of ion transfer (IT) within a general framework of non-equilibrium thermodynamics for bond-breaking Faradaic reactions. Simple analytical approximations for the reaction rate will be presented for CIET at metal electrodes with only a few key parameters: the reorganization energy, the red/ox ion transfer energies, and the electronic coupling, which can be predicted by quantum computation or fitted to experimental data. Experimental evidence will be presented that CIET is the mechanism for lithium-ion intercalation, as well as diverse processes in electrodeposition and electrocatalysis, which may also involve electrokinetic phenomena.

Using nanofluidic channels for neuromorphic circuits: Hysteresis, impedance, and synaptical behaviour

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Instituto de Tecnología Química (Universitat Politècnica de València-Agencia Estatal
Consejo Superior de Investigaciones Científicas), Valencia, Spain

Based on the emergence of iontronic fluidic components for brain-inspired computation, we discuss the general dynamical behaviour of nanopore channels. The main memory effects of fluidic nanopores are obtained by the combination of rectification and hysteresis. Rectification is imparted by an intrinsic charge asymmetry that affects the ionic current across the nanopores. It is accurately described by a background conductivity and a higher conduction branch that is activated by a state variable. Hysteresis produces self-crossing diagrams, in which the high current side shows inductive hysteresis, and the low current side presents capacitive hysteresis. These properties are well captured by measurements of impedance spectroscopy that show the correspondent spectra in each voltage wing. By applying a series of voltage pulses, the pore current undergoes synaptic properties of current change, showing potentiation of depression, which can be used in neuromorphic liquid circuits and logic gates. potentiation of the membrane conductance following voltage pulses (spikes) is observed. The detailed properties of hysteresis and transient response are determined by the relaxation time of the gating variable, that is inspired in the Hodgkin-Huxley neuron model. The classification of effects based on simple models provides a general guidance of the prospective application of artificial nanopore channels in information processing and signal conversion in iontronic hybrid devices.

Electrokinetic Devices and Systems for Biomedical Diagnostics

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University of Southampton, Southampton, United Kingdom

Keywords: Single Cell Cytometry, Cell Deformability, Digital Microfluidics

Electrokinetics has been widely researched as a technology for fluid and particle manipulation and characterisation, with the promise of new systems capable of processing and analysing biological cells and particles. However, many challenges remain in translating lab-based experimental devices into tools and devices that can be routinely used in bio-medicine and health care. In this talk I will describe two new technology platforms that exploit electrokinetic principles. First a large scale programmable Digital Microfluidic (EWOD) platform technology that is now used for sample processing as part of a nanopore DNA sequencing system, and a Lab on Chip platform for cell-free synthesis of proteins directly from DNA. I will also describe a cytometer for single cell spectroscopy that measures the full frequency-dependent dielectric properties of thousands of individual cells and microorganisms at high throughput, typically hundreds of cells per second. The method has been used to measure the response of individual cells to drugs, and to understand how bacteria respond to treatment with antibiotics or phage (virus) infection. The technique has now been commercialised for rapid analysis of bacterial susceptibility to antimicrobials. This single cell cytometer can also measure the cell dipole along different axis and thus determine shape or deformation. Cells suspended in a viscoelastic medium that flow through a narrow channel deform under a shear stress. The change in shape can be measured electrically providing a new way of probing single cell mechanical properties and furthering our understanding of disease.

Diffusiophoresis-Enhanced Turing Patterns: Continuum And Particle-Level Simulations

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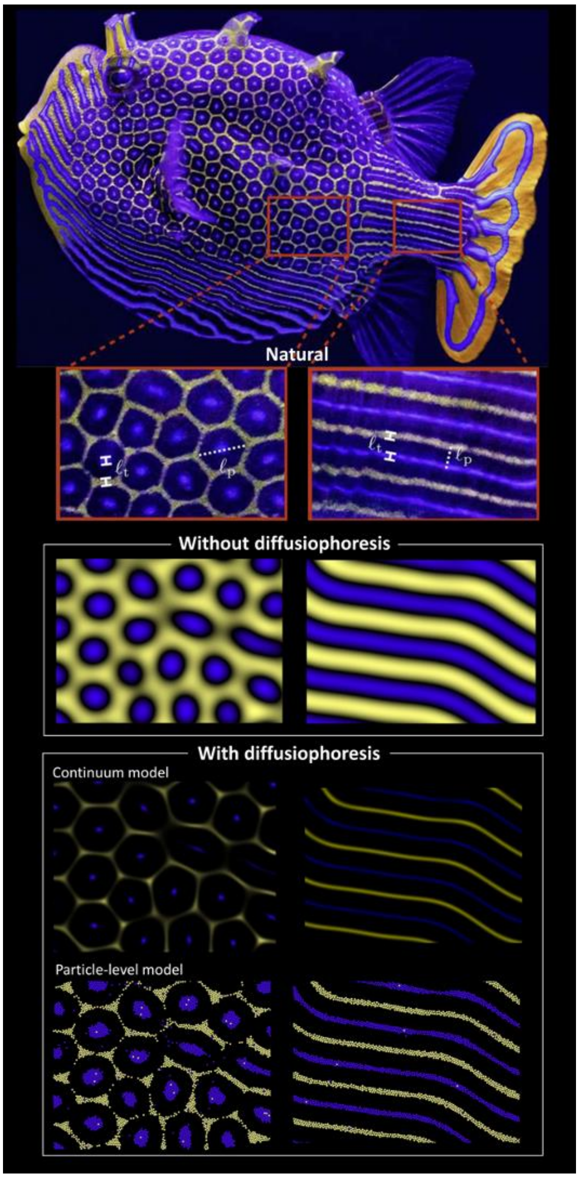
Keywords: Biophysics, Pattern Formation, PDE, Non-Equilibrium Assembly

Turing patterns, characterized by their origin from reaction-diffusion instabilities, are believed to be ubiquitous in biological systems like vertebrate skin patterns. However, these natural patterns often exhibit sharp concentration gradients, unlike classical Turing patterns which rely solely on diffusion and display shallow gradients. We address this limitation by proposing a two-tiered enhancement to Turing's theory. The first level utilizes continuum simulations, where cells respond to concentration gradients and undergo a transport mechanism called diffusiophoresis. This leads to the formation of diffusiophoresis-enhanced Turing patterns exhibiting sharper concentration gradients compared to classical patterns, with their sharpness controllable by the cell's Peclet number. The second level employs particle-level simulations, revealing realistic structural features not captured by continuum simulations. We quantify the impact of finite particle volume fraction and the limiting effect of particle size on pattern formation. Our findings demonstrate that while the particle-level model aligns well with the continuum model at low Peclet numbers and small particles relative to the pattern size, significant discrepancies arise beyond these boundaries.

References: Alessio and Gupta, Science Advances 2023. Mirfendereski and Gupta, under preparation



Pictured is an Ornate Boxfish with hexagon and stripe patterns. The simulated patterns are diffuse, by definition, from Turing's classical theory. We improve this prediction by inclusion of diffusiphoresis through both continuum level and particle level models.

Automatic On-Chip Aliquoting And Molecular Reaction Control Using Isotachophoresis

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Keywords: Isotachophoresis, Lab On A Chip, DNA Detection, Enzymatic Amplification

Portable and automated assay devices that can identify nucleic acid sequences starting from raw samples can have immense benefit for medical diagnostics in low resource settings. We are developing a device that uses isotachophoresis (ITP) to control nucleic acid purification, sample aliquoting, preconcentration, mixing, enzymatic reactions, and in-line detection. ITP is an electrokinetic technique that focuses target species based on their mobility into a self-steepening ion concentration shock wave. [1] ITP can purify DNA from complex samples like saliva and blood. As shown in Figure 1, we use ITP to achieve a novel method of aliquoting wherein the ITP zone is split at a series of bifurcations to achieve automated sample aliquoting into 4 to 16 parallel LAMP channels. ITP is further used to mix purified DNA with the reagents for enzymatic DNA amplification using loop-mediated isothermal amplification (LAMP). LAMP is achieved while sample DNA, primers, and amplicon simultaneously focus within the ITP zone between its leading electrolyte (LE) and trailing electrolyte (TE). The chip is mounted on a heated indium tin oxide (ITO) plate to enable optical access and effect LAMP at 60°C. We will present example dynamics of ITP bifurcation and a sample assay using four parallel LAMP reaction channels.

Figure 1A shows the assay protocol and chip architecture. DNA is selectively extracted from raw biological samples, preconcentrated, and purified from inhibitors on the basis of their electrophoretic mobility. [2] Below the chip schematic are superposed experimental epifluorescence images demonstrating the serial bifurcation process for an eight-channel chip. Figure 1B schematically shows the dynamics of the ITP-controlled LAMP reactions. All steps of this process are performed on-chip and controlled with electric fields, requiring no moving parts.

References
[1] A Ramachandran, and JG Santiago. Chemical Reviews. 2022. doi.org/10.1021%2Facs.chemrev.1c00640
[2] A Rogacs, LA Marshall, and JG Santiago. Journal of Chromatography A. 2013. doi.org/10.1016/j.chroma.2013.12.027

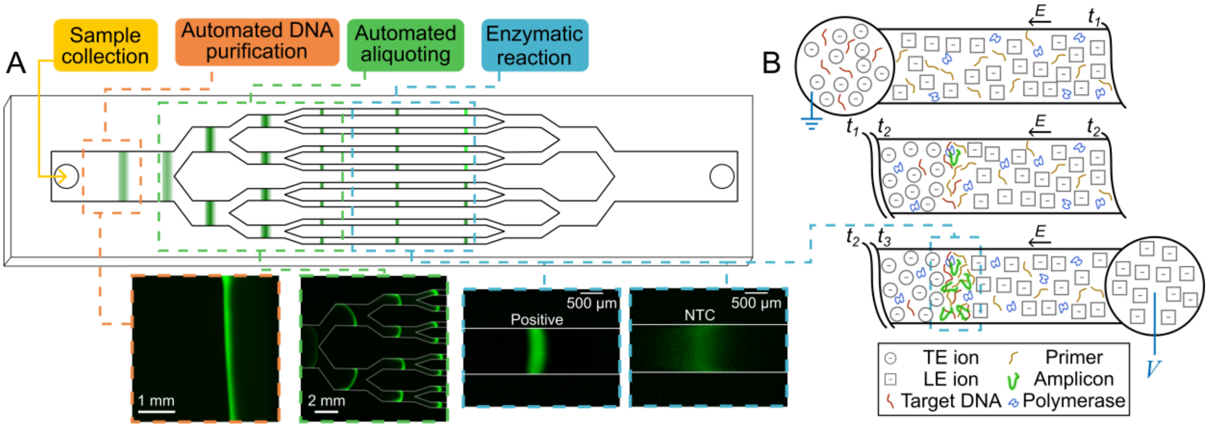

Figure 1. A Chip architecture and example images. Raw sample (e.g., whole blood or saliva) is injected in the inlet port of the microfluidic chip. ITP effects nucleic acid purification, aliquoting (in a novel multifurcation microchannel tree), mixing, and LAMP reactions. Beneath the schematic are experimental fluorescence images showing ITP multifurcation as well as example detection of amplicons in the positive and no template control (NTC) channels. B Schematic representation of the ITP-LAMP assay, including initial injection (t1), early-time focusing (t2), and amplicon production and focusing (t3).

Highly Multiplexed DCas9-Mediated Molecular Diagnosis By Nanoelectrokinetic Selective Preconcentration

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2. ProvaLabs, inc, Seoul, South Korea

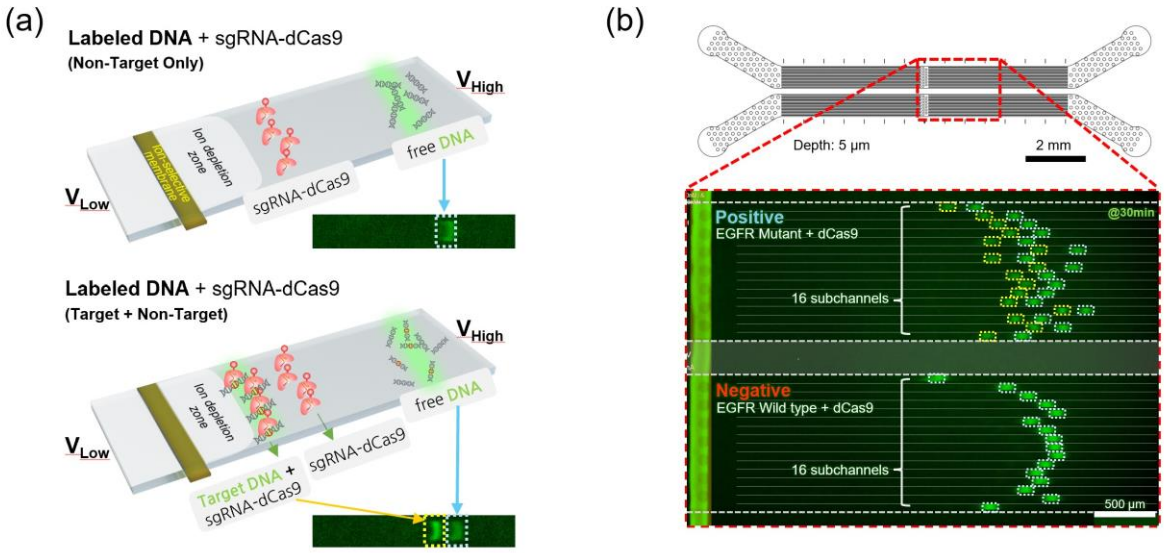
Keywords: Ion Concentration Polarization, DCas9, Selective Preconcentration, Molecular Diagnosis

This invited talk presents a liquid biopsy method designed for rapid and precise molecular detection from bloodstream DNA. By integrating sequence-specific labeling with CRISPR/dCas9 probe and ion concentration polarization (ICP) phenomena, the method shown in Figure(a) (i.e., one plug (negative) vs. two plugs (positive)), selectively concentrates targeted DNA molecules for direct detection, including single base substitution within Epidermal-Growth-Factor-Receptor(EGFR) DNA[1]. Theoretical analysis of ICP has elucidated electrophoretic mobility shift causing plug separation, which enabled rapid optical detection of target DNA at low concentrations without erroneous PCR[2].

While multiplexing is widely adopted in microfluidic platforms, ICP-based molecular detection has not yet utilized multiple channels for detection reliability. Direct and simultaneous comparison of test and control results in massively-parallel channels can significantly enhance detection sensitivity and statistical reliability and optimize signal-to-noise ratio as well. However, ensuring consistent operation of ICP is highly demanded, as the number of channels increases. Despite of precise fabrication, inherent electrokinetic instability remains nuisances because the characteristic length scale is the critical parameters that determines stability[3], especially, random vortices can significantly impact plug formations and their reproducibility. To mitigate this, a strategy of trapping the vortices within a gap between the membrane and the front-end of subchannels significantly reduces deviations. As a result, a highly multiplexed 32-channel device is introduced of which each group consists of 16 parallel-channels sharing a common inlet and outlet in Figure(b), enabling simultaneous execution of replicated diagnostic tests. The replicated plug separations statistically show reliable decision at LOD of 1.23 ng/μl of EGFR mutant DNA. This parallelism drastically reduces random noises and hand-on errors and, thus, aggregated data from multiple channels provide 4X more reliable results, compared to a single channel device. Consequently, the statistical reliability of the detection process is improved, yielding higher precision and accuracy.

Therefore, this study not only demonstrates the feasibility of multiplexed ICP-based DNA detection but also highlights its potentials for accurate molecular diagnostics without PCR procedure, but greater confidence.

[1] Lee, S. et al. Analytical Chemistry. doi.org/10.1021/acs.analchem.2c05539
[2] Lee, H. et al. Nano Letters. doi.org/10.1021/acs.nanolett.8b03224
[3] Nam, S. et al. Physical Review Letters. doi.org/10.1103/PhysRevLett.114.114501


(a)
Labeled DNA + sgRNA-dCas9
(Non-Target Only)
V_High
ion depletion zone
ion-selective membrane
sgRNA-dCas9
free DNA
V_Low
Labeled DNA + sgRNA-dCas9
(Target + Non-Target)
V_High
ion depletion zone
sgRNA-dCas9
free DNA
V_Low
Target DNA + sgRNA-dCas9
(b)
Depth: 5 μm
2 mm
Positive
EGFR Mutant + dCas9
@30min
16 subchannels
Negative
EGFR Wild type + dCas9
16 subchannels
500 μm

Electrokinetic Separation of DNA From an E-Coli Cell Lysis

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Keywords: Electrokinetic Separation, Microfluid Device

A microfluidic process incorporating coupled flow and electric fields is used to separate long strands of DNA from proteins and other cellular debris. The separation relies on an electrokinetic migration of polyelectrolytes to the bounding walls of a microfluidic channel. A DNA molecule in the channel is stretched into a cigar shape (on average) with the long axis rotated at a small angle to the flow field. A parallel electric field then drives a transverse migration of the DNA due to the anisotropic mobility tensor of the stretched molecule. At the wall the fluid velocity vanishes and DNA is returned to the inler by electrophoresis. The migration is specific to long polyelectrolytes, and the remaining components of the lysate are flushed by the pressure-driven flow.

In this talk I will outline the mechanism for migration and then describe recent work to design a microfluidic device for extracting DNA from a cell lysate. A small (10 mL) sample of an E-coli (~5 Mb) lysate is injected into a microfluidic device with a TE buffer solution flowing through it. A step change in the channel width creates a region where the DNA remains trapped while all the other components are removed – the process takes about 15 mins. After that, the DNA is drawn to an extraction port by an electric field and the sample is taken with a syringe or a pipette. Qubit measurements show sample concentrations in the range 1-2 ng/muL and gel electrophoresis confirms that the samples are unfragmented up to the maximum read length of the tapestation (60 kb). The purity of the sample was confirmed by successful PCR amplification, but the residual protein could not be quantified as the concentration falls well below the sensitivity of the Qubit. As a proxy we took mixtures of lambda phage DNA (10 ng/mL) and BSA (30 mg/mL), spiked with 5% FITC to give a strong illumination of the protein signal. Measurements from the extract showed that the protein concentration was below 0.3 ng mL, which corresponds to an A260/A280 ratio of 1.8.

Electro-Optical Sensing of Single Protein Biomarkers in Nanopores and Nanochannels: Towards Digital Proteomics

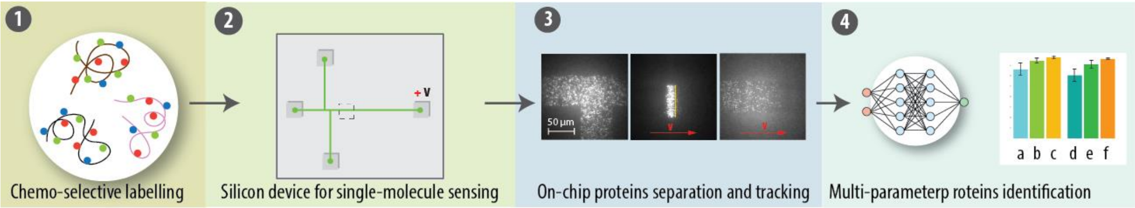
Amit Meller

Technion - IIT, Haifa, Israel

Keywords: Nano-Channels, Nanopores, Single-Molecule Sensing,

Nanopores are single molecule biosensors that utilize electrokinetic forces to focus, linearize and detect individual biopolymers, such as DNA and proteins. [1] Solid-state nanopores are mechanically robust, versatile sensors, that lend themselves for integration in sophisticated devices designed to processes and detect biological samples. Our lab is pursuing this technology to advance wide range of biomedical needs. Here I will provide several recent examples, including: (i) Threading and imaging of an extremely long genomic DNA (~0.5 Mbp) into solid-state nanopores and engineering the Electro Osmotic Forces (EOF) to facilitate the sensing of extremely short DNA (<50 bp) in sub 5 nm pores. (ii) An amplification-free mRNA quantification sensors to replace RT-qPCR for SARS-CoV-2 and for quantification of the early-stage Colorectal cancer marker MACC1. Moving beyond nucleic acids, I will discuss our latest efforts towards the use of electrophoretic single protein molecule separation by mass/charge ratio in sub-wavelength, nanometric channels.[2,3] Two color sensing and dynamical tracking of dually labelled proteins enable proteins identification using 4D information. This antibody-free sensing methodology permits discrete quantification of a cytokine panel, for the discrimination among viral versus bacterial infections host's response. Moreover, we show that this method allows identification of close VEGF protein isoforms, with diverse biological role, but can evade immuno sensing. This method can be integrated upstream of the many other single molecule methods including nanopore sensors and fluorosequencing for enhanced, high-throughput proteome profiling

[1] Ying, Y.-L.; et al. Nat. Nanotechnol. 2022, 17 (11), 1136–1146.
(2) Alfaro, J. A.; et al. Nat. Methods 2021, 18 (6), 604–617.
(3) Ohayon, S.; et al. Adv. Mater. 2024, e2314319.



A Highly Selective and Energy Efficient Approach to Boron Removal Overcomes the Achilles Heel of Seawater Desalination

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Keywords: Bipolar Membranes, Seawater Desalination

Selective removal of trace contaminants from water remains a significant challenge in water treatment. Boron is a trace contaminant that is ubiquitous in seawater and has been widely detected in groundwater. Current boron removal methods, such as multi-stage reverse osmosis and ion-exchange adsorption, are chemical and energy intensive, necessitating the development of more sustainable technologies. Here, we address this challenge by developing novel surface functionalized microporous electrodes that enable boron-selective bipolar membrane assisted electrosorption.

Our study demonstrates that micropore functionalization with oxygen-containing (hydroxyl, lactone, and carboxyl) and boron-selective (dopamine, 3-methylamino-1,2-propanediol, and N-Methyl-D-glucamine) functional groups significantly improves electrode performance for boron removal and selectivity. The functionalized electrodes exhibit a boron removal selectivity that is an order of magnitude higher than that of pristine electrodes, facilitating energy-efficient boron electrosorption. We identify hydroxyl groups as the key factor in enhancing boron removal performance and selectivity during electrosorption. Molecular dynamic simulations demonstrate the underlying mechanisms of boron selectivity, highlighting the role of hydrogen bonding between hydroxyl groups and boron in governing the boron selective electrosorption process.

Electroconvection and Water Splitting in Electrodialysis with Ion-Exchange Membranes

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Keywords: Electrodialysis, Desalination, Intensive Current Regime

Electrodialysis (ED) with ion-exchange membranes is a widely applied method of desalination, concentration and separation of electrolyte solutions. Its main restriction is the low ion transfer rate limited by ion diffusion through the boundary layer. Electroconvection is considered as a promising phenomenon, which could enhance mass transfer rate in ED processes. Electroconvective microvortices formed within diffusion layer at the membrane surface deliver “fresh” solution from the bulk to the surface and remove depleted solution. However, at intensive overlimiting current densities, another phenomenon occurs during ED of aqueous solutions: generation of H+/OH− ions. The most discussed mechanism of this phenomenon is the dissociation of water molecules enhanced by a strong electric field and proton-transfer reactions involving membrane functional groups. This mechanism is known as “water splitting” [1]. We show that electroconvection and water ion generation are two antagonistic phenomena: when creating favorable conditions for enhancing electroconvection (e.g. by forming patterns on the membrane surface), the rate of water splitting decreases; conversely, when water splitting is increased (e.g. by introducing highly catalytic functional groups in the membrane), electroconvection is reduced. The latter is due to the fact that the H+/OH− ions generated at the depleted solution/membrane surface enter the extended space charge, for which they are coions (having the opposite sign of charge), and thereby reduce it [2]. Therefore, increasing mass transfer in ED means not only creating special-designed patterns on the membrane surface to stimulate electroconvection, but also preparing the membrane with a minimum water splitting rate. Approaches aimed at solving the above problems are discussed in the paper. We discuss also another mechanism of of H+/OH− ion generation, which is recently described in literature [3] and named “acid dissociation”. It is the dissociation of polybasic acid anions (such as H2PO4−) as they enter an anion-exchange membrane.

Acknowledgement. This study is supported by Rus. Sci. Foundation, proj. 24-19-00648.

References
1. R. Simons, Electrochim. Acta, 30 (1985) 275
2. N.A. Mishchuk, Adv. Colloid Interface Sci. 160 (2010) 16
3. O. Rybalkina et al., J. Memb. Sci. 651 (2022) 120449

Tuning Device Configuration for Enhanced Performance of Electrical Double-Layer Capacitors

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Keywords: Electrical Double-Layer Capacitors, Supercapacitors, Microporous Electrodes, Device Optimization

Electrical double-layer capacitors (EDLCs) consist of two porous electrodes separated by a permeable membrane to prevent short circuits. Understanding EDLC charging is crucial for developing these ecologically friendly devices for capacitive energy storage and conversion, water desalination, etc [1]. Prior studies have mainly focused on optimizing the structure of porous electrodes and ionic liquids, e.g. by matching the pore and ion sizes, while the relations between electrode and separator sizes received less attention. In this contribution, we use analytical models [2] and molecular simulations to investigate how the interplay between the membrane and electrode thicknesses affects the EDLC charging [3].

Acknowledgments
This work was supported by the Polish National Science Centre (NCN) under a grant No. 2021/40/Q/ST4/00160.

References

[1] Kondrat, S. et al. Chemical Reviews. doi.org/10.1021/acs.chemrev.2c00728
[2] Verkholyak, T. et al, The Journal of Chemical Physics. doi.org/10.1063/5.0066786
[3] Paolini, D. et al. ChemElectroChem, accepted.

Molecular Simulations and Theoretical Models of the Stability and Mobility of Nanobubbles in Aqueous and Non-Aqueous Liquids

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Keywords: Nanobubbles, Stability, Mobility, Simulations

Nanobubbles, gas-filled bubbles with diameters in the ~100 nm range, have only recently come under focused scientific investigation. They have been confirmed to exist in bulk aqueous solution and there are more limited reports for some non-aqueous liquids. While several features of nanobubbles are consistently reported, most notably their unexpected stability over extend periods, there remains considerable uncertainty and debate regarding the nature and properties of bulk nanobubbles. Nevertheless, bulk nanobubbles have aroused considerable interest across a wide range of real-world applications, from medical imaging to water treatment and agriculture. This presentation will begin by providing a more general overview of nanobubbles, their properties, and some of controversy surrounding nanobubbles and their unexpected features. It will then have a more detailed look into possible explanations for nanobubbles and their behaviour. Specifically, I will introduce a simple physical model that is able to account for both the stability and mobility of bulk aqueous nanobubbles. This model uses the polarization of the air/water interface, considering dipole and quadrupole contributions, together with the spherical bubble geometry to account for forces giving rise to both nanobubble stability and mobility. This presentation will also report results from molecular simulations of nanobubbles in both water and in an non-aqueous liquid (cyclopentane). I will demonstrate that both short-range and long-range interactions in these systems must be treated with care in order to correctly determine the pressure in the system. Results for the movement of aqueous nanobubbles in electric fields will be report. The predictions of the proposed physical model will be demonstrated to be consistent with the results from these molecular simulations.

Enhancing Kinetics of Physicochemical Wastewater Treatment Process by Nanobubbles Convective Aeration.

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Keywords: Nanobubbles, Convective Aeration Process, Waste, Wastewater Treatment

Traditional wastewater treatment methods, despite their efficacy, face limitations in energy consumption and contaminant removal efficiency, particularly for emerging contaminants such as pharmaceuticals and endocrine-disrupting chemicals. Conventional bubble aeration systems have a low oxygen transfer efficiency (around 2% SOTE), leading to high energy costs. The adoption of nanobubbles (NB´s), which exhibit a much higher SOTE (around 85%) due to their stability, small size (70-200 nm), and surface charge, provides a solution for the optimization of physicochemical processes for the removal of pollutants from municipal wastewater. Integrating NB´s into a modular plant for wastewater treatment offers a significant enhancement in contaminant removal efficiency. This study presents the development and evaluation of a novel convective nanobubble aeration system coupled to a 1.3 m3 batch tank designed to improve the performance of three well-established wastewater treatments: flotation, coagulation-flocculation, and advanced oxidation processes (AOPs).

Results show that using O3 NB´s improves pollutant removal compared to air NBs. The flotation process resulted in a 160% improvement in suspended matter removal. In the coagulation-flocculation process, the use of chitosan as a natural coagulant, in conjunction with O3 NB´s, resulted in an 80% reduction in chemical oxygen demand (COD), outperforming the 70% reduction achieved with air nanobubbles. The advanced oxidation process, facilitated by O3 NB´s, achieved a remarkable removal efficiency of 99.8% for total suspended solids (TSS) and 93% for COD. Based on the COD removal results, kinetic analysis showed that the process is carried out in two stages: the first stage is coagulation where models were established for the 3 processes and the second stage is floc formation where the pollutant is removed by flotation processes.

In conclusion, this study demonstrates the superior performance of a modular nanobubble-assisted wastewater treatment plant. The integration of flotation, coagulation-flocculation with chitosan, and advanced oxidation processes using O3 NB´s significantly enhances contaminant removal efficiency, reduces energy consumption and mitigates the environmental impact of wastewater treatment.

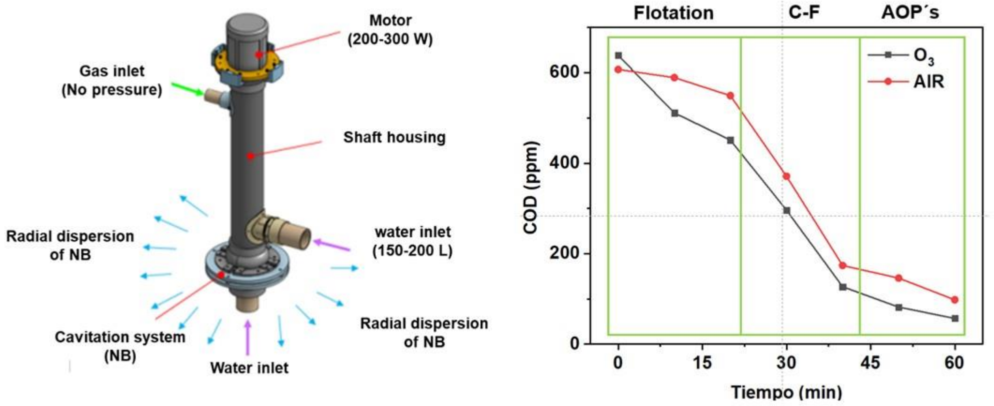

Figure 1. COD on real-time of the treated water as a function of the treatment time by air NB's and O3 NB's

Electrokinetic Characterisation Of Electric-Field-Generated Nanobubbles

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Keywords: Nanobubbles

We detail the electrokinetic characteristics of a new class of highly metastable and long-lived nanobubbles generated by the application of an external electric field to a liquid-gas mixture. Here, we study, inter alia, the zeta potentials, bubble-size distribution and other electrokinetic properties of both air and CO2 nanobubbles in an effort to understand their unique stability and longevity. In so doing, we seek insight into mechanistic origins of this stability, aided by theoretical and numerical modelling and simulations.

Electrophoresis of Nanobubbles

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Keywords: Computer Simulation, Electrolyte

Nanobubbles can be formed in various natural and industrial processes including liquids. In water, the bubbles often acquire an electric charge due to the preferential adsorption of certain ions on the bubble surface. In that case, the bubbles would respond to an external electric field and exhibit electrophoresis. Several experimental works have reported a dramatic variation of the bubble electrophoretic mobility in different electrolytes, including anomalous mobility in electrolytes containing polyvalent cations. In this work, we performed a computer simulation study of bubble electrophoresis in aqueous electrolytes using dissipative particle dynamics simulations. We compare the cases of monovalent divalent and trivalent salts. We observe the rich behaviour of the electrophoretic mobility of the bubbles as a function of salt concentration, in agreement with experiments, and discuss the mechanisms of the bubble mobility variation and inversion in solutions of polyvalent electrolytes.

Giant Carbon Geosequestration Potential with Supercritical CO_2 Nanobubbles In Brine

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Keywords: Nanobubbles, Molecular Dynamics, Solubility Trapping, Carbon Sequestration

Storing excess CO2 in underground saline aquifers is an important technology for the low carbon future. Direct dissolution of CO2 molecules in connate brine (solubility trapping) is one of the safest carbon geosequestration method, yet was underexplored due to the perceived slow process. Here, we show that injecting supercritical CO2 (scCO2) nanobubbles in saline aquifers can considerably boost the solubility trapping. Molecular modeling predicts 1.5 to 2x CO2 oversaturation in brine with the presence of scCO2 nanobubbles. Furthermore, the nanobubble electrical double layers (EDL) are enhanced with reducing nanobubble sizes and increasing brine salinity, which indicate enhanced nanobubble stability against CO2 macro-phase separation in saline aquifers. The unique physiochemical properties of nanobubbles including high specific scCO2/brine interface areas and low buoyancy forces also greatly favor the solubility trapping processes. This study highlights that combining nanobubble technology in CO2 geosequestration is a promising new direction that worths more attention.

Electrokinetic phenomena strongly affect the removal of organic micropollutants in membrane separation processes

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Keywords: Membrane Separation Processes, Donnan Steric Pore Model, Removal Of Organic Pollutants

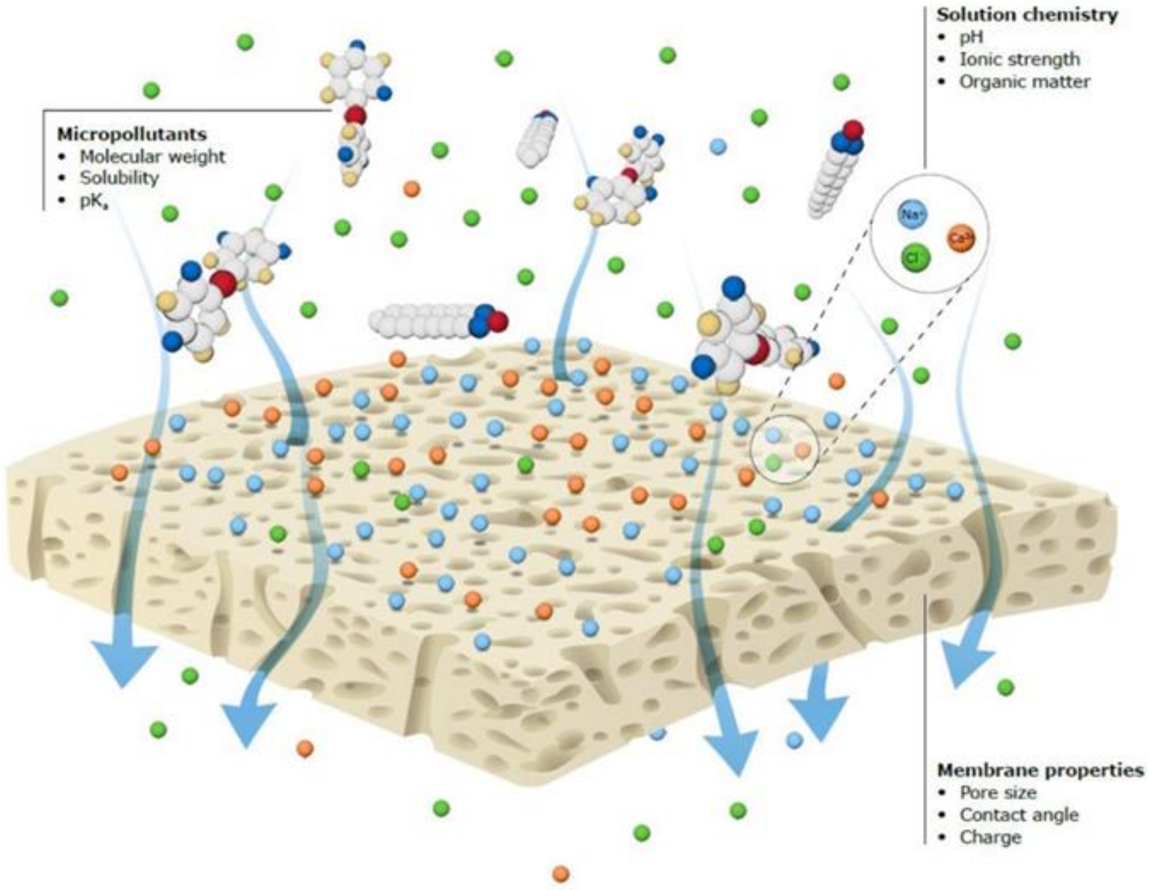
The removal of organic micropollutants (MPs) from water sources, present at very low concentrations, is often necessary to meet drinking water quality standards. Membrane filtration technologies, such as nanofiltration (NF), are effective for MP removal. While these technologies demonstrate high removal for many MPs, their effectiveness can be limited for certain MPs. To predict the removal of MPs, it is essential to understand the underlying mechanisms of MP removal using NF.

A common approach is to predict removal performance based on the charge and size of MPs. In this framework, components with a molecular weight larger than the membrane's molecular weight cutoff, as well as components with an opposite charge to the membrane, are considered to be effectively removed. However, the impact of an electric potential across the membrane, influenced by the ionic composition of the solution, is often neglected.

In this presentation, we examine the effect of an electric field on the rejection of organic micropollutants by membrane separation processes. This electric field is strongly influenced by the salt concentration in the feed water. We present a concise model and compare theoretical predictions with experimental data for the removal of seven MPs at five different salt concentrations using the nanofiltration NF270 membrane. Our findings indicate that the model accurately describes MP transport through nanofiltration membranes. The results show that salt concentration impacts MP rejection differently based on MP charge and size. Specifically, increasing salt concentration decreases the rejection of small, counter-charged MPs, while it increases the rejection of large, counter-charged MPs.

Furthermore, we investigate the effect of divalent ions on MP removal. Natural water sources often contain calcium at varying concentrations, which affects MP removal. We evaluate, both theoretically and experimentally, three mechanisms reported in the literature that influence MP removal. We developed an extended version of the Donnan steric pore model, which accounts for the formation of Ca-MP complexes and the effect of calcium on membrane charge density, and describe experimental data for MP removal. We provide further explanation of the phenomena impacting MP removal.

Reference: Castaño Osorio et al., Water Research, https://doi-org.ezproxy.library.wur.nl/10.1016/j.watres.2022.119130


Micropollutants
• Molecular weight
• Solubility
• pK_a
Solution chemistry
• pH
• Ionic strength
• Organic matter
Na^+
Ca^{2+}
Cl^-
Membrane properties
• Pore size
• Contact angle
• Charge

Modelling Polarization of and Salt Sorption by Floating Nanoporous Electrodes Using Homogeneous Approximation

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Keywords: Bipolar Electrode, Nanoporous, Salt Sorption, Current

Nanoporous electrodes are widely used in EDL supercapacitors and devices for Capacitive Deionization (CDI). Usually, two such electrodes are connected to leads and a voltage is applied. However, bipolar configurations are also being considered and can have considerable advantages [1].

Previously, homogeneous approximation has only been used for the description of “volumetric” capacity while ion transfer was explicitly modelled only in electroneutral “macro-channels” [2]. This made impossible analysis of the limiting case of no macro-channels. Meanwhile, there are emerging carbon nanoporous materials having a narrow pore-size distribution and an average pore size around 10 nm [3]. In the homogeneous approximation, due to the complete EDL overlap, electrostatic potential inside nanopores remains constant. Therefore, ion transport occurs only via diffusion, which is driven by concentration gradients arising due to inter-phase potential drops at the external boundaries. This simplifies the modelling considerably because inside nanopores there are just linear equations of non-stationary ion diffusion. However, equations for different ions are coupled by non-linear boundary conditions of interphase equilibria at the external boundaries. Bipolar configuration is especially interesting due realistic galvanostatic mode and a non-trivial steady state. The stationary solution is extremely simple because the concentration profiles inside a nanoporous slab electrode are just linear. Cations accumulate at one edge and anions at the other giving rise to a current-induced sorption of salt described by a very simple equation. Another simple expression can be obtained for the current voltage characteristics. Galvanostatic charging dynamics is especially simple in the case of cations and anions of equal mobilities where explicit analytical expressions in terms of Fourier transforms and their convolutions can be obtained. Remarkably, they depend only on dimensionless current and time whose definitions lump in such material properties as thickness, porosity, ion diffusion coefficient and current density.

In steady state, we could also obtain explicit corrections for a finite EDL overlap and, thus, define the scope of applicability of homogeneous approximation.

[1] J. Nordstrand, J. Dutta, Electrochim. Acta 467 (2023) 143000
[2] P.M. Biesheuvel, et al, Russ. J. Electrochem. 48 (2012) 580–592
[3] G. Hasegawa, J. Sol-Gel Sci. Technol. 2022 103:2 103 (2022) 637–679

Donnan Dialysis Under Non-Isothermal Conditions: How Temperature Gradients Could Accelerate/Manipulate Transport Of Divalent Ionic Species Through Nanofluidic Channels?

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Keywords: Donnan Dialysis, Water Pre-Treatment, Non-Equilibrium Conditions, Nanofluidics

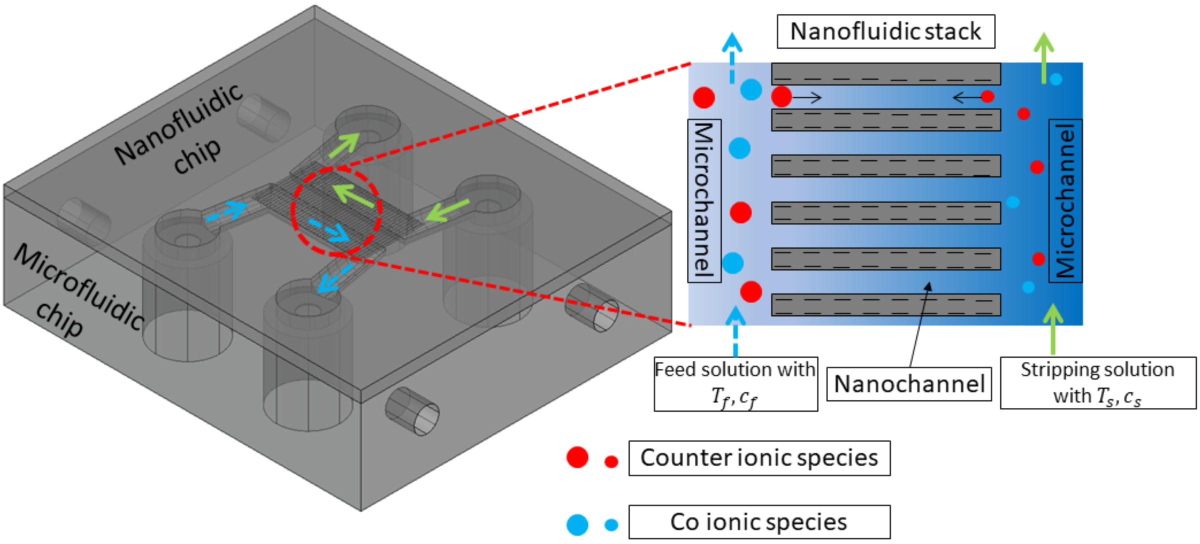
Desalination technology can harvest abundant water from saline sources such as seawater, groundwater, and industrial effluents. However, the energy intensity (EI) of desalination is a growing environmental, economic, and societal concern. One way to reduce EI is by using large amounts of low-grade waste heat for pretreatment in desalination plants. Another challenge is membrane fouling and scaling by divalent cations (e.g., Ca2+, Mg2+), which requires chemical dosing and pretreatment, limiting water recovery. Some existing pretreatment technologies use the concentration gradient between a feed and concentrate solution (Donnan dialysis) or direct ion exchange with ion exchange resins (IEX). While Donnan dialysis is economical, simple, and energy-saving [1], it is not widely used due to its slow kinetics. In this work, we demonstrate that adding thermodynamic forces, such as a temperature gradient, can accelerate the kinetics of Donnan dialysis.

To study the impact of temperature gradients on ion transport in Donnan dialysis, we designed a microfluidic/nanofluidic setup. This setup features stacks of 40 nanochannels, each with depths of 50 and 30 nm, connecting two parallel microchannels. Two accurate incubators control the temperature across the nanochannel stack. Our uniquely designed temperature and flow sensors measure the in-line solution temperature and flow rates, providing detailed insight into thermoosmosis and heat transfer between microchannels. A recirculation pumping system allows continuous processing of solutions for several hours.

Finally, we measure the concentration of ionic species using Ion Chromatography and determine the transport of ionic species as a function of the applied temperature gradient and solution composition. Additionally, we develop a robust theory based on non-equilibrium thermodynamics to solve the coupled heat, water, and charge transport. In this theory, the Soret and Dufour coefficients for each ionic species are obtained from our experiments.

This work aims to provide a deeper understanding of the potential for using temperature gradients to enhance the efficiency of Donnan dialysis in desalination processes, thereby addressing key energy and environmental challenges.

[1] M. Vanoppen, et al., Water Research. https://doi.org/10.1016/j.watres.2015.04.030



Schematic of Micro/Nanofluidic setup. The microfluidic chip is made of PDMS and the nanochannels are etched on silicon wafer. Two streams of high and low temperature with different ionic compositions will be flowed through the microchannels. The temperatrues are accurately controlled and measured via 4 sensors before and after each microchannel.

A Network Model for Ionic Transport in Charged Porous Materials

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Keywords: Supercapacitor, Equivalent Circuit, Energy Storage, Confinement

Matching the supply and demand of energy drawn from intermittent renewable sources, such as sun and wind, requires high-power energy storage devices, such as supercapacitors. These devices store energy through the fast electrostatic attraction of ions in solution to oppositely charged inner surfaces of electrodes under an applied voltage, forming charged electrolyte regions called electric double layers. Typically, supercapacitor charging is modeled through semi-empirical extensions of de Levie's equivalent circuit. The latter represents charge transport as a balance of Ohmic potential drops in an electroneutral pore bulk and capacitive attraction of counterions to thin double layers. However, recent materials research and industrial technologies have focused on designs of electrodes with average pore sizes in the order of nanometers for optimal capacitance per unit volume.

In this work, we propose an extension of de Levie's circuit to networks with narrow pores by accounting for the effects of finite double-layer thickness. To this end, we derive reduced-order forms of the Poisson-Nernst-Planck equations and corresponding boundary conditions and interpret the resulting equations as circuits of infinitely many elements. Due to a charge distribution throughout a cross-section, this circuit contains a critical change relative to de Levie's. Namely, charge fluxes from both the electric field and diffusion are present. To represent both fluxes through resistive elements, we define the electrochemical potential of charge, i.e., the valence-weighted average of the electrochemical potentials of the ions, which is conserved over a cross-section and across junctions of pores of different sizes. Through our computationally affordable reduced-order equations, we solve networks of nearly 5,000 pores in 6 min. We use the framework to develop insights on the impact of pore structures and size dispersity on electrode charging dynamics, particularly on the time scale, energy density, and power density of capacitive charging. We postulate the use of this scalable methodology in the interpretation of geometric effects on electrode impedance spectroscopy measurements and to inform the design of 3D-printed electrodes.

Anomalous Electrokinetic Phenomena in Confinement

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Keywords: Electrokinetics, Angstrom Channel, Ionic Blockade

There is still a knowledge gap for the understanding of molecular sieving, fluidic structure, and thermodynamics in Angstrom-channels [1]. Here we studied the critical impacts of surface charge for the flow and ionic transport at surface as well as in the Angstrom-channel. We demonstrate the slip length dramatically reduced at a heterogeneously charged surface, while have less decrease at homogeneously charged surface [2]. We found that cations are tightly bound to the surface charge, blocking ionic transport in a single-file water channel and resulting in nonlinear I-V cure, which we named as "Counterion blockade" [3]. The ionic conduction gradually becomes Ohmic as surface charge density increases, which quantitatively explained the discoveries in our experiments [4]. In addition, we first-time found the streaming conductance increases as applied pressure in the Angstrom channels, which is known as a constant in classical theories. We approximate the dissociation probability of counterions from the surface charge, thus increasing the streaming conductance. We theoretically investigate the anomalous electrokinetic phenomena in Angstrom channel by non-equilibrium statistics and MD simulations. We give new Onsager reciprocal factors of electrokinetics in confinement, which well described the pressure dependent streaming conductance as we found in experiments.

References:
[1] Samuel Faucher et al., J. Phys. Chem. C 2019, 123, 21309−21326.
[2] Yanbo Xie, Li Fu, Thomas Niehaus, and Laurent Joly, Physical Review Letters 125, 014501 (2020).
[3] Shusong Zhang, Li Fu, Yanbo Xie, arXiv preprint arXiv:2304.13355
[4] Yanbo Xie, Deli Shi, Wenhui Wang, Ziheng Wang, Nanoscale, 15, 9560–9566 (2023)

Poster Presentations Abstracts

Poster #1

The Time-Averaged Motion of a Dielectric Nanoparticle With a Thick Double-Layer in an Oscillating Electric Field Using the Maxwell-Stress-Tensor Approach

Bing-Yang Shih[1], Senne Fransen[1], Radin Tahvildari[1], Willem Van Roy[1], Kherim Willems[1], Ying Ting Set[1], Cesar Javier Lockhart De La Rosa[1], Pol Van Dorpe[1,2], Maarten Rosmeulen[1]

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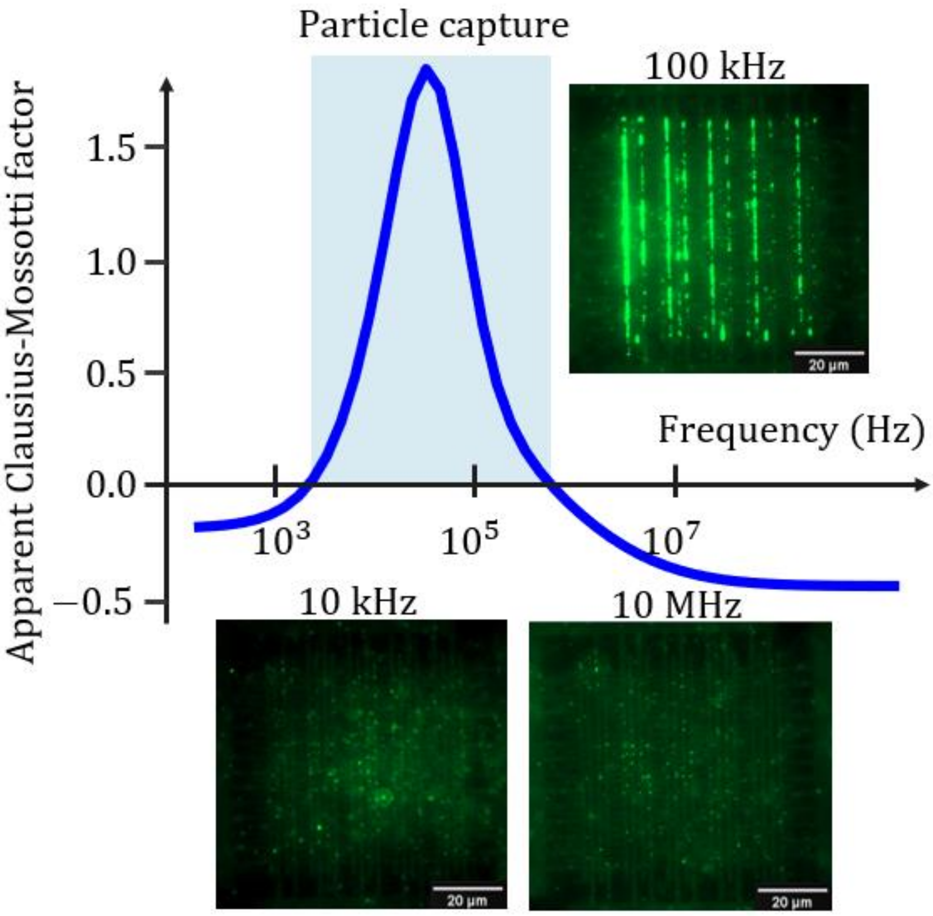
Keywords: Dielectrophoresis, Maxwell Stress Tensor, Standard Electrokinetics Equations, Time-Averaged Electrokinetics

Previous studies on the behavior of non-conducting nanoparticles in an oscillating non-uniform electric field have used both the effective dipole moment approach as well as the Maxwell stress tensor approach to investigate the particle's dielectrophoretic movement. Typically, the effective dipole moment approach has been applied to particles with a thick double layer [1], whereas the Maxwell stress tensor approach has been used to investigate particle-wall or particle-particle interactions when the double-layer is infinitely thin [2]. However, there seems to be some controversy when applying the Maxwell stress tensor approach to cases where the double layer is thick [3]. In this talk, we present a model and numerical methodology for investigating the time-averaged response of dielectric nanoparticles using the Maxwell stress tensor approach. Then, by applying perturbation theory consistently up to the second order, we show that the Maxwell stress tensor approach naturally includes three contributions: 1) the dielectrophoretic response as found from the effective dipole moment approach, 2) the movement due to induced charge electrophoresis, and 3) second-order corrections to ordinary electrophoresis. We discuss the importance of each contribution depending on the particle's surface charge density and external field's oscillation frequency. Lastly, we critically evaluate the merits and shortcomings of the model and compare our predictions with experimental measurements using functionalized polystyrene particles.

[1] Zhao, H. et al. Journal of Colloid and Interface Science. doi.org/10.1016/j.jcis.2009.01.056
[2] Ai, Y. et al. Journal of Colloid and Interface Science. doi.org/10.1016/j.jcis.2013.11.034
[3] Zhao, Y. et al. Biomicrofluidics. doi.org/10.1063/1.4979014


Particle capture
100 kHz
20 µm
Apparent Clausius-Mossotti factor
1.5
1.0
0.5
0.0
−0.5
Frequency (Hz)
10^3
10^5
10^7
10 kHz
20 µm
10 MHz
20 µm

Poster #2

Nanofiltration Through Cylindrical Nanopores with Ion Adsorption

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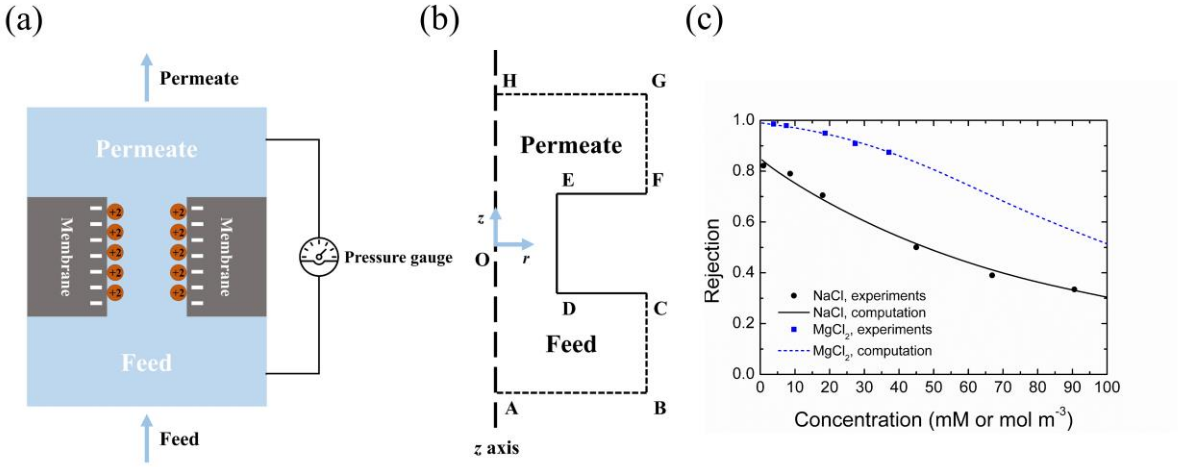
Keywords: Site Binding, Dielectric Exclusion, Hindered Transport, Charge Polarity Reversal

A continuum model is adopted to investigate the effects of ion adsorption on nanofiltration and is validated against experimental results [1]. Considering the confined space within the nanopore and the layered structure of water near its surface, we have incorporated hindered transport and anisotropic dielectric exclusion to account for their influence on interfacial ion adsorption. The distinction caused by ion adsorption is demonstrated and compared with the system without ion adsorption. Charge polarity reversal may occur when multivalent ions are present in the system. Ion adsorption decreases the rejection of NaCl slightly, but it alters the rejection of CaSO4 significantly due to the lowering in surface charge density magnitude. In particular, ion adsorption improves the rejection of asymmetric electrolytes due to the charge polarity reversal. With ion adsorption, the susceptibility of rejection to pH changes diminishes, and the dependence of rejection on feed concentration decreases. Owing to the counteracting effects of increasing surface charge density and more severe ion screening on surface charge as feed concentration increases, the rejection of CaCl2 and Na2SO4 displays a maximum under specific pH ranges. 2D surface plots illustrate the dependence of rejection on concentration and pH. In addition, hindered transport leads to improvements in rejection. As the diffusivities of cations and anions drop or the diffusivity ratio of coion to counterion decreases, the rejection increases pronouncedly. Lastly, dielectric exclusion results in a higher negative surface charge density, thereby causing a shift of the isoelectric point towards lower pH values. The results presented in this work may unravel the influence of ion adsorption on nanofiltration in the presence of various electrokinetic effects.

[1] Schaep, J. et al. Journal of Membrane Science. doi.org/10.1016/S0376-7388(99)00163-5



(a) Schematic diagram of the nanofiltration system under investigation. (b) Schematic diagram of the computational domain with associated boundaries. (c) Comparison of model predictions (lines) with experimental data from Schaep et al. [1] (symbols) on rejection rates.

Poster #3

Measurement of an Eddy Diffusivity for Chaotic Electroconvection

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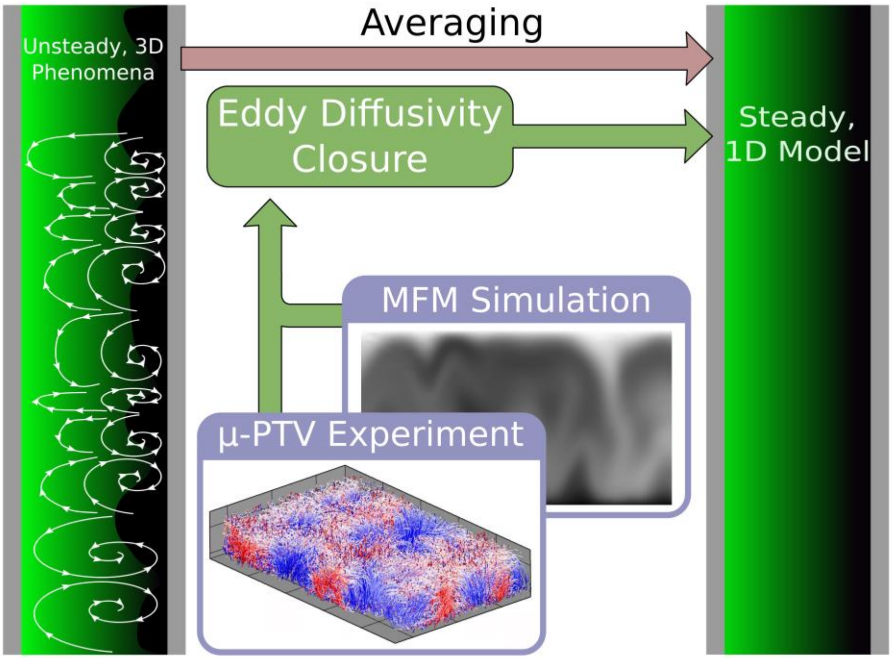
Keywords: Electroconvection, Model Reduction, Reynolds Averaging, Eddy Diffusivity

In electrodialysis, the coupling between ion transport, fluid flow, and electrostatics may give rise to electroconvection, a hydrodynamic instability that eventually transitions to a chaotic flow. In the chaotic regime, the flow is characterized by unsteady, three-dimensional vortices with a wide range of length scales and is accurately described by the Poisson-Nernst-Planck-Navier-Stokes (PNPNS) equations. However, 3D simulations of the PNPNS equations are extremely expensive due to inherent stiffness in the system. In practice, knowledge of the averaged ion concentration, velocity, and electric potential fields would be sufficient to predict essential performance benchmarks like the current-voltage curve. Unfortunately, the application of Reynolds-averaging to the PNPNS equations leads to a closure problem, thwarting direct computation of the averaged fields. In this work, we combine the macroscopic forcing method, a numerical technique for measurement of closure operators in Reynolds-averaged equations, with high-fidelity experimental data to close the Reynolds-averaged PNPNS equations. We show that the unclosed fluxes may be represented to the leading order as a gradient-diffusion term with a spatially varying eddy diffusivity, and we measure the eddy diffusivity from space-time-resolved experimental velocity fields. This finding allows direct computation of the averaged fields at a fraction of the cost of 3D PNPNS simulations by enabling use of the 1D Poisson-Nernst-Planck equations with supplementary eddy diffusivity. The resulting current-voltage curve exhibits strong agreement with experiments.

See graphical abstract, used with permission from Balaji-Wright, A. et al. Physical Review Fluids. https://doi.org/10.1103/PhysRevFluids.9.023701



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Poster #4

Hybrid Continuous-Flow and Digital Microfluidics Platform for Manipulation of Nanoliter Droplets

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Keywords: Electrowetting, Droplets, Hybrid, Microchannel

The presented hybrid platform for integrating continuous flow microchannels with electrowetting-on-dielectric (EWOD) based digital microfluidics (DMF) enables the utilization of the benefits of both microfluidic systems in direct connection, automatically, and without any need for pipetting. As such, discrete droplets can be extracted from a microchannel where the liquid is being pre-processed, and be manipulated to perform various lab-on-a-chip applications. Previously reported platforms that integrated microchannels with DMF include the generation of discrete droplets using a microchannel with oil flow and their manipulation using DMF [1], droplet generation from electrowetting microchannels [2], and droplet transfer from the DMF part to the microchannel by electrowetting [3]. The current study further extends these to enable the generation of droplets from a continuous flow within a microchannel followed by their manipulation using EWOD in air without an oil phase. Our hybrid chip included a 500 µm wide main microchannel with a 300 µm side microchannel of 25 µm height. The side channel’s end reached a hydrophobic barrier and contacted the first EWOD electrode. The last EWOD electrode within the side microchannel is interfaced to an array of 3×5 500×500 µm EWOD electrodes as depicted in figure 1. Preliminary tests concluded that in order to generate a droplet from a channel, the liquid front must be pulled to the side from its original path (as seen in figure 2d). Since the force generated from electrowetting acts on the three-phase contact line at the liquid front, cutting a droplet requires obtaining a three-phase contact line on both sides of the liquid [4]. When the liquid front was pulled down its original path only, the channel acted as an infinite reservoir of liquid and droplet generation was not possible.

References:
[1] Ahmadi et al., Lab Chip 19, 524 (2019)
[2] Banerjee et al., Micromachines 6, 172 (2015)
[3] Sathyanarayanan et al., Adv. Mater. Tech. 5, 2000451 (2020)
[4] Mugele F., Heikenfeld J., "Electrowetting: Fundamental Principles and Practical Applications", Weinheim: Wiley-VCH, 2019.

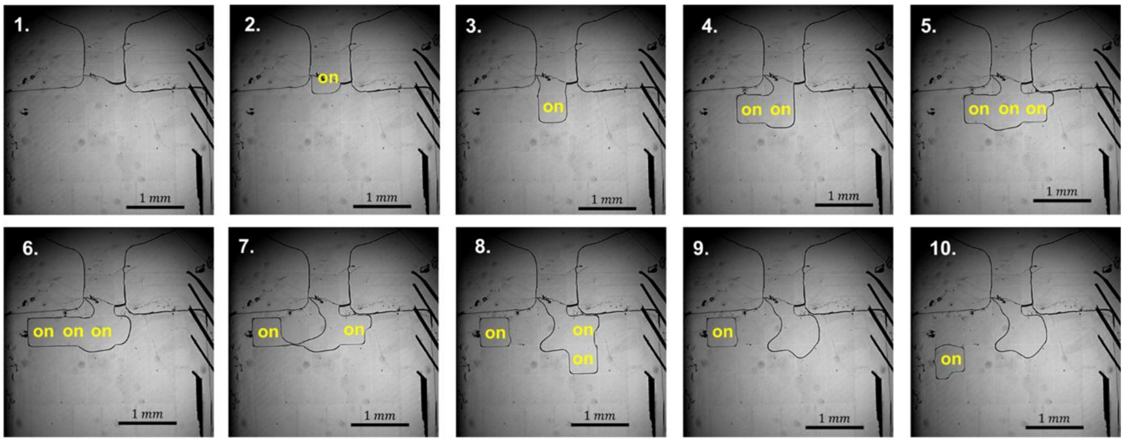

Figure 1: Droplet generation from a microchannel using electrowetting-on-dielectric

Poster #5

Ionic Associations and Hydration in the Electrical Double Layer of Water-In-Salt Electrolytes

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Keywords: Electrostatics, Chemical Thermodynamics, Electric Double Layer, Interfacial Properties

Concentrated electrolytes have a broad set of promising and exotic properties, such as fire-extinguishing and high stability, with potential applications in electrochemical energy storage. A well-established super-concentrated electrolyte is Water-in-Salt-Electrolytes (WiSEs). In contrast to dilute electrolytes, WiSEs have only a small amount of water dissolved in a salt, leading to cations being only partially hydrated and multi-ion clusters dominating interactions. WiSEs have demonstrated expanded electrochemical stability window, good conductivity, and non-Newtonian viscosity, among others. These distinct properties are thought to originate from the presence of an ionic network and interpenetrating water channels, which indicates that species associations in the WiSEs are crucial to understanding their properties. Currently, species associations have only been investigated in the bulk, while little attention has been given to the electrolyte structure near electrified interfaces. Here, we develop a theory for the electrical double layer (EDL) of WiSEs where we consistently account for the thermoreversible associations of species into Cayley tree aggregates. The theory predicts an asymmetric structure of the EDL. At negative voltages, hydrated Li^+ dominate. Additionally, cluster aggregation is initially slightly enhanced before they disintegrate at larger voltages. At positive voltages, clusters are strictly diminished. The theory can capture trends observed in molecular dynamic (MD) simulations and experiments. The gained insights highlight the critical role of ionic associations in the equilibrium interfacial structure of WiSEs. Furthermore, we posit that this knowledge is important in not only understanding reaction kinetics near electrified interfaces and the formation of the solid electrolyte interphase but also may shed light on surface force measurements near electrified interfaces.

Poster #6

Electrical Response for Nanoporous Carbons During Imbibition and Drying

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Nanoporous electrically conductive materials filled with aqueous electrolytes are promising candidates for electrical energy harvesting and conversion. Of particular interest is the process of formation and destruction of the electrical double layer in the pore space during drying and imbibition. In contrast to supercapacitors, where this process is initiated by the application of an external potential difference, the spontaneous adsorption and desorption of ions on the surface during drying and imbibition is investigated here. In this process, in the absence of an applied external potential difference, although the total charge of the system is zero, a local charge accumulates at the interface. The amount of adsorbed ions is determined by the chemical composition of the material, the bonds on the surface, and, due to the spontaneity of this process, significantly by the surface area, which determines the potential for energy harvesting. The ability to utilize the energy stored in such a system is related to the potential difference between electrodes with different interfaces and adsorption properties.

This study examines the electrical response of nanoporous carbons to imbibition and drying. A combination of gravimetric measurements, zero resistance amperometry, and other open circuit electrochemical techniques is employed to investigate the effects of these processes on current relaxation and potential evolution. These key characteristics of charge redistribution and ion rearrangement at the interface are investigated.

Poster #7

Metal recovery from mine tailings: comparative solvent efficacy and bioavailability in electrokinetic leaching vs. static leaching

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Moving toward a low-carbon economy requires urgent development of new approaches in sustainable metal recovery from secondary resources, such as solid mine wastes. Within this in situ leaching (ISL) has emerged as a powerful technique due to its ability to remove target metals (pollutants or economically valuable) without physical excavation of the material. ISL has proven difficult, however, for mine tailings, due to their low permeability. To overcome this, electrokinetics (EK) has been proposed but work in this field remains in its infancy. Herein we have compared the effectiveness, extraction mechanisms, and bioavailability in EK assisted leaching versus static leaching from porphyry Cu mine tailings using twelve equimolar concentrations (0.5 M) of inorganic, organic, chloride-based, and deep eutectic solvents (DES). EK assisted leaching showed superior recovery of aluminum (Al), copper (Cu), iron (Fe), and manganese (Mn) from porphyry Cu tailings compared to static leaching, regardless of solvent type. Specifically, EK leaching achieved up to 50.0% Cu and 31.0% Mn recovery within seven days using 0.16 M ferric chloride, while static leaching reached up to 23.1% Cu recovery with 0.5 M malonic acid and 10.6% Mn recovery with 0.16 M ferric chloride over the same period. The lowest Cu recovery in both EK leaching (6.8% - 17.6%) and static leaching (0.7% - 3.6%) was observed in the DES group, due to the high viscosity of DES. The most efficient solvents for Cu recovery in EK leaching were 0.16 M ferric chloride (50.0%), 0.5 M citric acid (46.5%), and 0.5 M malonic acid (45.7%), while in static leaching, they were 0.5 M malonic acid (23.1%), 0.5 M hydrochloric acid (22.9%), and 0.5 M citric acid (22.4%). This indicates a more complex metal transport mechanism in EK leaching beyond routine dissolution-electromigration. Bioavailability assessments using diluted HNO3 and CaCl2 extractions revealed that EK can reduce long-term ecological risks by transforming more potentially available fractions into actually available fractions, facilitating easier removal through prolonged EK processes. EK metal recovery from tailings holds great promise for sustainability and circularity of secondary resources when optimized and combined with renewable energy sources like solar and bioenergy.

Poster #8

Polyelectrolyte Gels-Based Iontronic Memristors for Neuromorphic Systems

Zhenyu Zhang[1,2], Barak Sabbagh[2,3], Yunfei Chen[1], Gilad Yossifon[2]

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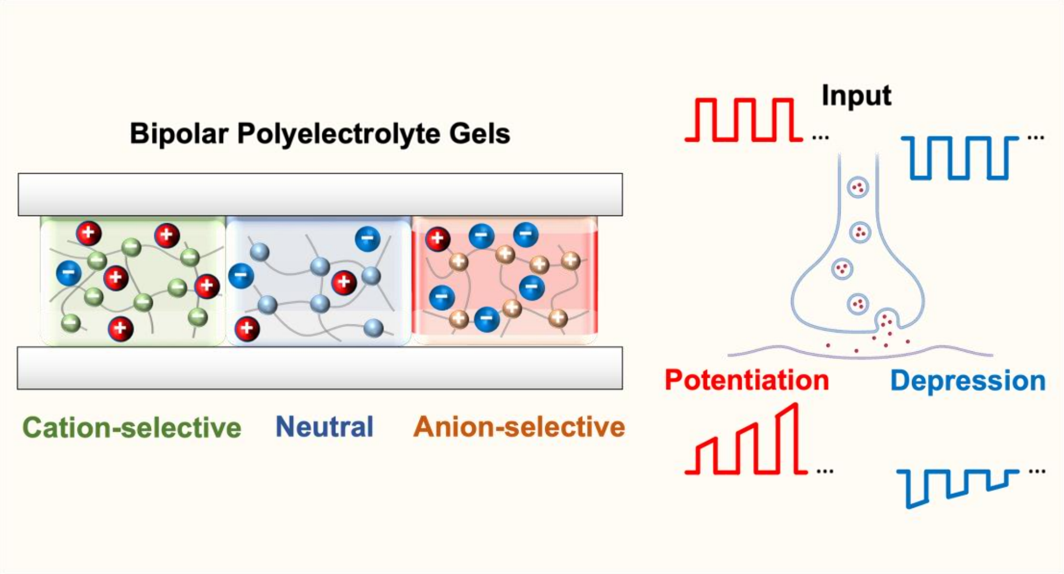
3. Technion–Israel Institute of Technology, Haifa, Israel

Keywords: Memristor, Polyelectrolyte, Iontronics, Nanofluidics

Iontronic systems, which utilize nanometer-sized ion permselective fluidic structures to mimic the energy-efficient information processing of biological systems, are garnering significant attention [1]. Compared to electronic systems, iontronics can transduce and process both electrical and chemical signals via the transport of various ions and charged molecules in aqueous solutions or polymers, reminiscent of signal transmission in biological systems. As a counterpart in electronics, iontronic fluidic memristors have been reported to realize neuromorphic functions by leveraging various mechanisms [1]. However, it is still challenging to achieve optimal temporal electrical performances, for example, large conductance ON/OFF ratio and long-term plasticity. Here we present a novel realization of iontronic bipolar memristors featuring a three-layer ion-selective polyelectrolyte gel structure [2,3]. The fabrication process is cost-effective, rapid and facile, eliminating the need for photolithography and etching procedures. The memristive capacities are highly robust, significant, and reproducible, with a geometrically scalable memory time from 200 to 4000 seconds, from short-term memory to long-term memory regimes. Numerical simulations have shown that these enhancements are due to the ionic concentration-polarization (ICP)-induced rectification ratio within the polyelectrolyte gels. The unique bipolar structure of these devices significantly prolongs memory times and improves the ion conductance switching ratio with a mesoscale (10-1000 µm) geometry precision, while exhibit memory dynamics akin to those observed in unipolar devices. These properties endow the devices with the capability of effective neuromorphic processing with pulse-based input voltage signals. The presented iontronic bipolar memristors are versatile and can be easily integrated into small-scale iontronic circuits, paving the way for advanced neuromorphic computing functionalities.

References

[1] Noy, A.; Li, Z.; Darling, S. B. Fluid Learning: Mimicking Brain Computing with Neuromorphic Nanofluidic Devices. Nano Today 2023, 53, 102043. doi.org/10.1016/j.nantod.2023.102043
[2] Sabbagh, B.; Fraiman, N. E.; Fish, A.; Yossifon, G. Designing with Iontronic Logic Gates─ from a Single Polyelectrolyte Diode to an Integrated Ionic Circuit. ACS Appl. Mater. Interfaces 2023, 15 (19), 23361-23370. doi.org/10.1021/acsami.3c00062
[3] Zhang, Z.; Sabbagh, B.; Chen, Y.; Yossifon, G. Geometrically Scalable Iontronic Memristors: Employing Bipolar Polyelectrolyte Gels for Neuromorphic Systems. ACS Nano 2024 (Accepted).


Bipolar Polyelectrolyte Gels
Cation-selective
Neutral
Anion-selective
Input
Potentiation
Depression

Poster #9

Reverse Electro-Dialysis: One Model To Rule Them All

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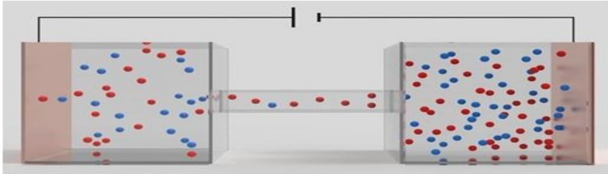
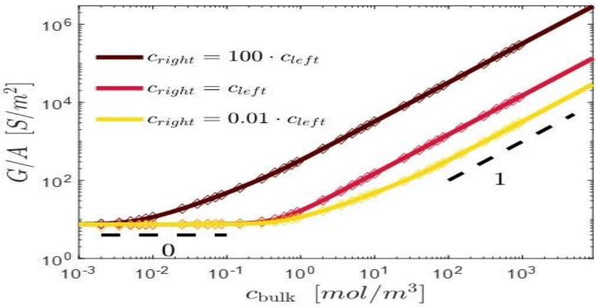
Keywords: Reverse Electro-Dialysis, Nanofluidics, Ion Transport

Reverse Electro-Dialysis (RED) is a process that leverages a difference in salt concentrations to harvest "free" energy. Namely, an electrical current can be harvested upon the introduction of a concentration difference across an ion-selective membrane or nanochannel. This concentration difference is natural and highly abundant – it can be found wherever freshwater rivers flow into the sea. Thus, RED presents the potential to introduce a sustainable source of electricity that could revolutionize the global energy market. While RED is a well-established process and has already been upscaled in the REDStack Afsluitdijk pilot power plant, the microscopic details are still not completely understood. As such, this has led to the conventional reliance on trial and error for tuning and improving RED systems.

To overcome the challenges associated with trial and error, we have theoretically formulated (using the Poisson-Nernst-Planck equations) a universal model for RED systems that accounts for the key parameters of these systems, including geometry, concentration differences, and surface charge density. We derived a nonlinear current-voltage response as a function of the key parameters.

In this talk, we will present our model and its results. We will first show that our model can be degenerated to previous known models. Thereafter, we will present our new results, which also include novel expressions for the electrical conductance and the offset voltage of nanofluidic systems subject to a concentration difference. Our theoretical results are backed by exact numerical simulations, which show remarkable correspondence. Our model and its outcomes can be used to improve the design of all RED systems.





Poster #10

Principles For Optimizing Electroosmotic Flows Induced By Electric Double-Layer Charging In Asymmetric Nanochannels

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Keywords: Nanochannel, Electroosmotic Flow, Shape Asymmetry, Optimization

In microfluidics, where particle motions are constrained by the fluid motion through the linearity and reversibility of the Stokes equations, net displacements demand complex mechanisms. In these settings, transport can be attained through nanochannels subjected to suitable driving forces. Recent research has expanded the potential of using electric double layers formed near electrodes with asymmetric geometries under alternate currents as the source of net flows for such applications. In particular, it has been shown that the frequency of the gate potential of a nanochannel can be used to tune the flow rate. However, the models developed so far have yet to offer insights into controlling the channel geometry to enhance these flow rates. In the present work, we develop a model that accounts for a variable channel cross-section and arbitrary double-layer thickness, providing an understanding of the principles for the optimization of the flows in the nanochannels.

To this end, we performed second-order asymptotic expansions of the Poisson-Nernst-Planck-Stokes equations for low applied potentials in long channels. In the first order, we capture the dynamics of double-layer formation in the channel with an arbitrarily variable cross-section. The model captures the local charging dynamics through an axially dependent effective diffusivity, which contains the concurrent electromigrative and diffusive fluxes, setting the local effective electrochemical potential of charge. We derive the WKB approximation of this potential for an arbitrary shape. This information is fed into the second-order flow generated, which is then used to calculate the net flow rate. We learn that the frequency-dependent flow rate is produced by a competition of two effects, an electric pressure difference across the ends of the pore, and an integral contribution of the gradient of electrochemical potential of charge throughout the symmetry axis of the channel. The high-frequency plateau of its temporal average is determined from Laplace’s asymptotic method for integrals to quantify the dependence of these opposing contributions on the geometry of the channel. Through the resulting relations, we establish principles for optimizing the electroosmotic flows.

Poster #11

Electrokinetics in Iontronic Devices to Enable Brain-Inspired Signalling and Computing in a Brain-Inspired Medium

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Keywords: Iontronics, Neuromorphics, Memristor

The ionic dynamics in emerging aqueous electrolyte-based devices present exciting opportunities for brain-inspired (neuromorphic) systems using iontronic devices, representing a departure from conventional solid-state devices by mimicking the brain's fluidic ion transport. From first-principles, we derive analytic solutions for voltage-dependent salt concentration polarization in iontronic channels, showing that the voltage-driven net salt flux and accumulation surprisingly combine into a diffusionlike quadratic dependence of the concentration polarization time on the channel length. Building on this, we develop quantitative theories describing the dynamic conductance of iontronic channels and consequently extract neuromorphic features. We will discuss both the i) signalling and ii) the computing side of neuromorphic iontronics, enabled by fluidic memristors (memory resistors). i) We show how characteristic features of neuronal signalling can be extracted from an iontronic circuit containing these channels (Fig. 1(a)) [1,2]. ii) By combining theory with experiment we then show how microfluidic channels that embed a rigid colloidal structure can be employed as an artificial synapse to carry out neuromorphic reservoir computing tasks (Fig. 1(b)) [3]. These results pave the way for neuromorphic systems that more closely resemble the brains fascinating aqueous processes.

[1] Kamsma, T.M. et al., Phys, Rev, Lett. (2023), doi.org/10.1103/PhysRevLett.130.268401
[2] Kamsma, T.M. et al., Neuromorph. Comput. Eng. (2024), doi.org/10.1088/2634-4386/ad40ca
[3] Kamsma, T.M. & Kim, J. et al., PNAS (2024), doi.org/10.1073/pnas.2320242121

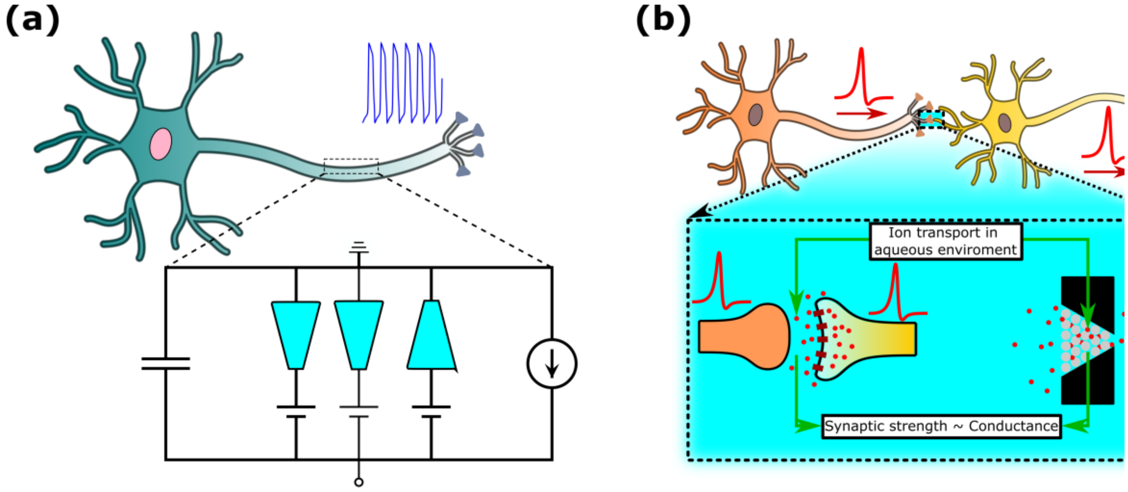

Figure 1. Neuromorphic signalling (a) and computing (b) features extracted from artificial fluidic ion channels. (a) A modelled microfluidic iontronic circuit containing conical channels exhibits characteristic features of neuronal spiking such as all-or-none action potentials and spike trains [1]. (b) A tapered microfluidic channel filled with a rigid colloidal structure that embeds a conducting network of fluidic nanochannels emulates synaptic short-term plasticity and is implemented as an element for neuromorphic reservoir computing [3].

Poster #12

Trapping of Particles in Microfluidic Constrictions Driven by AC Electric Fields

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Keywords: Microfluidics, Trapping, Dielectrophoresis, Concentration Polarization

Alternating electric fields are commonly employed to trap and separate micro- and nano-particles within channel constrictions in microfluidic devices. Trapping mechanism is typically attributed to the electrostatic forces caused by the non-homogeneous electric field in the constrictions, and the phenomenon is known as insulator-based dielectrophoresis (iDEP). We recently reported experimental trapping of 500 nm and 1 um particles that cannot be explained by DEP forces alone [1] (Fig. 1).

In this work we show further experimental verification of particle trapping that cannot be explained using electrical forces only. Instead, we report numerical simulations showing observed trapping can be explained as the result of at least two different phenomena: flow vortices around the constrictions and hydrodynamic repulsion of the particles with the channel walls. Both mechanisms arise from Concentration Polarization Electroosmosis (CPEO) [2,3]. It is also shown that strong negative DEP prevents trapping, in agreement with experimental observations for particles larger than 2 micron. On the other hand, small particles follow the fluid flow (CPEO vortices) and no trapping is observed. Fig 2 (a) shows a diagram of the particle behaviour regimes as a function of Clausius-Mossotti factor (CM) and particle size. Fig 2 (b) is an example of a simulated particle trajectories leading to trapping. Thus, dominant DEP acts against trapping, contrary to classical claims on the origin of the trapping.

[1] R. Fernández-Mateo et al. Anal. Chem. 2021, 93, 44, 14667–14674. doi.org/10.1021/acs.analchem.1c02849
[2] R. Fernández-Mateo et al. Physical Review Letters 2022, 128(7), 074501. doi.org/10.1103/PhysRevLett.128.074501
[3] R. Fernández-Mateo et al. J. Fluid Mech. 2021, 924, R2, doi:10.1017/jfm.2021.650

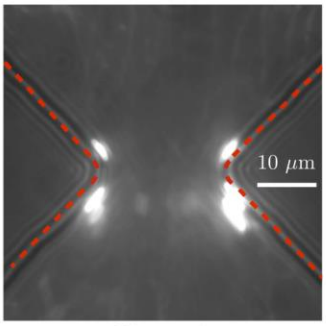

Figure 1

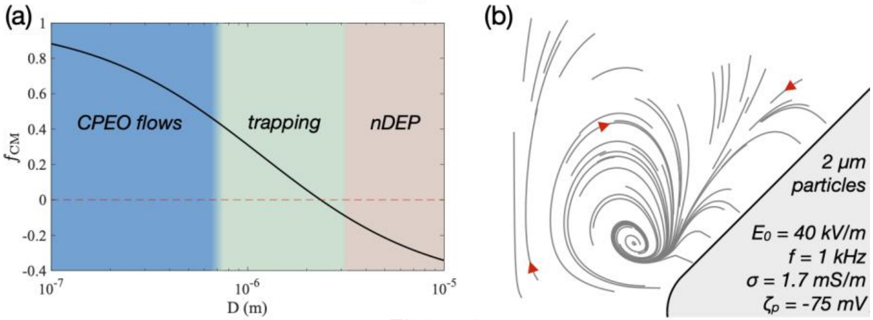

Figure 2

Poster #13

Fluid-sphere electrophoresis: Interfacial-exchange kinetics and interfacial-charge mobility

Reghan J. Hill

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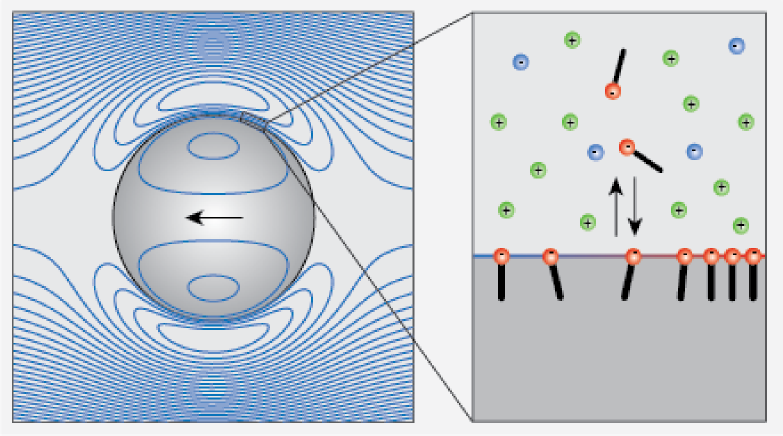
Keywords: Nano-Bubbles, Nano-Drops. Zeta-Potential, Electrophoretic Mobility, Interfacial Exchange; Interfacial Charge

Electrophoretic characterization of nano- and micro-meter scaled bubbles and drops is increasingly important in environmental and health related sciences. For example, nano-bubble existence and colloidal stability hinge on the interfacial charge, but this is invariably ascertained from electrophoresis experiments under the assumption that bubbles behave as rigid spheres. This work examines how coupling interfacial conservation relationships for spherical bubbles and drops to the standard electrokinetic model affects the electrophoretic mobility and apparent ζ-potential. Systematically varying the interfacial kinetic-exchange rate and surface-charge mobility unveils a variety of novel outcomes, reflecting subtle balances of hydrodynamic and electrical forces. In this talk, comparisons will be made with extant analytical theories and the computations of Baygents and Saville (J. Chem. Soc. Faraday Trans., 1991). The model will then be applied to ascertain interfacial charge densities for nano-bubbles and micro-bubbles, drawing on electrophoretic mobilities and ζ-potentials available in the literature.



Poster #14

Experimental Study of the Electro-Orientation of Metallodielectric Janus Particles

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Universidad de Granada, Granada, Spain

Keywords: Electro-Optics, Anisotropic Particles, Janus Paticles

The application of electric fields to Janus particles systems has revealed fascinating individual and collective phenomena [1, 2]. Despite the multiple studies of the dynamics of these particles based on microscope visualization, measuring the interaction between electrically polarized particles is required for a proper characterization of this complex phenomenology. In this context, characterizing the electrokinetic response of individual particles may help to understand the behavior of the whole system.

In this work, we focus on the less explored metallodielectric Janus particles that are also elongated. This additional anisotropy in the geometry of the particles not only broadens the interest of the system, but also the number of properties that can be explored. On this occasion, we have investigated the electrical birefringence of the system, a macroscopic property that allows obtaining information about the electro-orientation of the polarized particles [3]. In addition, we analyzed particles with different aspect ratio and compared these results with those of a morphologically similar system without metallization, i.e., not Janus and hence passive particles, providing a more complete view of their properties and behavior.

[1] Peng, C., et al. (2014). Phys. Rev. E 90(5), 051002.doi.org/10.1103/PhysRevE.90.051002
[2] Yan, J., et al. (2016) Nat. Materials 15(10), 1095-1099. doi.org/10.1038/nmat4696
[3] Arenas-Guerrero P. et al. (2018). Langmuir 35(3), 687-694.
doi.org/10.1021/acs.langmuir.8b03122

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Poster #15

Sliding Electrification and Surface Potential of Hydrophobic Surfaces

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Max Planck Institute for Polymer Research, Mainz, Germany

Keywords: Sliding Electrification, Hydrophobicity, Interfaces, Surface Potential

When a droplet slides on a hydrophobic surface negative surface charges are spontaneously deposited behind the drop, a process known as sliding electrification. The fundamentals of this phenomenon are still under debate and several hypothesis for explaining the origin of the charging were proposed. One of the most accepted explanations is that the surface charges causing the electrical double layer are partially left behind on the free solid surface.

Here we address the question whether it is possible to obtain zeta potentials of the solid-water interfaces by measuring the charge of sliding droplets. In Bista et al. (2023) [1] a model for predicting surface potential from the charge of sliding drops was presented were it is stated that, after a critical sliding distance, the drop charge reaches a constant value and then a constant surface potential is assumed.

In this work, spontaneous charging of sliding droplets on hydrophobic-coated surfaces and their experimental zeta potential were measured. By applying Bista et al model a comparison between the as obtained surface potential and experimental zeta potential is possible. This results show that Bista et al model accurately predicts zeta potential at low and neutral pH, while a discrepancy between model prediction and experiments appears as pH increases. The origin of this difference is not fully clear yet but several effects may be taking place, as adsorption kinetics of ionic species, screening of surface potential at high pH and possible solvent penetration and degrafting of the coating layer when increasing basicity in the aqueous phase. Finally, time dependence of zeta potential for the hydrophobic-coated surfaces will be discussed as a possible source of differences between the model and the experimental zeta potential, which evidences the complex nature of charging phenomena at liquid - solid interfaces.

[1] Bista, P. et al. J. Phys. Chem. Lett. doi.org/10.1021/acs.jpclett.3c02864

Poster #16

Capacitive Deionization in Microchannels Using Soft Electrodes: Experimental Results and Theoretical Predictions

Juan Antonio Lirio Piñar[1], Juan Calvo Yagüe[2,3], Silvia Alejandra Ahualli Yapur[1,3]

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3. Modeling Nature (MNat) Research Unit of Excellence, University of Granada, Granada, Spain

Keywords: Capacitive Deionization, Mathematical Modelling, Soft Electrodes, Polyelectrolyte Coating

Techniques based on electrochemical processes, that do not require high temperatures or pressures, have attracted a lot of interest as a possible alternative for next-generation water treatment and purification. One of the most developed emerging techniques in the field of charge transfer is the so-called capacitive deionization (CDI) known for its cyclic efficiency and reversibility. The basis of this technique lies in the capacitive property of the Electric Double Layer. The CDI process entails the movement of ions from a solution to the electrical double layer built in the porous electrodes, thereby leaving the solution partially desalinated. The use of functionalized electrodes with a polyelectrolyte coating, named as Soft Electrodes, substantially improves the efficiency of this method (Figure 1).

Based on previous models [1-3], we elaborate a one-dimensional theoretical model, for a CDI cell considering the polyelectrolyte coating electrodes. In this work, we have solved the equations that governing the ionic motion, the charge transfer, and the ion adsorption in micropores. The equations are numerically solved using the finite element method.

The theoretical predictions are compared with experimental results obtained using the CDI experiments carried out in microchannels using Soft Electrodes. The temporal and spatial evolution of the ion concentration profiles can be observed using fluorescent solution.

Theoretical and experimental results seem to indicate that the use of Soft Electrodes results in a decrease of approximately 20% in the number of ions remaining in the cell. This method could therefore prove to be a significant enhancement in large-scale implementation, for instance, in CDI based desalination plants.

[1] Nordstrand, J. et al. Nano Select. doi.org/10.1002/nano.202100270
[2] Hemmatifar, A. et al. The Journal of Physical Chemistry C. doi.org/10.1021/acs.jpcc.5b05847
[3] Suss, M. et al. Environmental science & technology. doi.org/10.1021/es403682n

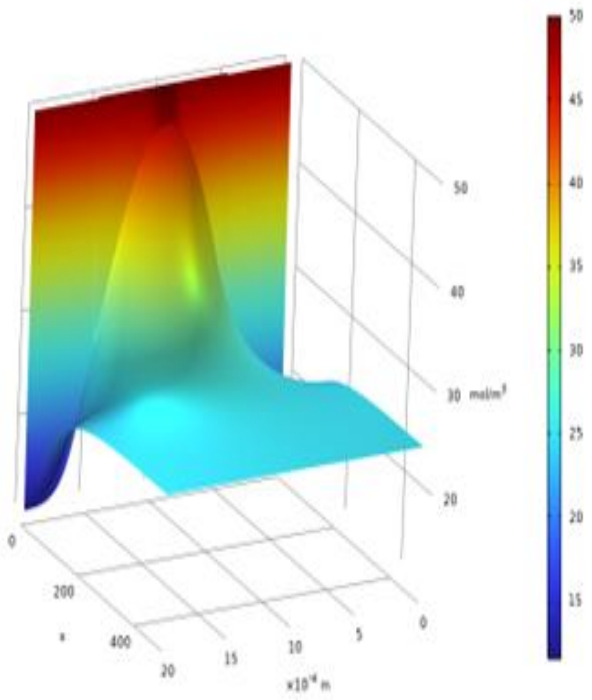

Figure 1: Concentration surface as function of spatial and temporal variables in a CDI cell.

Poster #17

Selection On Flocculation and Optimal Mixing Ratio for Enhanced Electro-Osmotic Dewatering of Waste Sludge

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Keywords: Flocculant, Electro-Osmosis, Waste Sludge, Dewatering

Accumulation of fine-grained waste sludge with high water content is nowadays increasing dramatically in China. Adding flocculant is a must-taken step for initial solid-water separation to reduce transportation and storage costs. Electro-osmosis is gaining increasing attention as an environmentally friendly technique for secondary dewatering. However, the optimum type and dosage of flocculant for self-weight settling and electro-dewatering is not necessarily the same. One dimensional sedimentation and electro-osmotic tests were performed on the effects of various flocculant additions with waste sludge from shield tunnelling site of one metro construction in Hangzhou. It is found that: 1) polymeric flocculants improve electro-dewatering rate by 17% ~ 71% for the first 12 hours, which is attributed to the increased pore size and permeability of slurry after flocculation treatment proved by the results of specific resistance to filtration and mercury intrusion porosimetry tests; 2) the larger dosage of flocculant, the faster the electro-osmotic rate decays during late stage of electro-osmosis. Therefore, the optimal dosage of flocculant for electro-dewatering is 0.2%, which is lower than 0.8% for sedimentation; 3) no significant difference between anionic and cationic flocculants is found in both settling and electro-dewatering performance for slurry treatment; 4) the excessive addition and higher molecular weight of flocculants indicate small benefit for the early stage of electro-osmosis, whereas its impact on the decrease of electro-osmotic rate for the later stage is much more significant, and the main reason is non-uniform distribution of pH and Zeta potential induced by electrolysis reactions under higher electric current; 5) higher dose of flocculant leads to higher electric current, which does not contribute to the enhancement of electro-osmotic flow, but results in the rise of energy consumption instead. In conclusion, the combined flocculation and electro-osmosis is very promising for dealing with waste sludge. Electro-osmotic behavior should be considered for selection on flocculation and optimal mixing ratio, which would not only enhance electro-dewatering but also avoid the environmental, economic and energy consumption problems caused by over-addition. The pH gradient should be conditioned for maintaining electro-dewatering efficiency. More investigations on various types of waste sludge are still demanding in further research.

Poster #18

The Charge of Dielectric Surfaces in CO 2 -Containing Aqueous Electrolytes

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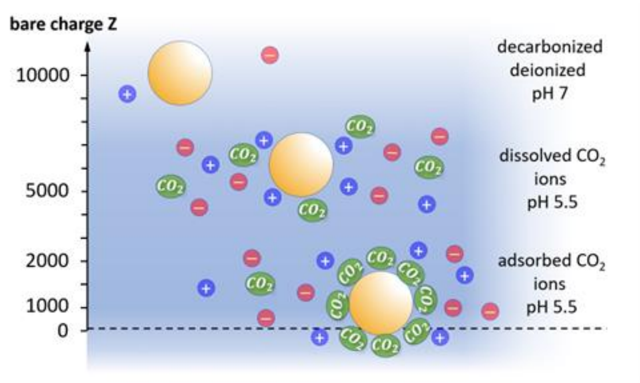
Keywords: Neutral CO2 , Electrode Charging, Dielectric Surfaces, Electrokinetics

Charged dielectric surfaces in contact with aqueous electrolytes are ubiquitous. We studied the behaviour of model surfaces by electro-kinetic experiments, Poisson Boltzmann Cell Model calculations with pH-driven charge regulation and Molecular Dynamics (MD) simulations [1,2,3,4]. Starting from hydrophobic or hydrophilic surface in contact with thoroughly deionized and de-carbonized water, we find that dissolved molecular CO2 leads to a drastic decharging of the surfaces. The effects go way beyond the expected decharging effects due to the dissociation products (screening and pH-driven charge regulation). MD-simulations show the formation of a diffusively adsorbed monolayer of molecular CO2. We propose, that in the CO2-loaden state, the local dielectric constant is significantly decreased and induces a dielectric charge regulation, i.e., an increased intramolecular interaction within surface groups and an increased interaction between neighbouring groups. Both can explain the observed decrease in effective surface group pK A and the corresponding shift of the i.e.p. As a consequence, cation-exchange properties are suppressed and co-ions switch from screening dominated behaviour to adsorption and surface re-charging at increasing CO2-concentrations. While an overview is given in the corresponding talk, the poster presents ample details on methods and models and a full set of results. Given the importance of charged surfaces in contact with aqueous electrolytes, we anticipate that our observations bear substantial theoretical challenges and important implications for applications ranging from desalination to biomembranes.

[1] P.Vogel. et al., J. Am. Chem. Soc. 144 (2022), 21080-21087.
[2] P.V., T.P., J. Colloid Interface Sci. 656 (2023), 280-288.
[3] P.V. et al., Soft Matter (submitted 2023). CO2-induced Drastic Decharging of Dielectric Surfaces in Aqueous Suspensions
[4] D. Botin, et. al., J. Chem Phys. 152, 244902 (2020).


bare charge Z
10000
5000
2000
1000
0
decarbonized
deionized
pH 7
dissolved CO_2
ions
pH 5.5
adsorbed CO_2
ions
pH 5.5
CO_2

Poster #19

Discriminating Electrokinetic Phenomena on Corrugated Membranes Using Micro-Particle Tracking Velocimetry

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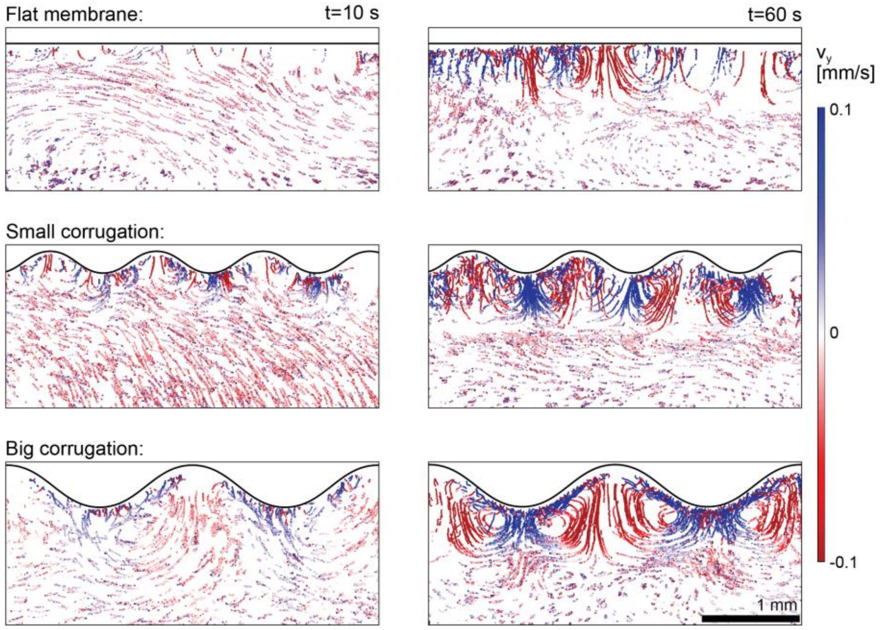
Keywords: Electroconvection, Overlimiting Current, Ion-Exchange Membranes, Electrodialysis

In this work, the impact of geometrical membrane corrugation on electroconvective and ion transport was investigated. A high-precision micro-particle tracking velocimetry setup is used to visualize the temporal evolution of electroconvective vortices on different membrane surface geometries while simultaneously evaluating mass transport through the monitoring of current-voltage curves.

A significant change in electro-hydrodynamic response inside a lab-scale electrodialysis cell was observed at overlimiting current densities for different corrugation sizes. A correlation between corrugation feature size, electroconvective vortex size, and their contribution to ion transport was revealed. Also, the superposition of small and large electroconvective vortices was observed, each coexisting at distinctly different velocities. Electroosmotic forces caused by the membrane corrugation were recognized to stabilize the typically chaotic electroconvective vortices. More extensive membrane features led to more stable vortices, aligning their counter-rotation with the membrane's geometry. A threshold for stable and unstable vortices was determined, and a characterization of transitioning to a chaotic and destabilized state was derived. Finally, the contribution of stable vortices to ion transport was evaluated, finding that stable, larger vortices lead to enhanced transport. These findings contribute to the proposal of optimizing membrane designs for electrodialysis application as a possible solution to overcome ion transport limitations at overlimiting current densities.

Temporal evolution of electroconvective vortices on corrugated ion exchange membrane surfaces



Poster #20

Electrostatic Interactions Influence Biomolecular Phase Separation and Wetting of Biological Surfaces

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Keywords: Phase Separation, Electrostatics, Capillary Forces, Microtubule Nucleation

The microtubule-based spindle organizes and segregates chromosomes during cell division. Thousands of microtubules nucleate rapidly and exhibit complex cooperative behavior, which is facilitated by numerous microtubule-associated proteins. A biomolecular condensate of the microtubule-associated protein TPX2 has been found to wet microtubule surfaces, in order to recruit and concentrate factors important for microtubule nucleation. Here, using atomic force microscopy, we directly measure the attractive capillary interactions on TPX2-coated microtubule surfaces. We find that the capillary interactions are significant and can therefore underly the functional role of TPX2 in microtubule nucleation and organization. The capillary interactions are dependent on the concentration of salt, which can also affect the phase boundary of TPX2 condensation. Taken together, these results indicate that electrostatic interactions between charged residues on TPX2 can drive its phase separation and influence the surface tension of the condensed phase. We construct thermodynamically-consistent mathematical models based on a modified Voorn-Overbeek theory to explain our observations.

Poster #21

Slip-Plane-Distance-Coincidences?

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Keywords: Zeta-Potential, Hydrodynamic Radius, Surface Complexation Model

Literature data for “apparent” slip-plane distances (taken as fit-values) are compared to changes in hydrodynamic radius for monodisperse particles with changes in pH and salt level, also available in the literature. Interestingly, values fall into the same ranges, with excessively high values for at low salt levels.

Additional comparisons with data from non-linear optical experiments, yield the same trends after scaling. These experiments are related to the orientation and/or the number of ordered water molecules. The relative changes from these experimental techniques in the extracted literature data also point to significant changes in the thickness of ordered water layers. However, they disagree with conclusions from crystal-truncation-rod measurements, which suggest structured water is not extending to the same extent to the solution side of the interface. The crystal-truncation-rod data are in agreement with the generally accepted view that the water structuring does not extend beyond the first few layers.

With increasing salt content, the non-linear optical data are possibly affected by the effect adsorbed ions have on the water structure, which could resolve the apparent contradiction to crystal-truncation-rod experiments.

In the case of the hydrodynamic radii the use of the published data is based on the presence of monodisperse particles. Some preliminary own measurements seem to support the published data.

To what extent all the observations can be brought together will be discussed, and additional observations suggesting long range ordering of interfacial water will be included in the discussion.

Poster #22

Pattern Formation in Planar Electrophoretic Cells

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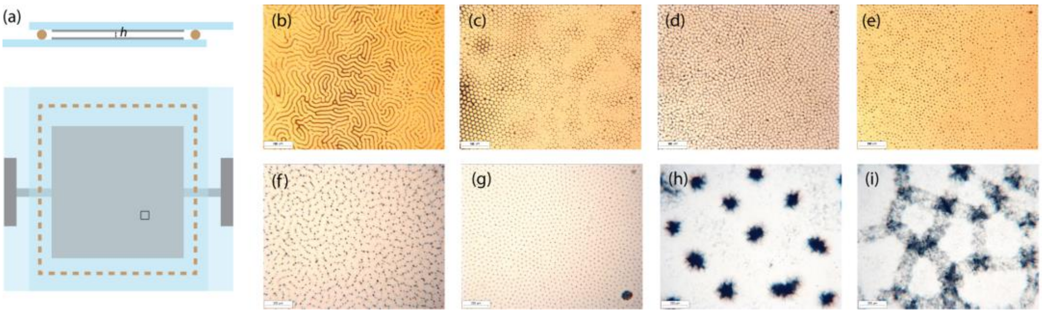
Keywords: Electrophoresis, Pattern Formation, Planar Cell, Nonpolar

In experiments on planar electrophoretic cells with nonpolar solvent and surfactant we observe an intriguing pattern formation of suspended pigment particles (see figure). The observed dependency of the patterns on concentrations, cell dimensions and applied voltage profile is so far not understood. A possible explanation is that the phenomenon is an expression of spinodal decomposition. We compare our observations with earlier reports of pattern formation in different environments [1, 2, 3]. The results are also part of a recently started project that aims to better understand electrokinetics in complex geometries and nonpolar environments.

[1] Rendos, A., Cao, W., Chern, M., Lauricella, M., Succi, S., Werner, J.G., Dennis, A.M., Brown, K.A., 2022. Electric field induced macroscopic cellular phase of nanoparticles. Soft Matter 18, 1991–1996. https://doi.org/10.1039/D1SM01650D

[2] Trau, M., Saville, D.A., Aksay, I.A., 1997. Assembly of Colloidal Crystals at Electrode Interfaces. Langmuir 13, 6375–6381. https://doi.org/10.1021/la970568u

[3] Lin, T., 2013. Dynamics of Charged Colloids in Nonpolar Solvents. Doctoral dissertation, Harvard University.



(a) Side and top view of a planar electrophoretic cell: two parallel ITO electrodes (1cm2) are a distance h apart. Patterns observed in the small square for h = 10 µm (b-e), 20 µm (f,g) and 50 µm (h,i) for various voltage amplitudes and frequencies. Suspension is composed of 0.2 wt% monodispersed TiO2 particles with an average diameter of 165 nm, dispersed in 0.5 wt% OLOA11000 dissolved in n-dodecane.

Poster #23

Coupling Ion Concentration-Polarization Based Analyte Preconcentration and On-Chip Electrochemical Sensing for Enhancement of Detecting Signal

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Keywords: Ion Concentration-Polarization, Electrochemical Sensing

Here, we integrated two key technologies within a microfluidic system, an electrokinetic preconcentration of analytes by ion Concentration Polarization (CP)1,2 and local electrochemical sensors3 to detect the analytes which can synergistically act to significantly enhance the detection signal. The combination of both techniques can produce synergetic effect with a significant improved sensitivity4, however, the current study4 for CP-based electrokinetic preconcentration and electrochemical sensing have been completely decoupled from each other. It is essential to gain a deeper fundamental understanding of their interaction, as potential adverse effects may arise, such as cross-talk between simultaneously applied electrically driven CP and electrochemical sensing electric fields as well as gaining continuous monitoring of analytes. This study presents an on-chip electrochemical sensing system that integrates CP-based preconcentration and local electrochemical sensing, facilitating both decoupled and coupled operation modes for continuous monitoring. This synergistic combination was validated by the intensified fluorescent intensities of CP-preconcentrated analytes and the associated enhanced electrochemical response using differential pulse voltammetry and chronoamperometry. The system performance was evaluated by varying the location of the active electrochemical sensor, target analyte concentrations, and electrolyte concentration using fluorescein molecules as the model analyte, and Homovanillic acid (HVA) as the target bioanalyte within both phosphate-buffered saline (PBS) and artificial sweat solution. The combination of on-chip electrochemical sensing with CP-based preconcentration renders this generic approach adaptable to various analytes. This advanced system shows remarkable promise for enhancing biosensing detection in practical applications, while bridging the gap between fundamental research and practical implementation.

REFERENCES

1. Li, M. & Anand, R. K. Analyst 141, 3496–3510 (2016).
2. Park, S. at al. Nanoscale 12, 23586–23595 (2020).
3. Ben-Yoav, H. et al Biosens Bioelectron 38, 114–120 (2012).
4. Lee, G. H. et al. Sci Rep 7, (2017).

Poster #24

Electrode Reaction-Free Electric Potential Probing For Precise Electrokinetic Response

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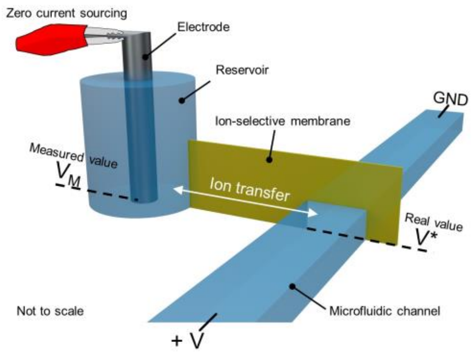
4. Inter-university Semiconductor Research Center, Seoul, South Korea

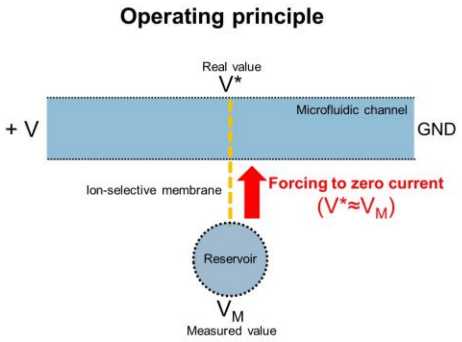
Keywords: Electric Potential Probe, Electrode Reaction-Free

Accurate measurement of electric potential in electrokinetic systems is critical for unraveling the complex electrokinetic and electrochemical phenomena, enabling researchers to estimate electric fields and resistance for detailed system characterization and manipulation. Recently, micro/nanofluidic devices have been increasingly employed in the field of bioanalysis, chemical separations, and environmental sensing, where in situ measurement of electric potential and(/or) electrolyte concentration is critical in those applications. Typically, electric potential is measured using patterned electrodes embedded in microfluidic chips, which operate through electron transfer at electrode-solution interface. However, applying an electric field to floating electrodes can cause phenomena such as faradaic ion concentration polarization [1] and induced-charge electro-osmosis [2], altering electrode reactions and flow. This interference can lead to inaccurate measurements, as the electrodes themselves may affect the channel.

In this study, we introduce an ion-selective membrane-based probe integrated into the microfluidic device, designed to measure potential without electrode reactions. While electron transfer at electrodes inevitably induces electrode reactions, ion transfer through the ion-selective membrane could minimize these reactions. Furthermore, to minimize the side effect on the channel, we connected the microfluidic channel and the measurement reservoir using a self-sealed patterning method [3], advantageous for visualization while minimizing the contact area. By sourcing zero current on the electrode of the measurement reservoir, the potential difference between the microfluidic channel and reservoir is maintained close to zero, allowing for the estimation of the actual value through the measured value. In the meantime, we evaluated the probe system's accuracy, bandwidth, and dynamic range. Our results demonstrated that the input impedance and current resolution of the probe system significantly influenced its accuracy. We also explored how parameters impacted the bandwidth of both the microfluidic and probe systems and found that ion transfer-based potential measurement enhanced the dynamic range. Therefore, we expect that our probe system would be an effective tool for desalination devices and feedback control systems that require in situ measurement of potentials or concentrations without external interference.

[1] Dhopeshwarkar et al, Journal of the American Chemical Society, doi.org/10.1021/ja8036405
[2] Squires et al, Journal of Fluid Mechanics, doi.org/10.1017/S0022112004009309
[3] Kim et al, Analytical Chemistry, doi.org/10.1021/ac800157q





Poster #25

Nonlinear Response of Streaming Current in Microchannels Coated by a Highly Charged Nanoporous Layer

Sehyuk Yoon[1], Hyomin Lee[2], Jihee Park[1,3], Sung Jae Kim[1,3,4]

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4. Inter-university Semiconductor Research Center, Seoul, South Korea

Keywords: Streaming Current, Nanoporous Layer, Nonlinearity, Surface-Engineering

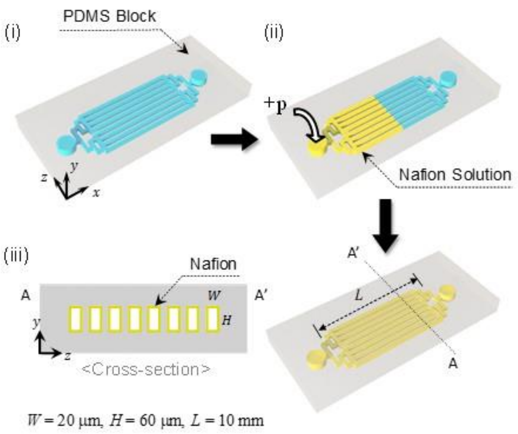
When an electrolyte is driven through a microchannel by external pressure, it stimulates the movement of cations within the electrical double layer near the channel walls, resulting in the generation of streaming current.[1] This phenomenon, known for its conversion of mechanical flow into electricity, presents considerable potential across various applications.[2] This study investigates the mechanisms behind streaming current generation within microchannels whose surface is coated with a highly charged layer, Nafion, particularly focusing on ion transport through the layer.

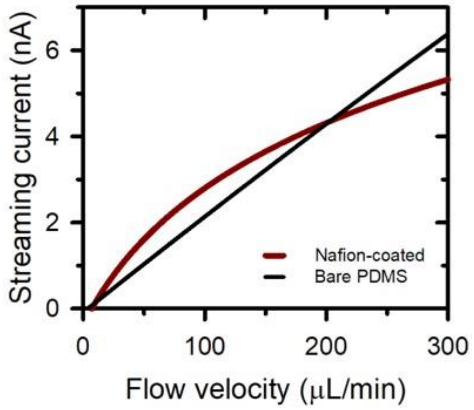
To intensify surface effects for precise analysis, we fabricated a microfluidic device using polydimethylsiloxane configured with a tournament channel layout. While uncoated microchannels showed a linear correlation between streaming current and flow rate, Nafion-coated channels exhibited an unpredicted nonlinear response to the flow rate.[1,2] Our numerical simulations unveiled a substantial conduction current flow within the Nafion layer, attributed to an induced electric field opposing the external pressure.

To reduce this nonlinearity and enhance the applicability of streaming current, we experimentally and numerically analyzed the influence of the thickness of the Nafion coating on the channels.[3] Thinner Nafion layers consistently demonstrated a reduction in nonlinearity and an enhancement in current production. We also developed a scaling law to summarize the factors influencing streaming current nonlinearity, including electrolyte concentration, and membrane properties as well as Nafion membrane thickness.

Coating the channel surface with a highly charged nanoporous layer to enhance streaming current can result in a nonlinear relationship between the streaming current and flow rate, making interpretation and application challenging. Through rigorous analysis, we were able to characterize the coated layer to reduce nonlinearity, while simultaneously enhancing streaming current itself. This improvement demonstrates easier interpretation of the streaming current, thereby opening up new possibilities for practical applications.

[1] van der Heyden, et al. Physical Review Letters. doi.org/10.1103/PhysRevLett.95.116104
[2] Yu, Longteng, et al. Advanced Materials Technologies. doi.org/10.1002/admt.201800430
[3] Kim, Junsuk, et al. Scientific Reports. doi.org/10.1038/s41598-017-04646-0





Poster #26

Concurrent Desalination and Hydrogen Production by Nanoelectrokinetic Ion Separation

Sehyuk Yoon[1], Sungjae Ha[2], **Jihee Park**[3], Sung Jae Kim[1,3,4]

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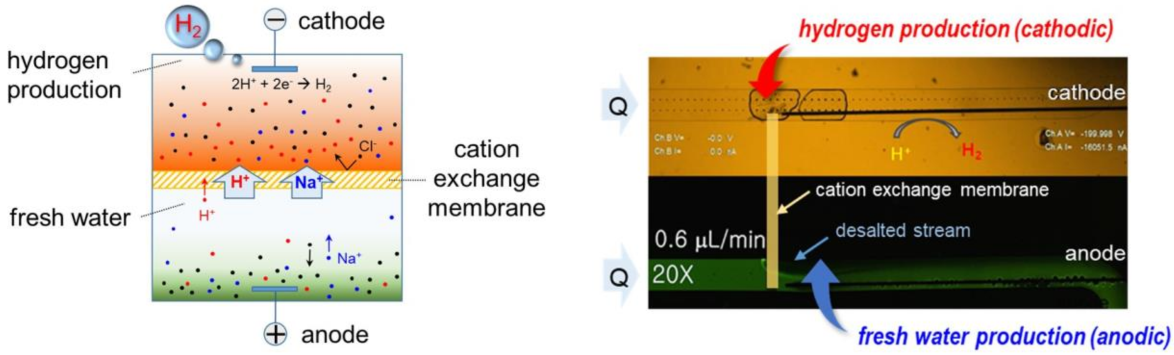
Keywords: Ion Concentration Polarization, Desalination, Hydrogen Production

The clean water scarcity and energy shortage are one of the most critical challenges nowadays. These two issues are interconnected, known as the "water-energy nexus," as providing clean water requires energy, and producing energy requires clean water. Recently, energy research has been exploded in the electrochemical production of hydrogen as an energy source, which bears a striking resemblance to electricity-powered desalination technique such as electrodialysis. Starting from this resemblance, we aim to develop a system that enables simultaneous production of fresh water and hydrogen gas by precisely regulating ion transport through ion exchange membranes. Our system utilizes the nanoelectrokinetic transport of ions through unipolar ion exchange membranes and their surrounding fluids[1,2], while electrodialysis utilizes bipolar membranes where hydrogen retrieval is challenging [3]. By applying a voltage to a cation exchange membrane, an ion depletion zone (IDZ) is formed on the anodic side and an ion enrichment zone (IEZ) on the cathodic side, a phenomenon known as ion concentration polarization (ICP). Our approach is to produce desalted water from the IDZ, while proton is reduced to hydrogen gas at cathodic electrode. First, we use micro-nano devices filled with pH indicator to demonstrate the generation of acidic brine for hydrogen production in the IEZ. By introducing microelectrodes inside the channels, we visualize simultaneous gas bubble formation at the reduction electrode during desalination. The fluid turns to be basic after the hydrogen gas formation, evidenced by the color change of pH indicator of the solution collected at the cathodic reservoir. This hydrogen gas can potentially be used to save an external power input to run the ICP desalinator if it is converted to an electrical energy source using a fuel cell. Furthermore, we analyze the transport of sodium ions and protons competing through the membrane at various experimental conditions. This nanoelectrokinetic study for the ion transport through the membrane will play a critical role in realizing simultaneous water desalination and electrolytic hydrogen production.

[1] Kim, S. J. et al. Physical Review Letters. doi.org/10.1103/PhysRevLett.99.044501
[2] Kim, S. J. et al. Nature Nanotechnology. doi.org/10.1038/nnano.2010.34
[3] Al-Amshawee, S. et al. Chemical Engineering Journal. doi.org/10.1016/j.cej.2019.122231



Schematics and experimental demonstration of simultaneous desalination and hydrogen production by nanoelectrokinetic selective ion separation

Poster #27

Brownian Dynamics Of Interacting Particles Confined In An Aqueous Hybrid Electro-Optical Trap

Carlos David González Gómez[1,2], Emilio Ruiz-Reina[2], Raúl A. Rica[1]

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Keywords: Dielectrophoresis, Paul Trap, Optical Trap

The manipulation of micro/nanoparticles dispersed in a liquid is highly demanded for various applications in both basic science and industry. Trapping in aqueous solutions can be achieved e.g. using optical tweezers, where a tightly focused laser beam is able to trap individual dielectric particles in several applications in biophysics, stochastic thermodynamics, to name but a few [1]. Nonetheless, it has some drawbacks, like limited applicability with light-absorbing particles. Moreover, trapping multiple particles in the same optical well leads to aggregation, and the individual dynamics cannot be resolved.

Alternatively, trapping of charged particles of any material can also be achieved with electric fields (EF), making use of either Paul trapping [2], dielectrophoresis [3,4], or both [5]. Here, we present an electro-optical trap that is able to trap tens of particles in a microfluidic device combining the benefits of the two techniques. The dielectrophoretic trap is constructed by two gold microelectrodes deposited on borosilicate glass with ring geometry and implemented together with an optical tweezers setup, which allows us to create the aforementioned hybrid trap. First, we characterize the trap by video tracking the diffusion of a single particle in the potential well. We estimate the EF distribution with the help of the optical tweezers. Furthermore, we track the trajectory of several particles simultaneously and extract information of their interactions from the analysis of their mean squared displacement using two types of polystyrene particles, one of which strongly polarize in presence of an AC electric field and tend to form chains. We also study the difference in trap stiffness between DEP trap, optical trap, or hybrid trap. Finally, we discuss the prospects of such a device.

[1] J. Gieseler et al., Adv. Opt. Photon. 13 74–241 (2021).
[2] W. Guan, et al., Proceedings of the National Academy of Sciences 108 9326-9330 (2011).
[3] P. Y. Weng et al., Biomicrofluidics, 10 011909 (2016).
[4] M. R. U. Rahman, et al., Biomedical Microdevices 23 33 (2021).
[5] W. Guan, et al. Nanotechnology 22 245103 (2011).

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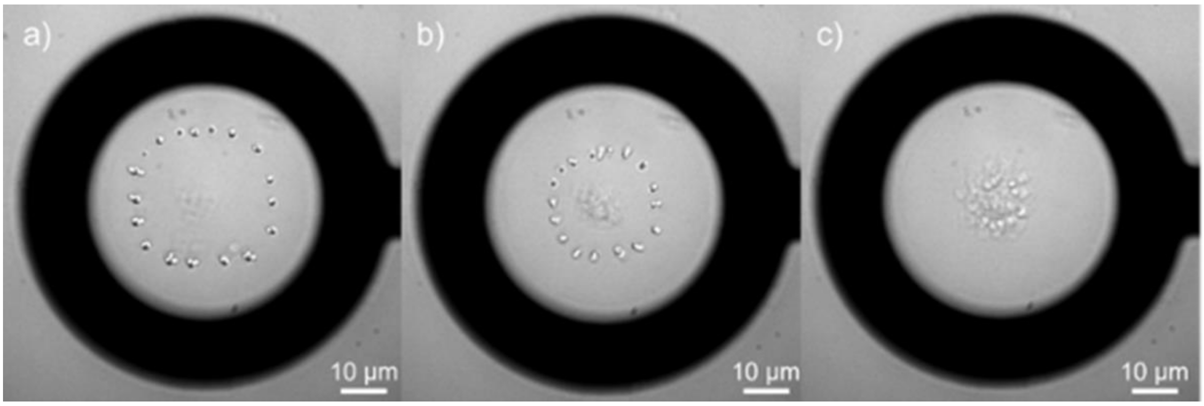

Figure 1: a) 1 μm SiO2 particles optically trapped within the DEP trap. b) and c), after we switched off the optical traps, the particles quickly moved to the center of the DEP trap, where the potential is lower.

Poster #28

Nanopatterning With Polyelectrolytes: Influence Of Substrate And Surface Coverage On The Apparent PAMAM Dendrimer Charge

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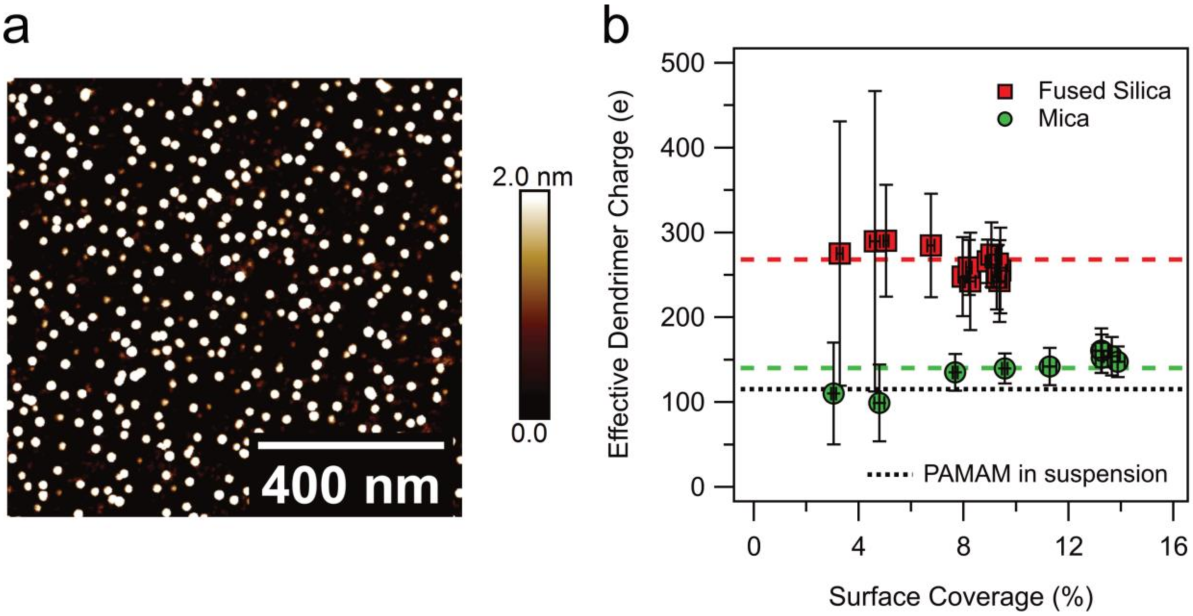
Keywords: Streaming Potential, Atomic Force Microscopy, Adsorption, Nanopatterning

The electrokinetic behavior of heterogeneously charged surfaces is essential for many applications, such as protein adsorption or surface coatings. The adsorption of polyelectrolytes is a well-established approach to tune the overall surface charge [1]. However, to deduce surface properties from electrokinetic techniques to a high degree of accuracy, effects due to the interaction of polymeric adsorbate and the collector surface must be considered, most importantly charge regulation [2]. Here, we used poly(amidoamine) (PAMAM) dendrimers as model system. PAMAM dendrimers are a class of highly defined polyelectrolyte macromolecules with very high surface charges and a well-defined shape [3]. Their adsorption follows the so-called random sequential adsorption (RSA) model and leads to a fractional surface coverage. Due to their size and characteristic shape, their surface coverage can be determined directly from AFM imaging, making PAMAM an ideal model system for studying heterogeneous charge distributions by electrokinetics and direct force measurements [2]. In this study, we propose an approach to quantify adsorbent-substrate charge regulation and inter-PAMAM charge regulation by combining the streaming potential technique and atomic force microscopy.

The adsorption of polyelectrolytes does not only lead to charge neutralization of the substrate but also to charge inversion, depending on the adsorbed amount on a given collector substrate. Various parameters have an influence, such as surface chemistry of the substrate, ionic strength, and pH. The zeta-potential and, thus, the overall surface have been directly determined from the streaming potential measurements on flat substrates of mica and silica. Thus, the effective charge Zeff of the adsorbed dendrimers can be determined as a function of fractional surface, which has been determined independently by AFM-imaging. Thereby, we could demonstrate the effective charge of the dendrimers strongly depends on the substrate (charge regulation with the substrate) but only weakly from the surface coverage (inter-dendrimer charge regulation). Hence, the often-inherent assumption of a linear proportionality between overall zeta-potential and surface coverage should be, in most cases, fulfilled.

[1] Morga, M. et al. Journal of Colloid and Interface Science. doi.org/10.1016/j.jcis.2015.05.044
[2] Popa, I. et al. Physical Chemistry Chemical Physics. doi.org/10.1039/b925812d
[3] Pericet-Camara, R. et al. Chemical Communications. doi.org/10.1039/b612249c



(a) AFM image of the PAMAM G10 dendrimers adsorbed onto a fused silica surface in the saturation limit and (b) effective dendrimer charge as function of the PAMAM surface coverages on fused silica and mica at pH 5 and an overall ionic strength of 5 mM in KCl.

Poster #29

PH Hysteresis of Zeta Potential and Electroviscosity in Alumina Porous Membrane

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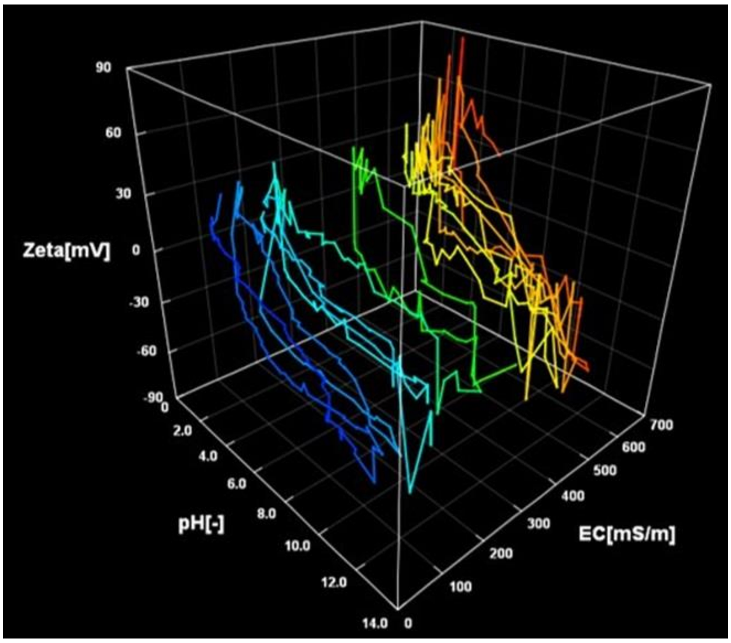
Keywords: Porous Membrane, Filtration, PH Hysteresis, Surface Reaction Kinetics

The microfiltration/ultrafiltration processes are one of the most attractive application area of electrokinetic phenomena because they are widely used in industries or basic social infrastructures due to their ability to produce highly-quality effluent by removing particulate materials or solutes. The basic phenomena occurred in the filtration process are liquid flow in porous media and the interaction between pore surface and particles or solutes in feed stream, which are typical electrokinetic phenomena. The challenges of these filtration processes are generally recognized the prediction of separation performance and the reduction of energy consuming and the zeta potential of pore surface and the electrovisocusity are directly useful for understanding the filtration phenomena and for enhancing their performances [1].

In this study the responses of streaming potential and electroviscosity of an alumina microfiltration membrane with a pore size of 0.2 μm to a wide range of pH and KCl concentrations using the newly developed high-throughput measurement setup. The detail profiles of the streaming potential and electroviscosity against KCl concentration were discussed from the viewpoints of EDL overlapping in pore structure. The pH profiles of zeta potential of pore surface showed pH hysteresis depending on pH change direction. This pH hysteresis was discussed from the kinetics of the surface reaction between H+ or OH- and surface hydroxyl groups. These findings will be useful for designing novel membrane materials and for developing novel procedure of filtration processes.

[1] G. Kaur. Et al. J. Memb. Sci. doi.org/10.1016/j.memsci.2023.121550.



Response of zeta potential against wide range of pH and KCl concentration

Poster #30

Nanobubble-Assisted Formation of Non-Gaseous Nanoparticles in Water

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Keywords: Nanobubble, Nanoparticle

For the past decade, there has been a heated debate regarding the existence of stable bulk nanobubbles in water [1]. To differentiate between gaseous particles, solid particles, and liquid droplets, it is crucial to measure the mass density of the nanoparticles. In this study, the mass density of nanoparticles generated during the nanobubble formation process was determined by observing sedimentation equilibrium and Brownian motion using dark-field microscopy. The size of the nanoparticles was about 450nm whereas the measured mass density ranged from 1.06 to 1.07 g/cm3, which was higher than that of water. This indicates that the nanoparticles, often referred to as stable bulk nanobubbles, are not gaseous. A comparison between treated and untreated solutions revealed that nanobubble generation aids in the formation of non-gaseous nanoparticles, which then sediment under gravity in water [2].

[1] D. Rak, M. Ovadova, and M. Sedlak, J. Phys. Chem. Lett. 10, 4215 - 4221 (2019).
[2] R. Miyazaki, Y. Kimura, and Y. Uematsu, submitted (2024).

Poster #31

Peculiarities of Electroosmotic Transport of Uncharged Impurities in Natural Fine Disperse Systems

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Keywords: Diffusion Coefficient, Electroosmotic and Hydrodynamic Flows, Hydrophobic Compounds, Solubilisation

The electric field is widely used in the processing of concentrated dispersions, including the electroosmotic removal of uncharged undesirable impurities from natural disperse systems. Among the most studied features of the electrotreatment of such dispersions is the regulation of the pH of the pore solution and, accordingly, the electrokinetic potential of the particles. However, due to the heterogeneity of the surface charge of particles that are components of natural dispersed systems, and the complex geometry of the pore space, electroosmotic transport of uncharged impurities through the dispersion is accompanied by a number of complicating factors. In particular, this applies to hydrophobic compounds that must be solubilized for removal.

It is shown that the optimal option is the use of nonionic surfactants, which cannot change the surface charge of dispersion particles to the opposite or cause electrophoresis of the compound/surfactant complex in the opposite direction to electroosmosis. Due to the possible adsorption or localization of the complexes in too narrow pores, their diffusional transport is also important.

To find out the factors that affect the movement of uncharged impurities in the dispersion medium, a special technique for determining the diffusion coefficients of compounds or their aggregates with surfactants and a theoretical model for the speed of their diffusion and electroosmotic spread in the dispersion were developed, which made it possible to establish the peculiarities of the transport of impurities. The results obtained for the kaolinite-based model system showed that the effective diffusion coefficient of these aggregates is different in the absence and presence of an electric field.

Due to the narrowing of the pore space when using an electric field in the dispersion, local pressure drops occur, which lead to the formation of hydrodynamic flows opposite to electroosmosis. At the same time, the different character of electroosmotic and hydrodynamic flows is important, which leads to a sharp change in the direction of movement of liquid near the surface of kaolinite particles and increases the effective diffusion coefficient, promotes the desorption of impurities and their transport from stagnant areas to the area of intense electroosmotic flow with subsequent removal from the dispersion.

Poster #32

Numerical Analysis of The Stationary Electrical Response of Ion-Exchange Membrane Systems Under Reverse Electrodialysis Conditions

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Keywords: Electrodialysis, Desalination, Reverse Electrodialysis, Network Simulation Method

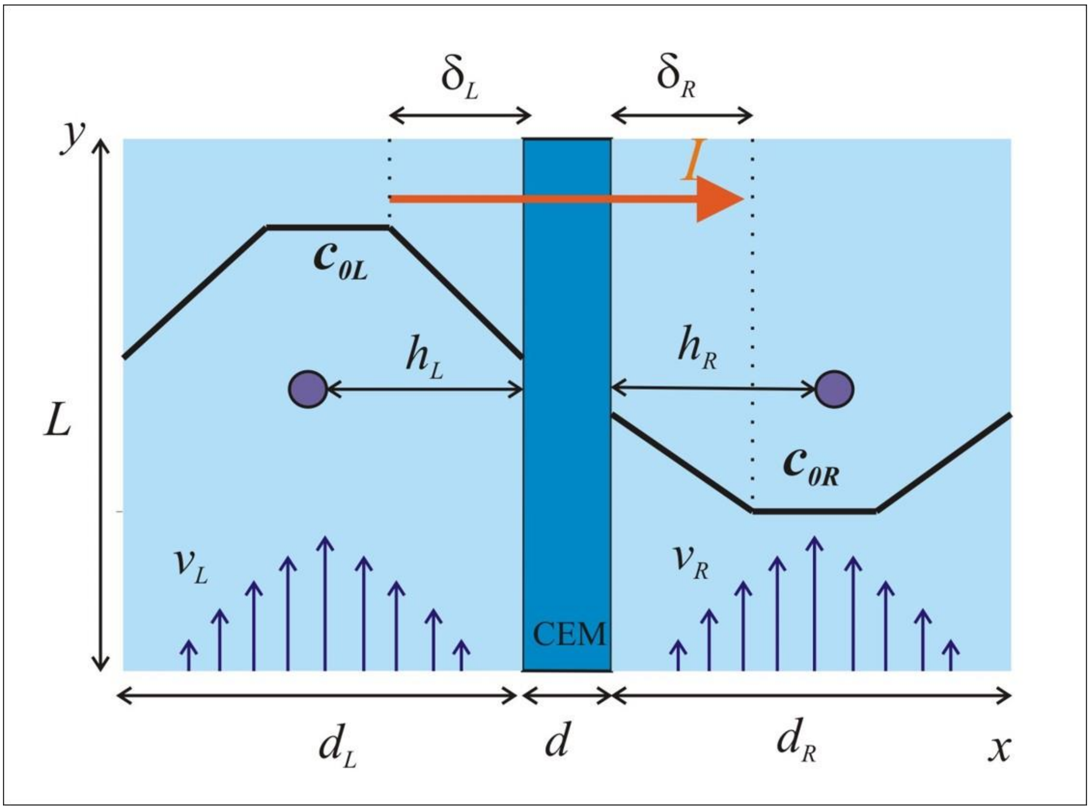
Nowadays, studies on ionic transport through ion-exchange membrane systems are receiving considerable attention because of the interesting environmental applications of these systems in different fields of science and technology such as electrodialysis for seawater desalination, or renewable energy harvesting.

Reverse electrodialysis (RED) is one of the emerging membrane-based technologies that can capture the available energy when waters with different salinity mix. RED stacks contain alternating anion and cation exchange membranes that separate salt solutions with different concentration. Selective transport of ions through the membranes creates an electric potential across each one, which drives electric current through an external electric circuit.

Evolution with direct electric current of the electric power supplied to the load resistor is well known in ion-exchange membrane systems under RED conditions, although theoretical studies have focused on ideally selective membranes, which are fully impermeable to the co-ions. However, ion-exchange systems with membranes permeable to both counter- and co-ions in solution are specially affected by the salinity gradient characteristic in a RED stack.

In this work, we present the results of a numerical study on the stationary electrical response of an ion-exchange membrane system under RED conditions by using the network simulation method [1], which is based on a finite differences scheme. The ionic transport processes are described by means of the Nernst-Planck flux equations and the electrical neutrality condition not only in the diffusion boundary layers (DBLs) but also in the membrane, and the Donnan equilibrium relations at the interfaces. The study is done for different values of the membrane fixed-charge concentration and the water flow velocity inside the intermembrane channels. The fluid flow velocity and the thickness of the DBLs are related by numerically solving a 2D diffusion-convection problem, using a parabolic velocity profile, in an intermembrane channel in the limiting current regime. Evolution with electric current of the voltage across the load resistor and the supplied electric power are analyzed for different values of the membrane fixed-charge concentration and the water flow velocity.

References:
[1] Moya A.A., Desalination. doi.org/10.1016/j.desal.2016.04.016392



Sketch of the reverse electrodialysis stack

Poster #33

Impedance-Frequency Response of Electrolytic Cells: Effect of the Back Flow of Fluid Induced by the Motion of the Ions.

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Keywords: Impedance, Ionic Size, Electrolytic Cells

When studying the impedance-frequency response of electrolytic cells with blocking electrodes, the theoretical model based on the Nernst-Planck flux equations and the Poisson equation is one of the most widely used. In this model, the electrolyte solution made of the solvent and the suspended ions is treated as an incompressible assuming furthermore full dissociation and point-like charges with equal mobilities. Although the standard formulation of the Poisson-Nernst-Planck (PNP) model and the associated boundary conditions are widely used, the numerous discrepancies among the theoretical predictions and the experimental determinations pointed to the necessity to review the assumptions used in the theoretical model. In this sense, in the last decades, several authors modified the PNP model to eliminate the point ion approximation. Most of these works use a Bikerman-type expression to include the ion-ion interactions due to finite volume of the ions in the Nernst−Planck flux equations.

Although this modification predicts important changes of the system in equilibrium, there is hardly any influence of the finite ionic size on the small-signal frequency response of electrolytic cells except for high applied DC voltages and low AC frequencies. However, it should be noted that the inclusion of steric effects in the PNP model does not necessarily imply that ions have a finite size: there is only a restriction on their ability to approach one another. On the contrary, a finite ion size implies that ions have a finite volume that can no longer be occupied by the suspending medium, which leads to the movement of matter in the system and produces the appearance of ion-ion and fluid-ion interactions. In effect, when ions move from the electrical double layer towards the bulk electrolyte solution and vice versa a movement of the solvent due to the volume occupied by the ions occurs: the solvent back flow.

The main purpose of this work is to include this solvent back flow induced by the ionic motion in the theoretical model and study how the impedance-frequency response of electrolytic cells is affected.

Poster #34

Physicochemical Characterization of Polysaccharide Films Embedded with Bioactive Substances

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Keywords: Crosslinking; Encapsulation; Carboxymethylcellulose; Citric Acid

This study involved the preparation and comprehensive evaluation of bioactive films made from sodium carboxymethyl cellulose (CMCNa), crosslinked with citric acid (CA), with a particular focus on their suitability for various applications, notably food packaging. The films exhibited favorable characteristics such as appropriate thickness, transparency, and moisture content, all crucial for effective packaging. Moreover, they demonstrated exceptional moisture absorption rate and barrier properties, attributed to the high concentration of CMCNa and the incorporation of CA. Mechanical strength, as determined by tensile strength and elongation at break values, remained unaffected by crosslinking and the presence of bioactive components. Thermal stability was evident through distinct weight loss events at different temperature ranges, with crosslinking contributing to slightly improved thermal performance. Additionally, the films exhibited varying levels of antioxidant activity, influenced by temperature and film solubility in different media, indicating their potential for diverse applications. Overall, these bioactive films showed promise as versatile materials with desirable properties for food packaging and related uses, particularly in scenarios where the controlled release of bioactive components can enhance the shelf life and safety of food products. These findings contribute to the expanding research in biodegradable and functional food packaging materials.

Poster #35

Physico-Chemical Study of Curcumin and its Application in O/W/O Multiple Emulsion

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Keywords: Curcumin Multiple Emulsion; Delivery System; Emulsion Stability; Encapsulation

Curcuma, renowned globally for its myriad health benefits, was the subject of this study. The research entailed conducting physicochemical analyses on both a curcumin standard sample and multiple emulsions containing curcumin. Over a span of 21 days, the emulsions underwent scrutiny for thermal behavior and stability. Confocal Laser Microscopy (CLSM) was utilized to visualize the encapsulation within the emulsions. Through Modulated Differential Scanning Calorimetry (MDSC) and HPLC techniques, various curcuminoids (including curcumin, demethoxycurcumin, bis-demethoxycurcumin, and cyclocurcumin) were identified in the curcumin standard.

Moreover, MDSC proved to be a viable alternative to HPLC in determining curcuminoid substances. The analysis revealed a curcumin release equilibrium value of 0.18 w.% after 14 days. Additionally, an enlargement in the emulsion size was noted by the study's conclusion at 21 days, while the emulsion stability index (ESI) showed a 55.8% increase between days 7 and 21. CLSM observations distinctly captured nano droplets of the oil phase containing dispersed curcumin particles confined within water-based carboxymethylcellulose micelles.

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