



Location:

Marinus Ruppertgebouw A
Leuvenlaan 21, 3584 CE Utrecht

Date: Friday, 11 October 2019

Time: 9:30 – 18:00

Morning 9:50 – 12:30, Place: Ruppert A

9:50 – 10:00, Opening

10:00 – 10:30, Surface forces generated by the action of electric fields across electrolyte films, **Susan Perkin**

10:30 – 11:00, Ion transport in membrane processes, **Rob Lammertink**

****break****

11:15 – 11:45, Concealed Colloidal Charge, **Ben Erne**

11:45 – 12:00, Giant thermoelectric response of nanofluidic systems driven by water excess enthalpy,
Laurent Joli

12:00 – 12:30, Electrochemistry in micro- and nanochannels controlled by streaming potentials, **Serge Lemay**

****lunch****

Afternoon: 13:30 – 17:00, Place: Ruppert Wit

13:30 – 14:30: poster session in the hallway next to Ruppert Wit

14:30 – 15:00, Ion adsorption, hydration, and the structure of the electric double layer: recent insights from high resolution Atomic Force Microscopy, **Frieder Mugele**

15:00 – 15:45, Limiting current and electro-osmotic flows in alkaline water electrolysis, **Willem Haverkort**

Dynamic Perturbation of the Electrical Double Layer with an Electrochemical AFM for Confined Metal Electrodeposition, **Mark Aarts**

Dissolution couples flow to surface charge, **Willem Boon**

15:45 – 16:15, Continuum modeling of electrodialysis including acid-base reactions and electrostatic cooling, **Maarten Biesheuvel**

16:15 – 16:45, Light metal hydride nanocomposites as room temperature solid electrolytes, **Petra de Jongh**

16:45 – 17:30, Break-out session and future directions

Closing

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INVITED TALKS

Surface forces generated by the action of electric fields across electrolyte films

Susan Perkin, Oxford University

Electric fields act across liquid or soft films in many technological and natural contexts, such as in liquid crystal displays, touch screens, and biological cell membranes. For dielectric fluids, the field scales inversely with film thickness such that micro-scale films require only small voltages applied to create an electric field sufficient to compete with thermal forces and manipulate the fluid structure and interactions. With electrolytic films, however, the effect of field is more complex (and interesting).

In my laboratory we perform high-resolution measurements of the force between surfaces across liquids using a Surface Force Balance (SFB). With this approach we are able to confine liquids to thin films and study their structure and mechanical, electrochemical, optical, and other properties. In this talk I will present recent experiments with an SFB modified to incorporate two gold electrodes on the confining surfaces. An electric field is imposed perpendicular to an electrolyte film, and the resulting surface force is measured as a function of time (and voltage, frequency, etc). An alternating electric field induces a force which diverges substantially from the calculated static response of the electrolyte. The magnitude of the force is larger than predicted, and the approach to steady state in electrolyte is slow compared to both the electrochemical and viscous timescales of the system. The non-trivial electrolyte response in AC electric fields may be connected to several recent reports of unexpected and bifurcating forces driving colloids in AC fields.

Ion transport in membrane processes

Rob Lammertink, University of Twente

Ion selective membranes find a plethora of applications in many processes, including electrodialysis, fuel cells, and diffusion dialysis found in water treatment and food industry. Here, I will highlight our experimental advancements regarding the study of the ion transport through and near these charge selective interfaces. Examples will include electrodialysis with strong concentration polarization, microfluidic observations, as well as diffusion dialysis. Membrane types include conventional high fixed charge density membranes, weakly charged hydrogel based membranes, and ultrathin graphene membranes.

Concealed Colloidal Charge

Ben Erne, Utrecht University

The electric surface charge is a key property of liquid-dispersed colloidal particles. Usually, however, only part of the charge manifests itself in colloidal stability and electrophoretic mobility: the charge corresponding to the diffuse, outer part of the ionic double layer. More challenging to reveal is the compact, inner part of the double layer, with its adsorbed solvent molecules and ions. This so-called Stern layer is better known in electrochemistry, where it can more easily be shown that it often dominates the double layer charge at the solid-electrolyte interface. Here, present-day experimental methods will be discussed

Electrochemistry in micro- and nanochannels controlled by streaming potentials

Zinaida A. Kostiuhenko, Jin Z. Cui and Serge G. Lemay, University of Twente

Fluid and charge transport in micro- and nanoscale fluidic systems are intrinsically coupled via electrokinetic phenomena. While electroosmotic flows and streaming potentials are well understood for externally imposed stimuli, charge injection at electrodes localized inside fluidic systems via electrochemical processes remains to a large degree unexplored. Here we employ ultramicroelectrodes and nanogap electrodes to study the subtle interplay between ohmic drops, streaming currents and faradaic processes in miniaturized channels at low concentrations of supporting electrolyte. We show that electroosmosis can, under favorable

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circumstances, counteract the effect of ohmic losses and shift the apparent formal potential of redox reactions that either conceal or reveal the Stern layer at the surface of colloidal particles.

Ion adsorption, hydration, and the structure of the electric double layer: recent insights from high resolution Atomic Force Microscopy

Frieder Mugele, University of Twente

Surface charge and the distribution of ions in the vicinity of solid-water interfaces are governed by the balance of interactions between solid, solvent, and solutes. They play a central role for a wide range of phenomena and processes in nature, science, and technology. I will discuss recent insights into the adsorption of mono- and divalent ions at mineral electrolyte interfaces based on high-resolution Atomic Force Microscopy (AFM). Our results illustrate the complex structure of the inner part of electric double layer. Specifically, we show that short range hydration forces typically dominate over classical DLVO forces when the AFM tip approaches the solid surface to distances of approximately 1nm or less. The strength and robustness of these hydration forces, which is confirmed in MD simulations, suggest a pivotal role of hydration effects for macroscopic adhesion and friction and in particular also for any (electro)chemical reaction that requires intimate contact between a dissolved reactant and a solid electrode or catalyst surface, as frequently encountered in recent applications for energy conversion and storage.

Continuum modeling of electro dialysis including acid-base reactions and electrostatic cooling

Maarten Biesheuvel, Wetsus, European centre of excellence for sustainable water technology

Electrodialysis (ED) is one of the most powerful methods to (selectively) desalinate water using electrical field effects. The ED platform can also be used for related methods of energy harvesting (osmotic power, or blue energy), energy storage (blue battery) or CO₂ capture. We present theoretical continuum approaches to model performance of ED systems in terms of ion selectivity and energy use, which include ion-ion reactions (acid-base reactions) as well as coion and water flow through the membranes. We focus on self-developed semi-analytical computational methods without using commercial software such as Comsol. We show both experimentally and theoretically how in ED systems, there is not only local electrostatic heating, but also cooling can take place.

Light metal hydride nanocomposites as room temperature solid electrolytes

Petra de Jongh, Peter Ngene, Debye Institute for Nanomaterials Science, Utrecht University

A central goal in current battery research is to increase the safety and energy density of Li-ion batteries. Electrolytes nowadays typically consist of lithium salts dissolved in organic solvents. Solid electrolytes could facilitate safer batteries with higher capacities, as they are compatible with Li metal anodes, prevent Li dendrite formation and sulphur shuttling, and eliminate risks associated with flammable organic solvents. Less than 10 years ago, LiBH₄ was proposed as a solid-state electrolyte. It showed a high ionic conductivity, but only at elevated temperatures. Since then strategies have been developed to extend the high ionic conductivity of LiBH₄ down to room temperature, and other light metal hydrides have been explored as solid electrolytes [1].

Using LiBH₄ as an example we will discuss how the properties of solid electrolytes can be modified by forming nanocomposites with metal oxides, leading to an enhancement of the room temperature ionic conductivity of more than three orders of magnitude [2]. DSC measurements combined with solid state NMR allow to identify how the nanoconfinement and presence of interfaces modify the phase stability and the Li⁺ mobility. Systematic studies show how the ionic conductivity can be optimized by tuning the nanostructure and



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interfaces in these nanocomposites. [3] Finally, promising results have been obtained in using these materials as solid-state electrolytes in next generation all-solid-state lithium-sulphur batteries. [4]

Keywords: solid state electrolytes, lithium borohydride, nanocomposites

[1] de Jongh et al. J. Appl. Phys. A (2016), 122:251.

[2] Blanchard et al., Adv. Funct. Mater. 25 (2015), 182.

[3] Ngene et al. ChemPhysChem (2019).

[4] Blanchard et al, J. Electrochem. Soc. (2016).

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CONTRIBUTED TALKS

Giant thermoelectric response of nanofluidic systems driven by water excess enthalpy

Laurent Joly, Université Lyon 1 - Institut Lumière Matière, France

Nanofluidic systems could in principle be used to produce electricity from waste heat, but current theoretical descriptions predict a rather poor performance as compared to thermoelectric solid materials. I will present a recent work where we investigated the thermoelectric response of NaCl and NaI solutions confined between charged walls, using molecular dynamics simulations. We computed a giant thermoelectric response, two orders of magnitude larger than the predictions of standard models. We showed that water excess enthalpy - neglected in the standard picture -- plays a dominant role in combination with the electroosmotic mobility of the liquid-solid interface. Accordingly, the thermoelectric response can be boosted using surfaces with large hydrodynamic slip. Overall, the heat harvesting performance of the model systems considered is comparable to that of the best thermoelectric materials, and the fundamental insight provided by molecular dynamics suggests guidelines to further optimize the performance, opening the way to recycle waste heat using nanofluidic devices."

Limiting current and electro-osmotic flows in alkaline water electrolysis

J.W. (Willem) Haverkort, Delft University

Microporous separators are used in alkaline water electrolyzers to separate oxygen and hydrogen. However, potential differences induce an electro-osmotic flow that influences the gas purity. An insightful binary electrolyte Nernst-Planck model was developed and successfully compared with experimental results."

Dynamic Perturbation of the Electrical Double Layer with an Electrochemical AFM for Confined Metal Electrodeposition

Mike Aarts, Institute AMOLF

Understanding and directing electrochemical reactions below the micrometer is a long-standing challenge in electrochemistry. In this respect, electrodeposition using scanning probe microscopy provides an attractive platform, not only for additive nanoscale manufacturing, but also for the investigation of local dynamics such as mass transport and reaction kinetics. We report on the direct writing of copper nanostructures using an oscillating nanoelectrode operated with an Atomic Force Microscope (AFM) in aqueous solutions. The nanoelectrode is used to locally initiate electrochemistry, while the AFM allows for in-situ probing of the deposited material. We demonstrate the writing of arbitrary structures beyond cluster size with lateral dimensions in the order of the tip radius.

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Strikingly, this local writing is only possible in highly dilute electrolytes ($\sim 1 \mu\text{M CuSO}_4$). Moreover, we find a profound effect of the dynamic operation of the nanoelectrode on the deposition kinetics.

We explain our results by considering the extended screening length and slow charge dynamics of the dilute electrolyte, which allows the nanoelectrode to operate inside, and disturb, the electrical double layer (EDL) at the solid-liquid interface. We visualize these (dis)charging dynamics and their effect on the reaction directly through the electrodeposited structures, and experimentally observe the Debye time of the electrolyte as a threshold value for growth. Furthermore, we show that this threshold time increases as a function of applied potential.

Our results lead us to propose a reaction mechanism based on cyclic charging and discharging of the EDL, which facilitates local electrodeposition through direct electrostatic interaction between ions in the liquid and the nanoelectrode."

Dissolution couples flow to surface charge

Willem Boon, Utrecht University

Recent experiments have demonstrated that flow through a channel can reversibly alter the surface charge of silica and calcium fluoride. This observation led to novel hypotheses and theories trying to explain the coupling of flow to surface charge. Our theoretical predictions combined with the latest experimental observations of a surface charge heterogeneity shows that dissolution of the solid is responsible for the coupling, as I will explain in this talk.

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CONTRIBUTED POSTERS

Surface Reaction Driven flow

Abimbola Achaju, University of Twente

The autonomous motion of catalytic bimetallic nanorods within an aqueous peroxide solution has been reported in literature [1]. A single nanorod consists of a bimetallic couple that catalyzes the decomposition of an aqueous solution such as hydrogen peroxide, thereby creating the necessary gradients (electric, concentration) that actuate motion. This bimetallic catalytic system can be immobilized to generate convective flow that was quantified by a numerical study [2]. In this work, we focus on experimental and numerical analysis that provides fundamental insight on the key elements including the generated electric field, reaction kinetics and mass transport that impact the overall diffusio-electroosmosis phenomena. The surface reactivity pattern characterized by the dimensionless Damköhler number, that releases and depletes protons is related to the fluid flow. Such surface-induced convective fluid flow can be harnessed in systems to reduce mass transport limitations.

- [1] Kline, Paxton, Mallouk, and Sen, Catalytic nanomotors: Remote-controlled autonomous movement of striped metallic nanorods, *Angew. Chemie-International Ed.*, vol. 44, no. 5, pp. 744-746, 2005.
[2] S. M. Davidson, R. G. H. Lammertink, and A. Mani, *PHYSICAL REVIEW FLUIDS* 3, 053701 (2018) Predictive model for convective flows induced by surface reactivity contrast, vol. 053701, pp. 1-16, 2018.

Decay lengths in electrolytes

Peter Cats, Utrecht University

Electrolytes, liquids with mobile charge carriers, are of interest in many fields, and have been investigated for more than a century. However, not every mystery about them has been unveiled and there are still answers that need to be found to get a full understanding of these liquids. One mystery surrounding electrolytes is the decay length of the charge-charge correlations at high salinity. Experiments showed unexpected and unexplained behavior of these correlations, revealing huge qualitative deviations from the standard Debye screening length [1]. In this talk I want to divert to classical Density Functional Theory, a theory for inhomogeneous liquids, to explore the predictions that can be made within this framework. We look at the asymptotic far-field behavior of the electric double layer, make a link to earlier work done in this field [2], and show that the decay lengths predicted by both theories are consistent, but not commensurate with experiments. Somehow the key physics of these systems remains a mystery.

- [1] A.M. Smith, A.A. Lee and S. Perkin, *J. Phys. Chem. Lett.* 7, 2157 (2017)
[2] R.J.F. Leote de Carvalho and R. Evans, *Molecular Physics*, 83, 619 (1994)

The effect of surface structure on preferential ion adsorption in electrolyte mixtures

Max Dopke, Delft University

Competitive ion adsorption in electrolyte mixtures plays a key role in a broad range of natural and industrial processes, including ion sensing and separation, and colloid science. Molecular simulations can reveal not only which ions adsorb onto a surface, but also uncover the mechanisms responsible for selectivity of individual

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adsorption sites. Such information is not accounted for in surface complexation models and is hard to infer experimentally.

Using all-atom molecular dynamics simulations of aqueous NaCl, CaCl₂, and NaCl-CaCl₂ solutions confined by charged amorphous silica, we found that adsorption sites can show a preference toward sodium or calcium ions. In this talk, I will show that this preferential adsorption is determined by the local surface structure surrounding an adsorption site. The surface structure is found to be able to sterically hinder the first hydration shell of the calcium ion, thereby inducing specificity towards the sodium ion. The relation between structure and selectivity is quantified in a simple metric, providing a means to explain and predict preferential ion adsorption on silicon oxide surfaces.

We expect our findings and approach to be extendable to other oxide surfaces and electrolyte mixtures. This insight into the relation between local surface structure and preferential adsorption can have large impact on the future design of sensors, membranes for separation and help to explain the mechanisms underlying enhanced oil recovery.

Self-thermoelectrophoresis at low salinity

Joost de Graaf, Utrecht University

A locally heated Janus colloid can achieve motion in an electrolyte by an effect known as self-thermo(di)electrophoresis. We numerically study the self-propulsion of such a "hot swimmer" in a monovalent electrolyte using the finite-element method and analytic theory. We obtain excellent agreement between our analytic theory and numerical calculations in the limit of high salinity, validating our approach. At low salt concentrations, we employ Teubner's integral formalism to arrive at expressions for the speed, which agree semi-quantitatively with our numerical results for conducting swimmers. This lends credibility to the remarkably high swim speed at very low ionic strength, which we numerically obtain for a fully insulating swimmer. We also report on hot swimmers with a mixed electrostatic boundary conditions. Our results should benefit the realization and analysis of further experiments on thermo(di)electrophoretic swimmers.

Dynamic density functional theory for electrolyte relaxation

Cheng Lian, Utrecht University

Understanding the charging kinetics of electric double layers is a scientific challenge of fundamental importance for the design and development of novel electrochemical devices such as supercapacitors and batteries. In this work, we study the charging behavior of concentrated electrolytes using a classical dynamic density functional theory (DDFT) that accounts for molecular excluded volume effects and the electrostatic interactions. Going beyond the conventional continuum theories with DDFT gives rise to richer charging dynamics. The combination of excluded volume and electrostatic interactions gives rise to multiple time scales: the initial RC-circuit charging time followed by a slower diffusive adsorption process. Furthermore, the porous network effects on the charging processes are also investigated, and the corresponding time scales agree qualitatively with those observed in experiments.

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Optical Imaging of the Electric Double Layer Around Nanostructures

Kevin Namink, Utrecht University

The electric double layer (EDL) formed around charged nanostructures at the liquid-solid interface determines their electrochemical activity and influences their electrical and optical polarizability. We experimentally demonstrate that restructuring of the EDL at the nanoscale can be detected by dark-field scattering microscopy. Temporal and spatial characterization of the scattering signal demonstrates that the potentiodynamic optical contrast is proportional to the accumulated charge of polarisable ions at the interface and its time derivative represents the nanoscale ionic current. The material-specificity of the EDL formation is used in our work as a label-free contrast mechanism to image nanostructures and perform spatially-resolved cyclic voltametry on ion current density of a few attoamperes, corresponding to the exchange of only a few hundred ions.

Measuring the flow dependency of the surface charge of a microchannel

Peter Speets, Utrecht University

Flow induced inhomogeneity in the surface charge of microchannels has been observed by Backus et al[1]. This process is driven by dissolution of the capillary itself. The dissolution of the surface is a chemical equilibrium reaction at the surface where charge is exchanged with the solvent. The flow and its streaming potential changes the concentrations of reactants near the surface, therefore driving the reaction to a different equilibrium. Werkhoven et al. [2] predicted that conservation of ion number requires that the concentration of reactants to change along the length of the microchannel and therefore cause inhomogeneity of surface charge depending on flow rate and direction. This leads to a difference in surface conductivity measured upstream or downstream of the channel.

In this experiment we measure the difference in surface conductivity measured up and downstream in a microchannel with controllable height. The height of the microchannel is controlled by pressing on a PDMS microchannel on a glass microscope slide with a piezo element. The height is measured with spectral-domain phase microscopy. With this method it is possible to separate the contribution of the bulk from the contribution of the surface to the total conductance of the microchannel.

Preliminary results are not conclusive about the flow and charge interaction, but measurements performed with an electrode placed downstream of the flow seem to have a higher surface conduction than the measurements upstream. For higher flow rates, however, this small effect is lost.

[1] D. Lis, E.H.G. Backus, J. Hunger, S. H. Parekh and M. Bonn, Liquid flow along a solid surface reversibly alters interfacial chemistry, *Science*, 334(6188), 1138-1142, 2014.

[2] B.L. Werkhoven, J.C. Everts, S. Samin and R. van Roij, Flow-Induced Surface Charge Heterogeneity in Electrokinetics due to Stern-Layer Conductance Coupled to Reaction Kinetics, *Physical Review Letters*, 120(26),264502-264508, 2018.

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Measuring the heat of electric double layer formation in porous carbon electrodes

Joren Vos, Utrecht University

We recently developed two setups that allow the measurement of heat generated during electric double layer formation in a porous carbon electrode with a large specific surface area. One setup relies on a temperature difference measurement, using four Pt100 resistance thermometers in a Wheatstone bridge circuit. The other setup measures the flow of heat directly, using a gSKIN heat flux sensor. Both setups include a reference electrode, which enables the measurement of heat as a function of the potential difference between the carbon and reference electrodes. This, in turn, allows the electrolytes cations and anions to be studied separately by choosing a cathodic or anodic measurement range. The measured heat consists of entropic and enthalpic effects, which originate from changes in concentration, hydration, and adsorption of ions inside the electrodes pores. This poster provides a description of the experimental methods and presents the initial results.

Monitoring the charge of a single nanoparticle with optical tweezers electrophoresis

Bohdan Yeroshenko, Utrecht University

Most materials develop an interfacial charge in contact with water. This surface charge attracts ions from the solution and leads to the formation of the Electric Double Layer (EDL). The EDL plays a central role in many chemical, physical and biological processes such as catalysis, self-assembly, electrochemical conversion. Understanding the structure and dynamics of the EDL are hence very important for explaining these processes and for technological applications. The relaxation of the EDL around a microparticle takes several microseconds. As a result, the particle electrophoretic mobility depends on the driving frequency. Here, we present first measurements of the electrophoretic mobility of silica nanoparticles of different sizes, with high accuracy at a time resolution of 10 microseconds. These particles can be held in optical tweezers for a duration of several minutes, in order to observe its slow and fast temporal response. Based on these measurements, we experimentally study the relaxation dynamics of the EDL with high accuracy. Furthermore, we record the dynamic response of the nanoparticles charge to the changes of the pH of the surrounding liquid. Our results fill a major experimental void for understanding the dynamics of the EDL and can serve as a test for the most recent theories for electrokinetics at the solid-liquid interface.

Jamming and unjamming of nanoparticles in a microchannel

Zhu Zhang, Utrecht University

Electro-osmotic pumping is a common method of circulating fluids in microfluidic channels. This technique is the method of choice for nanofluidic channels with a cross section smaller than $1 \mu\text{m}^2$ because pressure-driven flow is not practical. Pumping colloidal nanoparticles into such small channels is an important challenge in designing lab-on-chip devices as the interaction between channel walls and the colloidal particles initiates a range of multi-scale processes. These processes can cause disproportionate transport of solute particles and molecules into the channels, which can be useful for filtration. However, it can also cause accumulation of nanoparticles at the sharp edges of the channel entry. Aggregation at the channel entry might cause blocking and failure of the device. In other situations, controlled aggregation can be advantageous, for example for concentrating proteins in a well-defined location or for inducing crystallization by the long-period aggregation of nanoparticles.



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Based on nanoparticle tracking measurements at the entry of microchannels, we find that the aggregation of nanoparticles, caused by electro-osmotic pumping, could be cleared by reversing the direction of the applied potential for a short time. The clearing happens on time scales that are an order of magnitude faster than jamming. In this way, the blocking of the channel entry can be avoided by applying an asymmetric square waveform potential, and net flow could be achieved by tuning the duty cycle of the waveform. This result is important for the general operation of micro/nanofluidic devices that require electro-osmotic pumping and for sensing applications that use membrane nanopores.