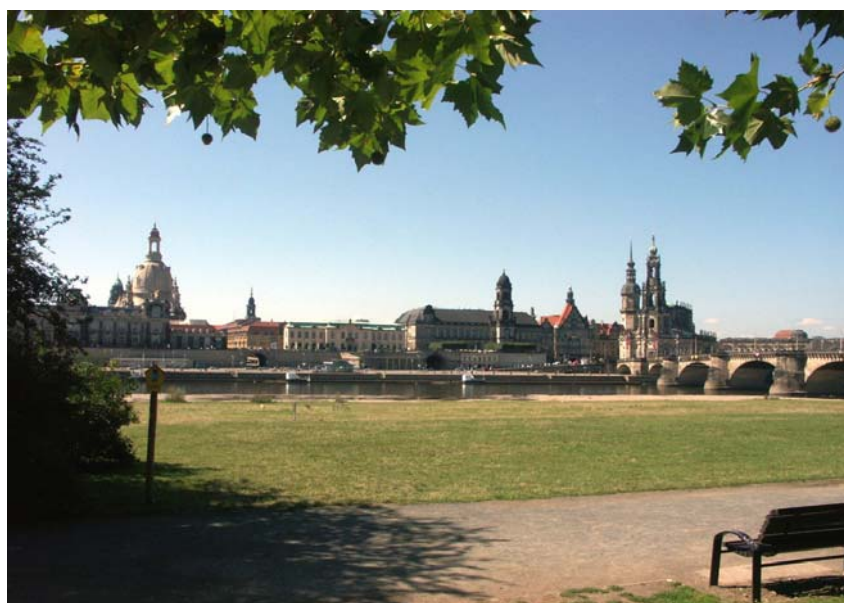


3rd Symposium on Electrosurface Phenomena in Advanced Materials Science



Dresden, September 24 - 25, 2009

Abstracts

Leibniz-Institut für Polymerforschung Dresden e.V.
Max-Bergmann-Zentrum für Biomaterialien Dresden
Hohe Straße 6, 01069 Dresden, Germany

Tokyo Institute of Technology, Department of Organic and
Polymeric Materials, Laboratory of Organic Materials Physics



Welcome to the third Symposium on Electrosurface Phenomena in Advanced Materials Science!

Again, we will face the challenge of bridging theoretical and experimental work as well as fundamental and applied research on electrosurface phenomena in a very small meeting. Moreover, the presentations will cover recent progress across a wide variety of projects ranging from research on ion specific effects over transport through nanomaterials to power conversion at aqueous interfaces. So, we can reasonably expect a flavour of many recent advances in the understanding and utilization of electrical charges at interfaces and we are happy that so many key individuals from complementary fields decided to contribute to this meeting.

The first symposium of this still rather young series took place in March 2006 at the Tokyo Institute of Technology as a part of the 2006 initiative “Germany in Japan”. In September 2007 a follow-up meeting with a larger number of participants was held at the Leibniz Institute of Polymer Research in Dresden. Throughout and after the previous symposia a majority of the participants expressed their appreciation of the stimulating atmosphere of the meetings. Therefore, we decided to organize another symposium with similar subject and format, held again in Dresden.

We are happy about the fact that our programme was very well received and look forward to a day full of new insights and inspiring discussions.

Financial support from the Tokyo Institute of Technology, the Leibniz Institute of Polymer Research Dresden and our industrial sponsors is gratefully acknowledged.

Carsten Werner on behalf of the team of organizers.

Programme

24th September:

19:00 Informal Get Together

25th September:

8:50 Carsten Werner
Opening

9:00 Hans Lyklema
Overcharging; solving the dilemma between physical and chemical interpretations

9:30 Akihiko Tanioka
Transport Phenomena across Nanomaterials

10:00 Roland Netz, Douwe Bonthuis and Dominik Horinek
Electrokinetics and Power Conversion at Aqueous Interfaces

10:30 Coffee Break

10:50 Werner Kunz
Specific Ion Effects at Interfaces

11:20 Pavel Jungwirth
Effects of alkali cations and halide anions on lipid membranes

11:50 David Küttner, Ralf Zimmermann, Lars Renner and Carsten Werner
Charging and Ion Specific Effects at Zwitterionic Supported Bilayer Lipid Membranes

12:20 Poster Presentation

12:40 Lunch

14:00 Hiroyuki Ohshima
Electrostatic Interaction between Soft Particles

14:30 Lydéric Bocquet
Nanofluidics within the Debye layer

15:00 Toshihisa Osaki and Shoji Takeuchi
Translocation of Linear Polymers through a Nanopore Membrane Protein in a Bilayer Lipid Membrane Microarray

15:30 Coffee Break

- 16:00 James K. Beattie and Angus Gray-Weale
The Force that Attracts Hydroxide Ions to Hydrophobic Interfaces
- 16:30 Jérôme Duval
ElectroHydrodynamics of Diffuse Soft Thin-Films supported by Charged Rigid Substrates
- 17:00 Ralf Zimmermann, Ana L. Cordeiro, Jérôme F. L. Duval and Carsten Werner
Temperature-dependent physicochemical properties of poly(N-isopropylacrylamide-co-N-(1-phenylethyl) acrylamide) thin films
- 17:30 Akihiko Tanioka
Concluding Remarks
- 19:30 Conference Dinner

ORAL PRESENTATIONS

Overcharging; solving the dilemma between physical and chemical interpretations

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Overcharging, or charge reversal, is the phenomenon that an electric double layer contains more countercharge than is needed to compensate the surface charge. Its occurrence can be established if the real surface charge and the effective surface charge, measured electrokinetically or inferred from interaction studies, are both measured and appear to have different signs. The phenomenon is often seen with ionic surfactants. For instance, cationic surfactants, adsorbing on negatively charged latices can induce overcharging, as evidenced by positive zeta potentials. The phenomenon can also be observed with inorganic electrolytes and this leads to the present theme.

For the interpretation two alternatives have been proposed, for the sake of simplicity distinguished as *chemical* vs. *physical*. According to the chemical interpretation overcharging is caused by specific bonding of counterions, that is bonding by non-electrostatic forces, such as complex formation, hydrophobic bonding and other water structure-determined interactions. The physical interpretation attributes overcharging to ion correlations, which become important if the double layer charge and the electrolyte concentrations are high.

Critical review of the vast literature indicates that virtually all reported cases can be interpreted in the chemical way, even those experiments that have been invoked as support for the action of ion correlations. Nevertheless, the theoretical grounds for ion correlations are convincing. Hence, the challenge is to find and interpret data for a system where the conditions are such that ion correlations should occur but where masking this phenomenon by chemical adsorption can be excluded.

In the presentation it will be shown that the double layer on negatively charged mercury in the presence of MgSO_4 solutions fulfills this condition, thus providing the first unambiguous proof for the operation of ion correlations in colloid science.

Work done in co-operation with Erik Wernersson and Roland Kjellander of Göteborg University, Sweden.
Publication in *J.Phys.Chem* pending.

Transport Phenomena across Nanomaterials

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Nanomaterials, including nano-scaled and nano-structured materials, have attracted much attention due to their unique properties and potential applications in many engineering fields. Filtration and separation are one of the exciting applications of nanomaterials. More recently, novel nanomaterials for separation (e.g., carbon nanotube pores and nanofiber-based membranes for ion or water transport) have been developed. Their surface electrochemical properties play an important role in their performance. The more advanced nanomaterials for separation will require understanding of transport and separation mechanism based on their structure of electrical double layer. We try to preview the research trends in this area for the future.

Electrokinetics and Power Conversion at Aqueous Interfaces

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Efficient conversion of power from one form to the other is nowadays a pressing issue. We study how to transform electric energy into mechanic energy by using aqueous interfaces in micro-fluidic devices. Previous Molecular Dynamics simulations suggested that the interfacial water structure inside a carbon nano-tube allows to directly convert a constant electric field into pressure gradients, suggesting applications in many directions and areas. We approach that problem using continuum theory and careful simulation techniques: First, we generalize the Navier-Stokes equation to include polar liquids and thereby treating antisymmetric contributions to the stress tensor. We explicitly show that a uniform electric field constant in time does not generate pressure gradients in any geometry. Reconsidering the Molecular Dynamics Simulations, we realize that imprudent use of cutoff schemes and cutoff lengths yields spurious pumping effects. Proper simulation conditions give zero pumping for fields constant in time, in agreement with continuum hydrodynamic theory. A rotating electric field, on the other hand, gives rise to an electro-osmotic flow, and thus to a simple shear flow for large channels. In asymmetric channels, it is possible to obtain net fluid transport. We conclude by proposing different practical schemes for electro/mechanic power conversion on the nano-scale.

Specific Ion Effects at Interfaces

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Specific ion effects are known and studied since more than one century, starting with the work of Poiseuille and Hofmeister. However, until recently, the attempts to explain or even to predict them, were not very successful. In the present contribution I try to give some striking examples of experimentally found specific ion effects with a special emphasis on interfaces. Further, I will resume some of the most promising attempts to model them and to understand the origin of these effects. Finally, I will present a simplified model that is probably able to predict the behaviour of ions near biological surfaces and surfaces of typical association colloids (micelles, polymers, liquid crystals etc.).¹

[1] *Nina Vlachy, Barbara Jagoda-Cwiklik, Robert Vácha, Didier Touraud, Pavel Jungwirth, and Werner Kunz, Hofmeister series and specific interaction of charged headgroups with aqueous ions, Advances in Colloid and Surface Science* **146** (2009) 42-47.

Effects of alkali cations and halide anions on lipid membranes

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Affinities of alkali cations and halide anions for lipid membranes such as DOPC in aqueous salt solutions are investigated by means of molecular dynamics simulations. The simulations reveal that sodium is attracted to the headgroup region with its concentration being maximal in the vicinity of the phosphate groups. Potassium and cesium, however, do not preferentially adsorb to the membrane. Similarly, halide anions do not exhibit a strong affinity for the lipid headgroups but merely compensate the positive charge of the sodium counter-cations. Nevertheless, larger halides such as bromide and iodide penetrate deeper into the headgroup region toward the boundary with the hydrophobic alkyl chain. Addition of alkali halide salts modifies physical properties of the bilayer including the electronic density profiles, the electrostatic potential, and the area per lipid headgroup.

We also present molecular dynamics simulations of a multicomponent asymmetric bilayer in mixed aqueous solutions of sodium and potassium chloride. Due to the geometry of the system there are two aqueous solution regions: one mimicking intracellular region and one extracellular. Ion specific effects are observed at the membrane/aqueous solution interface. Namely, at equal concentrations of sodium and potassium, sodium ions are more strongly adsorbed to carbonyl groups of the lipid headgroups and a significant concentration excess of potassium is needed for this ion to overwhelm in abundance sodium at the membrane. These simulations represent a step toward modeling of realistic biological membranes at physiological conditions.

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Charging and Ion Specific Effects at Zwitterionic Supported Bilayer Lipid Membranes

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Supported bilayer lipid membranes (sBLMs) are widely used as model systems for cell membranes.¹ As a big advantage sBLMs allow the application of various surface sensitive techniques to characterize their physicochemical properties. In natural environment biological membranes are surrounded by aqueous solution containing monovalent and divalent ions with different concentrations inside and outside of the cell. As lipid headgroups consist of various acidic and/or basics moieties the majority of lipids are charged in aqueous environments. The resulting electrostatic interactions between the ions and the lipids are crucial for membrane fusion, transmembrane transport, phase separation and influence important membrane properties as lipid density and lipid mobility. Furthermore, surface charge influences important processes such as cell adhesion, antigen-antibody binding, or cell drug delivery. Therefore detailed knowledge about the ionization of lipid headgroups and ion-specific interactions is required and a matter of particular interest.

In this study we applied streaming current measurements and fluorescence microscopy to investigate the charging and fluidity of sBLMs prepared from the zwitterionic lipid 1,2-Dioleoyl-sn-Glycero-3-Phosphatidylcholine (DOPC) in mono and multivalent electrolytes. Isoelectric points of about 4 and an almost linear dependence of the zeta potential on the solution pH revealed the dominating role of hydroxide and hydronium ions for the charging of the outer leaflet of the membrane in electrolytes with neither kosmotropic nor chaotropic ions.² The sign reversal of the zeta potential to positive values at pH < 4 was found to be correlated with a significant decrease of the lipid mobility in the bilayer. Increase of the chaotropicity of the anions in the solution was found to be accompanied by an shift of the IEP to lower values according to the following series: Cl⁻ ≈ Br⁻ < NO₃⁻ < I⁻ < ClO₄⁻. In contrary, increasing kosmotropicity of the cations in solution caused a IEP shift to higher values in the order NH₄⁺ ≈ K⁺ ≈ Na⁺ ≈ Li⁺ < Ca²⁺ < Mg²⁺ < La³⁺. The fluidity of the DOPC membranes was found to be strongly influenced in case of specific adsorption of chaotropic anions and multivalent kosmotropic cations. The data are discussed with respect to the interaction of the ions with polar sites in the lipid head group and their influence on the lipid packaging, headgroup orientation and interfacial water structure.

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Electrostatic Interaction between Soft Particles

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Electrostatic Interaction between colloidal particles plays an essential role in determining the behavior of colloidal suspensions. It is usually assumed that the particle-fixed charges are located only at the particle surface (of zero thickness). This model, however, is by no means a good approximation for the case where fixed charges are distributed over some depth on the particle surface, or the particle surface is covered with a polyelectrolyte layer. We call polyelectrolyte-coated particles soft particles [1]. A spherical soft particle becomes a hard sphere without surface structures, while a soft particle tends to a spherical polyelectrolyte when the particle core is absent. The purpose of the present paper to derive an approximate analytic expression for the electrostatic interaction energy between two dissimilar spherical soft particles (Fig. 1) [2]. The obtained expression covers various limiting cases that include hard sphere/hard sphere interaction, spherical polyelectrolyte/spherical polyelectrolyte interaction, soft sphere/spherical polyelectrolyte interaction, soft sphere/hard sphere interaction, and spherical polyelectrolyte/hard sphere interaction. The interaction between two cylindrical soft particles will also be discussed [3]. Two parallel cylinders and two crossed cylinders will be considered.

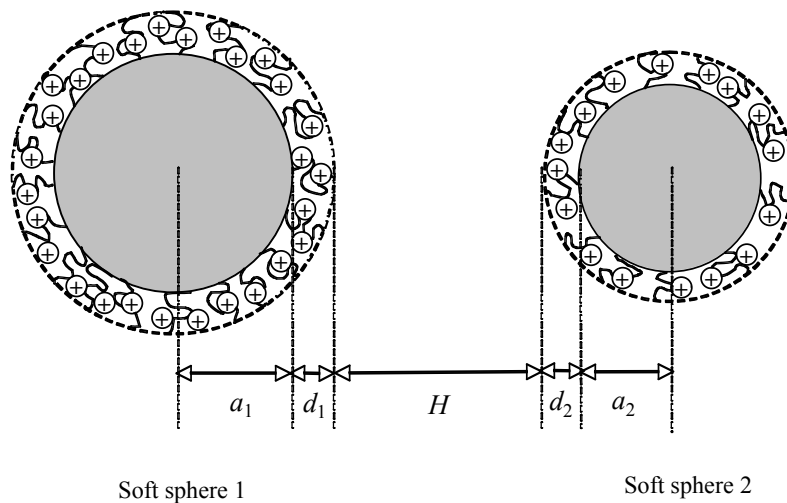


Fig. 1. Interaction between two soft spheres

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Nanofluidics within the Debye layer

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The progress made over the last ten years in the understanding of the dynamics of fluids at solid surfaces has shed a new light on nanofluidic transport within the electrical Debye Layer. Recent experimental and theoretical work has indeed shown that *hydrophobic* surfaces do exhibit low friction at the liquid-solid interface, as characterized by a large – but still nanometric – hydrodynamic slip length. This behavior has important implications for ion transport, due to the generic couplings occurring within the Debye layer. In particular the electro-osmotic mobility, which introduces the so-called *zeta potential*, is accordingly amplified by a (large) factor scaling like the ratio between the slip length to the width of the diffuse layer. This mechanism is generic to the ion dynamics within the diffuse layer and does not depend on the specific type of description of the diffuse layer. Molecular dynamics (MD) simulations of electro-kinetic phenomena do fully confirm this mechanism, both qualitatively and quantitatively [1,2]. MD results point furthermore to the importance of ion-specific effect for the electro-osmotic mobility.

Experimentally this problem was tackled in collaboration with P. Tabeling (ESPCI) using a newly developed nanofluidic tool allowing to measure the fluid velocity with typically a ten nanometers resolution. This combines a Particle Image Velocimetry (PIV) technique using nano-colloids as tracers, coupled to evanescent waves in TIRF setup (Total Internal Reflection Fluorescence). We measure velocity profiles and nanotracer concentration between 20 and 300 nm from the walls in a low salt electrolyte, at a hydrophilic (bare pyrex) and a hydrophobic (silanized pyrex) surface. Both pressure-driven and electroosmotic flows were investigated. These experiments demonstrates the large amplification of the electro-osmotic mobility by hydrodynamic slippage effects on the hydrophobic surface. In contrast, for the hydrophilic surface the zeta potential is shown to identify with the bare electrostatic potential [3].

We conclude by exploring interfacial transport at superhydrophobic surfaces. These surfaces are characterized by very large slippage effects at their interface, with an *effective slip length* in the *micrometer* range [4]. But although *a priori* very appealing, we will show that these nanotextured surfaces do not enhance further the electro-osmotic mobility. However a huge enhancement is demonstrated for other interfacial transport, and will be discussed in the context of diffusio-osmosis [5].

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Translocation of Linear Polymers through a Nanopore Membrane Protein in a Bilayer Lipid Membrane Microarray

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In this study, we examine the transport properties of linear polymers translocating through α -hemolysin nanopore (α HL, a bacterial membrane ion channel, [1]) that is reconstituted in a bilayer lipid membrane, using a microfluidic chip.

The microchip is fabricated with a common lithography process and stereolithography technology (Fig. a, [2]). An intermediate polymer film suspends the bilayer membrane at its patterned apertures and separates the upper wells and bottom channels (Fig. b). We achieve to form planar bilayer lipid membranes in an array format on the chip by a sequential injection of lipid/decane solution and aqueous buffer (Fig. c, [3]). The integration of α HL occurs at the membranes with addition of α HL solution at the upper wells. By the reconstitution of the nanopore the current increases with a defined conductance determined by the pore size (Fig. d). On the other hand, it is known that translocation of large molecules such as linear polymers through the nanopore significantly reduces the ionic current, and the pore diameter of 1.5 nm limits the size of the translocating molecules. Here we simultaneously monitor the current signals from the arrayed nanopores on the microchip and analyze the blocking events by a short and long polynucleotide molecules. Histograms of the half-width of the blocking peaks by these molecules demonstrate that the narrow pore size qualifies to discriminate the molecular weights and their distribution; the shorter the molecules are, the faster the translocation occurs [4]. Accordingly such a nanopore system has potentialities towards the applications for sensing, separation and identification of unknown molecules as a label-free, high throughput method.

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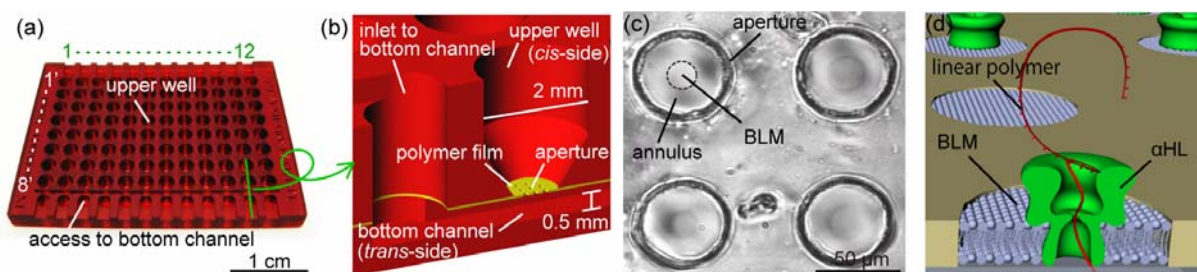


Figure. α HL-nanopore array: (a) Overview of the microchip. Eight top-wells on each of 12 bottom channels. (b) Cross-sectional view of the configuration of the chip. (c) Microscopic image of planar bilayer lipid membranes formed at the arrayed apertures on the polymer film. (d) Schematic diagram of α HL nanopore protein incorporated at a bilayer lipid membrane (BLM). The electrical current reduces with translocation of a linear polymer due to blocking of the narrow constriction.

The Force that Attracts Hydroxide Ions to Hydrophobic Interfaces

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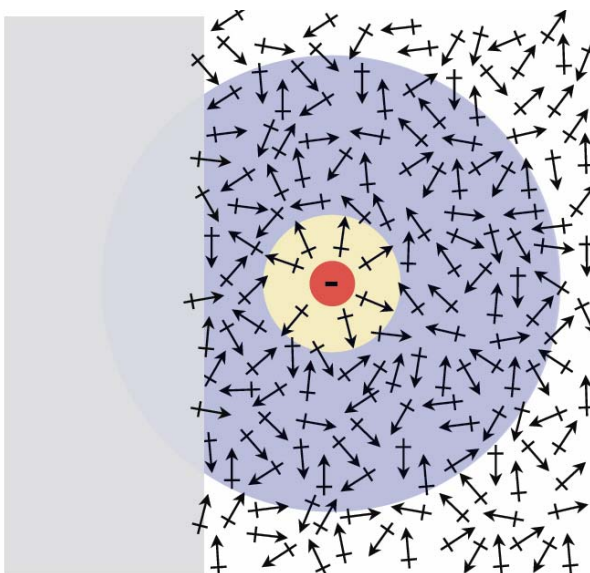
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Many authors have called for an explanation of the observations that water at mesoscopic hydrophobic interfaces acquires a negative charge through the preferential adsorption of hydroxide ions.¹ This occurs whether the hydrophobe is gaseous (air), liquid (oil), or an inert solid (e.g. Teflon).² The adsorption is strong, with an equilibrium constant of 10^8 - 10^9 , leading to an isoelectric point of pH 2-4, and a surface charge density of about $5 \mu\text{C cm}^{-2}$ (0.05 C m^{-2}).³ This corresponds to one hydroxide each 3 nm^2 .

We can now explain this phenomenon: it arises from the suppression of the collective dipole fluctuations of water molecules by ions.⁴ Hydroxide ions reduce the relative permittivity of an electrolyte solution more than other monovalent ions of similar size. The absence of these fluctuations leads to a Hamaker-like force on the hydroxide ion that attracts it to regions where the density of dipole-moment fluctuations is lower than in bulk water, in other words, to regions of low relative permittivity, the hydrophobic interface. By combining a simple model for this fluctuation force with a modified Poisson-Boltzmann equation, we reproduce the dependence of the zeta-potential on pH, including the low isoelectric point, the approximate magnitude of the experimental surface charge density, and the Jones-Ray data for the dependence of surface tension on electrolyte concentration. We propose an explanation for the absence of a signal from the hydroxide ions in surface spectroscopic measurements⁵ and the failure of some molecular dynamics simulations to reproduce the experimental results.⁶



This explanation has profound implications for many properties of water at interfaces. It provides predictions about the effect of pH and electrolyte concentrations on the surface tension, which are being tested.

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ElectroHydrodynamics of Diffuse Soft Thin-Films supported by Charged Rigid Substrates.

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In this presentation, a generalization/extension of previous electrokinetic models¹⁻³ for streaming current of charged gel layers is reported by tackling the most general situation where a diffuse charged thin gel layer is supported by a charged rigid surface.⁴ The theory does not suffer from any restrictions on the magnitude of the volume charge density of the gel, the electrokinetic potential of the supporting rigid surface and the thickness of the gel layer (nanometer to micrometer range). It further allows to introduce any diffuse distribution of the polymer segment density from the charged supporting surface to the outer electrolyte medium. A full analytical expression for the streaming current is given within the Debye-Hückel approximation in the practical limit where the thickness of the gel is well below the transversal dimension of the electrokinetic cell and for homogeneous distribution of polymer segments within the gel. In addition, explicit analytical expressions for the electrokinetic and hydrodynamic thickness of the gel are provided for the first time as a function of the relevant electrostatic and hydrodynamic parameters of the rigid surface and of the gel layer. Successful application of the formalism to streaming current data collected on poly(*N*-isopropylacrylamide)-*co*-*N*-(1-phenylethyl) acrylamide thermo-responsive thin films will be briefly presented. Throughout the presentation, emphasis will be brought on the analogy between the electrokinetic response (streaming current) of permeable thin-films and that (electrophoretic mobility) of core-shell soft (bio)particles⁵ like bacteria or red blood cells.⁶ Appropriately interpreted electrokinetic data for all these systems allow not only their characterisation in terms of charge and hydrodynamic permeability, but also contribute to the understanding of *e.g.* (i) the action of biospecific molecules like enzymes on cell surface structure,⁶ (ii) colloidal stability features for soft particles, or (iii) the dynamics of chemical reaction processes taking place at the interphase formed between soft permeable material and outer medium.⁷

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Temperature-dependent physicochemical properties of poly(*N*-isopropylacrylamide-*co*-*N*-(1-phenylethyl) acrylamide) thin films

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We report on the detailed characterization of a novel thermo-responsive copolymer thin film consisting of poly(*N*-isopropylacrylamide) (PNIPAAm) and *N*-(1-phenylethyl) acrylamide (PEAAm). The transition temperature of the copolymer was tuned to fit applications related to the control of marine biofouling, and was immobilized as a thin film onto Teflon[®] AF surfaces using a low pressure argon plasma treatment.¹ The temperature-dependent physicochemical properties of the thermo-responsive film were thoroughly characterized in deionized water, artificial sea water and KCl solutions. It was shown that the immobilized thermo-responsive film exhibits a reversible swelling / deswelling with temperature. Inverse contact angles were measured using captive air bubbles and analysed by axisymmetric drop shape analysis to study the wettability of the hydrated thin films at different temperatures. Streaming current measurements performed above and below the transition temperature of the thermo-responsive hydrogel (at 22°C and 4°C, respectively) indicated that the charging of the polymer / aqueous solution interface is mainly determined by the preferential water ion adsorption at the Teflon[®] AF surface. The contact angle results support the intrinsic properties of the thermo-responsive film, as surface hydrophilicity decreased with increasing temperature. The advancing water contact angle decreased with increasing temperature, which may be explained by the different molecular mobility at different temperatures, allowing or hampering the re-orientation of hydrophobic segments at the solid-liquid and solid-fluid interfaces.¹ The data of the streaming current measurements were further analyzed applying a recently introduced theory for the electrokinetics at diffuse soft interfaces.² The theory successfully reproduces the electrokinetic data for the P(NIPAAm-*co*-PEAAm) copolymer film at 22°C and 4°C over the whole range of pH and ionic strength examined. It was found that the threefold increase of the hydrogel film thickness with decreasing temperature from 22°C to 4°C (i.e. from 23 to 70 nm as measured by ellipsometry), is in line with homogeneous swelling and an increase of the hydrodynamic penetration length ($1/\lambda_0$) by a factor of ~1.6.

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POSTERS

Flexible and Highly Porous Carbon Nanofibrous Networks Produced by Electrospinning

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Flexible and highly porous carbon fiber fabrics with an average diameter in the range of 100 nm - 3.5 μm were prepared by electrospinning, followed by successive curing and carbonization. The addition of a high-molecular-weight polymer, poly (vinyl butyral) ($M_w = 340,000$), and electrolytes, pyridine and sodium carbonate, to the phenolic resin/MeOH solution enhanced formation of a thin smooth fiber by electrospinning. There was a close correlation between the fiber diameter and physical properties of the carbon fabrics; the fabrics with a thinner diameter showed a higher conductivity, a higher specific surface area, and flexibility. The prepared carbon fabrics with the thinnest average diameter of 109 nm had the highest electrical conductivity of 5.29 Scm^{-1} and highest BET specific surface area of $792.7 \text{ m}^2 \text{ g}^{-1}$. The flexible carbon nanofiber fabric is a promising material for flexible electronic and optical devices.

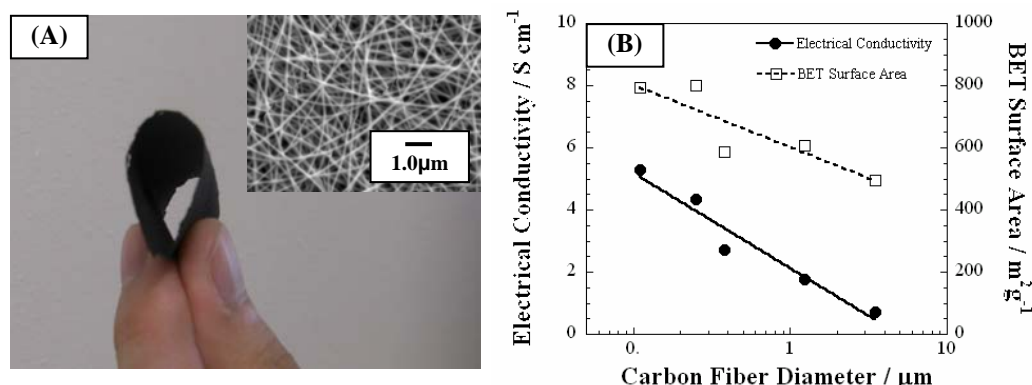


Figure (A) A photograph and (*Inset*) scanning electron microscope (SEM) image of a flexible carbon nanofiber fabric (fiber diameter; 109 nm), **(B)** The effect of carbon fiber diameter on electrical conductivities and BET surface area of carbon fiber fabrics.

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Wetting Behavior on Nanofiber Thin-Film Coatings

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The wetting behavior of a surface is determined by both its chemical composition and nanomicroscaled texture.¹ Superwetting properties on the textured surfaces, superhydrophilicity (i.e., water droplet contact angle $< 5^\circ$ within 0.5 s or less) and superhydrophobicity (i.e., water droplet contact angle $> 150^\circ$ and low contact angle hysteresis), have attracted much attention because of their potential practical applications as self-cleaning, anti-fogging, and anti-fouling surfaces. Textured surfaces have been produced by a range of chemical and physical methods: electrochemical polymerization, sol-gel method, electrodeposition, photolithography, micromolding, and so forth. Electrospinning is a straightforward and versatile method for forming continuous thin fibers from several nanometers to several tens of micrometers in diameter.² One major advantage of electrospinning is the one-step forming assemblies of nanofibers such as coatings, thin-films, and membranes.³ Recently, some researchers reported that the electrospinning process is useful for producing superhydrophobic surfaces.⁴ Our previous study showed that wettability on the electrospun nanofiber coatings could be controlled by changing the surface roughness.⁵ However, the wetting behavior on nanofiber coatings has not been understood in detail.

In the present study, nanofiber-coated surfaces were prepared by electrospinning from two kinds of acrylic resins. Their surface morphologies were observed using scanning electron microscopy and 3D profile microscopy. The wetting behaviors on the coated surfaces were characterized by static and dynamic contact angle measurements. The impregnation of water droplet was observed for the coated surface prepared from the resin A (hydrophilic-component rich). The coated surface prepared from the resin B (hydrophobic-component rich), on the other hand, showed the transfer from hydrophilic property to hydrophobic one. This phenomenon is well explained by the Cassie-Baxter model and the Wenzel model based on the roughness of textured surface and the area fraction of nanofibers.

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Charging and Swelling of Oxidized Cellulose Films

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Objectionable oxidation of cellulosic materials occurs during technical processes like pulping, bleaching and during aging/irradiation processes.¹ On the other hand oxidized celluloses gained a major interest due to their successful application for medical devices like absorbable hemostatic agents, wound dressings and immobilizing matrices for drugs, enzymes and proteins. In this context the properties and interactions of oxidized cellulose in aqueous media are of particular interest. To address this issue we investigated the charging and swelling of cellulose model layers² by pH-dependent streaming current/streaming potential measurements from microslit electrokinetic experiments³ and measurements of the layer thickness by ellipsometry in aqueous electrolyte solutions. Cellulose films were prepared with respect to their degree of oxidation which was adjusted by a graduated dissolution of the carbohydrate in NMMO·H₂O⁴ as well as through a subsequent oxidation of the reconstituted polymer film with the 2,2,6,6-Tetramethylpiperidine-1-oxyl radical (TEMPO).⁵ The charge formation of the cellulose films in aqueous electrolyte solutions is caused by the dissociation of carboxylic acid groups within the cellulose layer as well as an unsymmetrical adsorption of hydroxide ions within the alkaline pH-range. More in detail the charging of the topmost surface is reflected by streaming current data, the bulk phase of the polymer film is characterized by the surface conductivity. The pH-dependence of the surface conductivity was found to be significantly different from the trend of the streaming current as the carboxylic acid groups at the outermost surface dissociate as isolated functionalities whereas the electrostatic interactions of the ionizable groups within the polymer gel layer result in an altered dissociation of the acid functionalities and an increased swelling of the polymer film within the alkaline media. In solutions of lower ionic strength the dissociation of carboxylic acid groups is further decreased due to their local accumulation within the amorphous parts of the cellulose structure. In general the degree of oxidation of cellulose increases with rising dissolution time (increased surface conductivity) but can be further enhanced through a subsequent oxidation of the cellulose films with TEMPO.

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Influence of surface charge on the adhesion of *Escherichia coli* on poly(2-methyl-2-oxazoline) (PMOXA)-modified biopassive surfaces

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Bacterial contamination and colonization of biomaterials and medical devices, ranging from contact lenses and catheters to medical implants, is a wide-spread problem and potential risk for sustained infection. Physicochemical mechanisms of bacterial adhesion can be discussed based on the DLVO theory^{1, 2} in which adhesion is regarded as the total sum of Lifshitz-Van der Waals, acid-base and electrostatic interactions, whereas flagella, fimbriae, and other protein-receptors of bacteria promote binding via specific interactions. Since most of bacteria cells carry a net negative charge at physiological pH,²⁻⁵ electrostatic interaction between the bacteria cells and biomaterial surfaces is one of the important driving parameter in bacterial adhesion. In our study, the mechanism of interaction between bacteria and surfaces was investigated by varying the net surface charge via adjustment of the copolymer grafting density, the ionic strength of bacteria medium, and the type of *E. coli* strain. *E. coli* FimH AAEC191A and *E. coli* FimH ELT115 were used to study bacterial adhesion. Controlled loading of poly(2-methyl-2-oxazoline) (PMOXA) brush on Nb₂O₅ surfaces was performed by adsorption of poly(L-lysine)-poly(2-methyl-2-oxazoline) (PLL-PMOXA) graft copolymers with controlled grafting density (PMOXA/Lysine ratio). Self-assembly of the copolymers and their protein resistances on model substrate Nb₂O₅ were investigated using Optical Waveguide Lightmode Spectroscopy (OWLS). Streaming potential measurements were performed to determine the surface charges. Variable Angle Spectroscopic Ellipsometry (VASE) and water contact angle measurements were used to obtain surface coverage and hydrophilicity data. To study the interfacial forces associated with various PMOXA-modified Nb₂O₅ surfaces and the mechanism of bacterial resistance, adhesion of two *Escherichia coli* (*E. coli*) strains, AAEC191A (fim⁻) and ELT115 (fim⁺) respectively, was investigated in two different ionic strengths, 1 mM HEPES solution (HEPES 0) and 150 mM NaCl in 10 mM HEPES solution (HEPES II), respectively. Bacterial adhesion trends on different surface charge at different ionic strengths for the two different strains revealed that electrostatic forces and hydrophilicity play important roles in the interaction between bacteria cells and surfaces. PMOXA brush plays an important role in shielding the surface from bacterial adhesion.

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Local Surface Plasmon Resonance Sensor Fabricated on the Surface of Electrospun Nanofibers

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Because of localized surface plasmon resonance (LSPR), gold nanoparticle smaller than 100 nm shows the optical extinction in visible wavelength region. Then it has been used as one of color agents for stained glass in the Middle Age. In this decade, the LSPR character of gold nanoparticles has been paid much attention as a transducer of label-free chemical and biological sensor [1], since the resonance character of LSPR is considerably sensitive to the dielectric condition around the gold nanoparticles. In this paper we present new fabrication method of sensitive LSPR sensor with use of polymeric nanofiber fabricated by electrospinning. Gold nanoparticles were deposited on nanofibers of polyvinylidene difluoride (PVDF) prepared by electrospinning. Gold nanoparticles were deposited on PVDF nanofibers by vacuum evaporation. The deposition of gold nanoparticles was confirmed in backscattering electron image (BEI) obtained with scanning electron microscope (Figure 1). The shape of gold nanoparticles has been characterized by UV-visible polarized transmittance absorption spectroscopy. The sensitivity of the prepared nanoparticles was investigated by UV-visible transmittance absorption spectroscopy in various refractive index liquid ($n = 1.33$ - 1.405). The polarized absorption spectroscopy indicated anisotropy of the gold nanoparticles arising from large surface curvature of the nanofibers. The sensitivity of the LSPR increased as the diameter of PVDF nanofiber reduced (Table I). The highest sensitivity was 513 nm / RIU for the gold nanoparticles on a 114 nm-diameter PVDF nanofiber, which is comparable to the gold bipyramidal nanoparticles synthesized by reduction reaction [2].

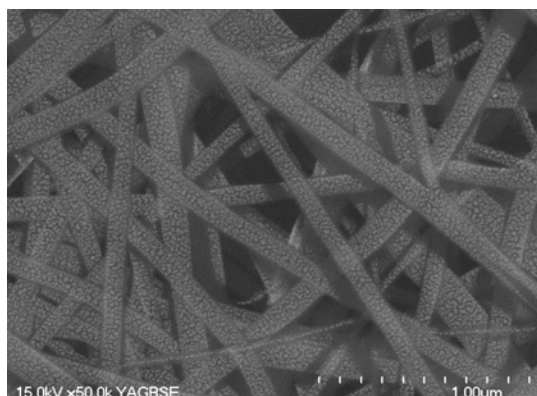


Figure 1. BEI of gold nanoparticles deposited on the surface of PVDF nanofibers

Table I. Sensitivity of LSPR sensors prepared on PVDF nanofibers

sample	mean diameter of PVDF nanofibers / nm	RIU / nmRIU ⁻¹
1	489 ± 106	255
2	211 ± 43	432
3	114 ± 32	513

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The role of oxygen in the sterilization process of dialyzers containing polysulfone/polyvinylpyrrolidone hollow fiber membranes

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Sterility is a basic requirement of disposable medical products used in dialysis [1]. The purpose of the sterilization process is to inactivate any microbial contaminations that may be present in the devices for extracorporeal blood purification therapy representing the last step of the manufacturing process. The fundamental action mechanism of sterilization procedure affect not only the microorganisms, but also materials of the dialyzers. [2].

Sterilization with ionizing rays is one of the most important ‘cold’ sterilization procedure for medical devices. During the absorption of gamma radiation by the dialyzer, the interaction with the bio- and synthetic materials leads to a generation of free radicals by destroying molecule chains. The recombination depends on the material, radiation time and radiation intensity. The ionizing radiation causes on the one hand elimination of microorganisms by decomposing RNA and DNA, but on the other hand material stress [3, 4] influencing the functionality and stability of the product.

Our research focuses on the interaction of gamma rays with polysulfone (PSU) membranes containing hydrophilizing component, polyvinylpyrrolidone (PVP), used in blood purification treatments. Non-sterilized membranes were included as controls. Furthermore, the effect of oxygen during dialyzer sterilization was studied. To clarify the importance of sterilization under oxygen-rich and -free atmosphere we investigate the physicochemical properties of the blood-sided inner surface of hollow fibers, associated with the effectivity and biocompatibility of the dialyzer, by analytical techniques.

Electrokinetic experiments on porous capillary membranes provided a direct access to the charge formation at solid surface in aqueous solution. In addition to the interfacial charges of functional groups wetting/swelling processes of the membrane are available by pH-dependent measurements. The amount of hydrophilic polymer PVP was quantitatively determined by X-ray photoelectron spectroscopy (XPS). Surface roughness and three-dimensional surface area were characterized on the observed inner surface by atomic force microscopy (AFM).

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