The Importance of Allowing for Realistic Conditions in Dynamic Electrophoresis of Spherical Particles in Aqueous Salt-Free Suspensions

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In this work the importance of taking into account the influence that water dissociation and CO2 contamination have on the dynamic electrophoretic mobility of a spherical particle in aqueous salt-free suspensions is stressed and analyzed in detail. This study has been carried out for different particle volume fractions, surface charge densities and particle radii. A pure salt free suspension (SF) is exclusively composed of charged particles and the added counterions that neutralize each particle charge. These added counterions stem from the particles and have been released to the solution as the particles get charged. On the other hand, in real aqueous suspensions other ionic species will be present, as H+ and OH- from water dissociation, and in many cases, ions produced by the atmospheric CO_2 contamination, as H+ and HCO3- from the partial dissociation of the carbonic acid generated by the dissolution of CO_2 in water. A salt-free model which include these real conditions is called “realistic salt-free (RSF)”.

To accomplish our aim, two models (SF and RSF) have been developed to compare and quantify their predictions. The models are based on the classical Poisson-Boltzmann theory, the standard electrokinetic equations and a cell model approximation to manage with electrohydrodynamic particle-particle interactions [1-3]. For the RSF model a non-equilibrium association-dissociation scheme for the chemical reactions in solution has been used [4].

The comparison of the dynamic electrophoretic mobility predictions according to SF and RSF models permit us to conclude: *i*) water dissociation and CO_2 contamination ions cannot be dismissed from a rigorous description of the electrophoresis in aqueous salt-free suspensions at low particle volume fractions and arbitrary particle charges. This is due to the larger concentration of those ions in comparison with that of the added counterions; *ii*) at higher particle volume fractions and not very low particle charges, the added counterions released from the particles are increasingly larger, screening the effect of water dissociation and CO_2 contamination ions. For these cases, SF predictions are good approximations for the dynamic electrophoretic mobility; *iii*) the discrepancies between the two models increase with the increase of particle radius at fixed particle charge density and volume fraction. This is due to the diminution of the added counterions concentration in solution in such conditions.

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Structural and Thermodynamic Properties of Water-Membrane Interphases: Significance for Peptide/Membrane Interactions.

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The thermodynamic properties of the lipid-protein interaction are governed by changes in the water activity of monolayers of different lipid composition according to the lateral surface pressure[1]. In order to clarify the role at the lipid-water interphase on the reactive properties of lipid monolayers to peptide adsorption and penetration we have compared and evaluated the compressibility of monolayers compressed gas phase lipid monolayers (GALMs) with self-assembly lipid monolayers (SALMs) obtained after the stabilization of the lipids in a force-free state.

According to water species present at the interphase, lipid membrane acts as a water state regulator, which determines interfacial water domains in the surface. It is proposed that those domains -formed by the contact between lipids themselves and between lipids and the water phase - are needed to trigger adsorption-insertion processes. The water domains are essential to maintain functional dynamical properties and are formed by water beyond the hydration shell of the lipid head groups. In this context, different water populations can be characterized below and above the phase transition temperature in relation to the CH_2 conformational states of the acyl chains[2, 3]. These water populations are congruent with the water pockets by which the partition of polar aminoacids into the membrane can be explained.

These confined water domains probably carries information in local units in relation to the lipid composition thus accounting for the link between lipidomics and aquaomics. The analysis of these results contributes to a new insight of the lipid bilayer as a non-autonomous, responsive (reactive) structure that correlates with the dynamical properties of a living system.

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Effects of Ethanol Based Disinfectant on Bacterial Zeta Potential

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Surface interfacial physiology is particularly important to unicellular organisms with regard to maintenance of optimal cell function (1). Bacterial cell surfaces usually possess net negative electrostatic charge on outer cell to induce the formation of electrical layers around each bacterial cell surface that interact with surrounding electrolyte (2). Aim of this study was to analyse the impact of ethanol base disinfection agent on zeta potential for three different bacterial strains: *E.coli*, *P.aeruginosa* and *S.aureus*. Cultivated strains were harvested by centrifugation at 10.000 rpm and washed with phosphate buffer solution with ionic strengths of 1 mmol/l (0.026 g KH_2PO_4, 0.047 g K_2HPO_4 in 1 l) and finally re-suspended in the same buffer to the final concentration of 10^7 CFU/ml (3). Electrophoretic mobility was measured using a Zetasizer Nano ZS. In this study, zeta potential was calculated from the electrophoretic mobility according to the method of Helmholtz-von Smoluchowski.

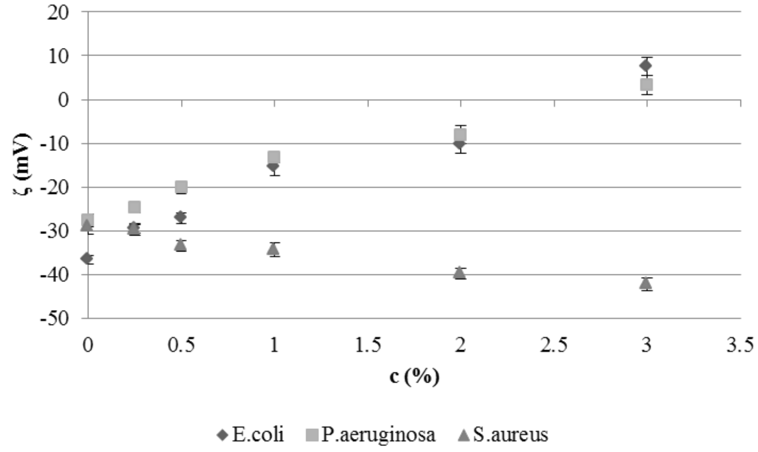

Fig. 1 Impact of ethanol based disinfectant to zeta potential of *E.coli, P.aeruginosa and S.aureus*

We demonstrated that ethanol based disinfectants increase zeta potential of *E.coli* and *P.aeruginosa*, whereas a decrease of zeta potential for *S.aureus* was observed. These results suggest that hydrophobic bacteria like *S.aureus* react to disinfectants differently compared to hydrophilic one. Results of our study also show that antimicrobials have potential to decrease bacterial zeta potential and disable its adhesion to material surface.

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Capacitive energy Extraction from Salinity Differences using Soft Carbon Electrodes

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Obtaining energy from the salinity differences in river mouths is a possible, but difficult task. Some approaches have been envisaged during recent years by the Capmix group (http://www.capmix.eu/). They are based on the capacitive variation of the solid/liquid interface when the salinity of the solution in contact is changed, and it has been shown that it is possible to convert the free energy of mixing directly into electric energy. There are two kinds of technologies, depending on the source of the voltage between the electrodes. One of them is CDLE (Capacitive energy extraction from Double Layer Expansion), in which porous carbon electrodes are charged in salt solution with an external DC power source or a supercapacitor, and discharged in contact with fresh water [1]. A different approach is known as CDP (Capacitive energy extraction based on Donnan Potential). In this case, the method is self-sufficient, since the origin of the voltage difference is the Donnan potential of the membranes that separate the solution from the carbon particles. Putting one electrode in contact with a cationic membrane and the other with an anionic one produces a voltage difference between both electrodes. From these methods we can learn that CDLE is a good candidate for being a cheap solution, whereas CDP teaches us that there is no need for external sources to provide the initial potential difference between both electrodes. We propose here a method that is based partially on both principles and at the same time avoids the disadvantages of each of them. We also work with a cell assembly with two electrodes separated by salt and fresh solutions pumped alternately, but we replace the carbon deposited on the electrodes by *soft* conductive particles made of a conductive core (activated carbon) coated by a polyelectrolyte layer of PDADMAC for the cationic electrode and PSS for the anionic one (Fig. 1). The method avoids the problems of cleaning and (bio)fouling associated to the use of membranes. Furthermore, the polyelectrolyte shell has not to be thick, and this makes the diffusion process fast, thus increasing the extracted power in comparison with CDLE.

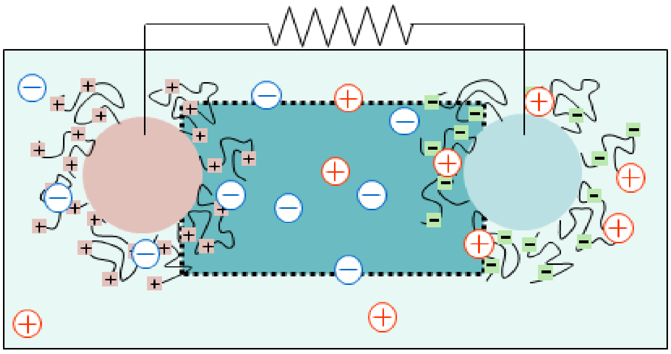

Fig. 1 Schematics of the soft electrodes for capacitive energy production.

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Effect of Flow Path Structure on Electroosmotic Dewatering

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The electroosmotic dewatering behaviors of various materials are discussed. The apparent liquid velocity u through the materials can be represented by Eq. (1). This is a variation of Darcy's equation under an electric field.

$$u = \frac{1}{\mu\alpha\rho_s}\left(E_{pg} + \frac{dp_L}{d\omega}\right) \tag{1}$$

Here μ is the viscosity of liquid, α the specific hydrodynamic resistance, ρ_s the true density of solid, and p_L the liquid pressure. ω is the moving material coordinate and denotes the net solid volume per unit cross-sectional area extending from the drainage surface up to an arbitrary position in the material. E_{pg} is the driving force of flow due to the electric field denoted by Eq. (2),

$$E_{pg} = \frac{f_s\varepsilon\alpha\rho_s D\zeta f}{\tau^2} i\rho_E \tag{2}$$

where f_s is the shape factor of the flow path, ε the porosity, τ the tortuosity of the flow path, i the current density, and ρ_E the specific electric resistance of the material. Here, we refer to E_{pg} as an electroosmotic pressure gradient. f in Eq. (2) is expressed by

$$f = 1 - \frac{2}{(\kappa D_e/2)}\frac{I_1(\kappa D_e/2)}{I_0(\kappa D_e/2)} \tag{3}$$

Here κ is the Debye-Hückel parameter, and D_e the equivalent diameter of flow path. I_1 and I_0 are the modified Bessel functions of the first kind of order one and zero, respectively. When the flow path is so narrow that the liquid is considered as homogeneously charged, then E_{pg} can be represented by

$$E_{pg} = \frac{\sigma_s}{\varepsilon} i\rho_E \qquad \text{(small pore model)} \tag{4}$$

where σ_s is the surface charge density per unit volume of solid. On the other hand, if the thickness of the electric double layer is neglected, E_{pg} is represented by Eq. (5).

$$E_{pg} = \frac{f_s\varepsilon\alpha\rho_s D\zeta}{\tau^2} i\rho_E \qquad \text{(large pore model)} \tag{5}$$

Empirical values of E_{pg} for swelling clay and superabsorbent hydrogel lie between the small and large pore models, suggesting some overlap of the double layers across the flow path of the materials. Based on Eq. (2), the electroosmotic dewatering is especially effective in removing liquid from highly compressible difficult-to-filter sludge, since it leads to a high electroosmotic pressure gradient.

Electroosmotic and Pressure Driven Dewatering of Clay Dispersions

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The treatment of disperse systems based on the use of electrokinetic phenomena presents an interest for a variety of industrial processes. In particular, dewatering of disperse systems is an important task for mining, food, paper and pharmaceutical industries, production of fertilizers, pigments and dyes, as well as for consolidation of sludge and wastes.

However, the possibility of electrotreatment of dispersions strongly depends on both surface and bulk properties of dispersed particles and is essentially limited by concomitant chemical and electrochemical processes. So, in spite of the wide use of electrokinetic phenomena in various practical areas, they need further systematic studies aimed at clarifying the main acting factors and optimization of the developed methods.

Analyzing electroosmotic dewatering of disperse systems it can be found that the efficacy of this process is determined by combination of two opposite factors. On the one hand, it is necessary to enhance the velocity of electroosmotic flow through the dispersion, i.e. to enlarge the surface potential of disperse particles. On the other hand, to promote the compaction of dispersion the electrostatic repulsion between the particles must be decreased, that is possible at the reduction of a surface potential. Taking into account that a surface potential of particles depends on the pH of the equilibrium porous solution, obtaining the optimal conditions is possible, but each type of dispersions requires a careful control of the characteristics of particles and liquids, and attention to the details of the treatment process.

That is why the experimental study of dewatering of dispersions consisted of two stages. The first stage was devoted to investigation of dispersion characteristics at different pH of the pore solution. The second stage deals with the dewatering process at electrical and pressure action. The investigations were conducted using a model system comprising the dispersion of kaolinite at different initial values of pH and moisture. It was shown that the applied pressure leads both to the compression of dispersion and to improvement of the contact of a treated dispersion with electrodes that accelerate electroosmotic dewatering in comparison with the application of an electric field only.

The established behavior of model dispersions at a wide range of pH, voltage and pressure is important for the development of electrokinetic technology because the obtained results allow predicting at which characteristics of dispersions one can obtain the stable and effective dewatering.

The obtained data may be also used for regulation of properties of disperse systems.

Electroosmotic Remediation of Fine Clay Soils Polluted by Uncharged Hydrophobic Organic Compounds

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Remediation of soils polluted with uncharged hydrophobic organic compounds is a very important and complicated ecological problem. Despite a number of rather successful attempts of soil decontamination from these matters, the efficacy of this process is still low and requires further researches and optimization.

For successful decontamination of soil the hydrophobic impurities should be transferred into the water-soluble form that can be realized by introduction of surfactants which provide desorption and movement of hydrophobic contaminants into the pore solution. Then it is necessary to provide a stable electro-osmotic flow, which removes the desorbed impurities from soil with their subsequent extraction from the cathode chamber. The efficacy of decontamination depends on many factors: soil chemistry and structure, sorption/desorption processes, ion exchange, polarization of soil particles and electrodes, electrokinetic mobility of pollutants etc.

Since the electroosmotic decontamination is the most acceptable method for fine clay soils, the rate and degree of soil remediation were studied using kaolinite polluted by different hydrophobic organic compounds (chlorobenzene, orthochlortoluene, cyclohexilbenzene).

Taking into account that the rate of electro-osmotic transport of contaminant depends on the electrokinetic potential of soil particles, which in turn depends on the pH of a pore solution, the important aspect of investigations was regulation of pH. That is why the electrohydrodynamic method of pH regulation was proposed and theoretically and experimentally substantiated.

The introduction of surfactants can change the surface potential of soil particles and charge the pollutants. Therefore the analysis of action of different surfactants was performed. Cationic surfactants cannot be used since clay soils have a negative electrokinetic potential, which decreases upon introduction of positively charged surfactants leading to a diminution of the electroosmotic velocity. Introduction of anionic surfactants increases the electrokinetic potential of soil particles accelerating electroosmosis, but in the same time these surfactants can charge the organic compounds leading to their electromigation in the direction opposite to electroosmotic flow, thereby also slowing down the rate of soil decontamination. Finally, nonionic surfactants do not charge the organic pollutants and soils and therefore do not affect the velocity of electrophoresis and electroosmosis. Thus, it can be supposed they are the most promising in soil remediation. To compare the efficiency of different surfactants the experimental remediation of soil was performed using non-ionic surfactants (Triton X-100, Tergitol 5-S-7, Neonol AF-9-12) and anionogenic surfactant (sodium dodecyl sulfate).

The conducted experimental investigations and subsequent theoretical analysis of all processes during soil remediation allowed finding the best conditions for soil decontaminations. It is shown, that correct choice of surfactant and effective regulation of electrokinetic potential of soil particles make possible to achieve a very high degree of model clay system and real soil decontamination from a number of hydrophobic organic impurities.

Modeling the Effect of Alternating Applied Electrical Fields on Tumor Cell Death

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While significant progress has been made in the treatment of cancer, effective delivery of drugs to cancer cells is still a formidable challenge because of the biobarriers imposed by the tumor environment at the cellular and tissue scales. One approach to overcome these biobarriers is by using applied electrical fields. Tumor treating fields (TTF) therapy using alternating applied electrical fields has recently been approved by the FDA for the treatment of patients with newly diagnosed glioblastoma multiforme (GBM, median survival rate with radiation and chemotherapy is 15 months) and has shown tremendous promise to become a new treatment modality to fight a wide variety of cancers. TTF therapy uses low intensity (1 – 2 V/cm) intermediate frequency (100 – 200 kHz) alternating electric fields to interfere with dividing cells and induce apoptosis (programmed cell death). It has been shown experimentally that alternating applied electrical fields induce tumor cell apoptosis through two mechanisms of action that disrupt mitosis in actively dividing cells. In the first, alternating applied electrical fields between 100 and 300 kHz become non-uniform in dividing cells and interfere with mitotic spindle formation via the dielectrophoretic movement of charged tubulin molecules, preventing them from polymerizing, thus arresting mitosis. The second disrupts the final step in mitosis, cytokinesis, in which an hourglass shaped cleavage furrow is formed, creating dense electrical forces in the center which move charged molecules within the cell toward the furrow, interfering with internal cell structure, thus leading to cell death [1, 2]. However, the effects of these applied electrical fields on drug delivery to tumor cells from a mechanistic perspective remain poorly understood and unpredictable. Thus, the resulting trial and error approach to designing devices and protocols for therapies has led to few commercially available treatment systems.

Here, we will present a mathematical model using idealized morphological descriptions of a single tumor cell during anaphase and cytokinesis under the influence of an alternating applied electrical field, viewing them as straight and diverging rectangular microchannels, respectively, with walls consisting of the inner part of the cell membrane which is positively charged, the inside of the microchannel containing the cell's cytoplasm (fluid domain) and charged molecules (solute domain) [3]. The electrokinetic-hydrodynamics (EKHD) approach [4] is used to link the fluid and solute domains to obtain effective transport coefficients (i.e., effective velocity and diffusivity) that are explicit functions of the physicochemical and geometrical parameters of the system. Based on these effective parameters, tumor cell death can be predicted.

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The Effect of Water on pH-Dependent Charge at Metal Oxide/Aqueous Electrolyte Interface

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For development application of surface complexation models and analysis of the surface reactions the properties of individual surface planes should be measured. The surface of colloids and nanoparticles consists of different crystallographic planes. Therefore, from measurements of surface charge density and electrokinetic potential of particles only the average surface properties could be evaluated.

Construction of single crystal metal oxide and silver halides electrodes enables measurements of inner surface potential of defined crystal planes. While streaming potential (or streaming current) measurements provide the electrokinetic zeta-potential of defined crystal plane. The comparison and analysis of those two measured potentials leads to interesting and surprising findings.

For some metal oxide crystal planes the measured Ψ_0(pH) function is nonlinear with a broad zero-potential region around the point of zero potential. This result could be interpreted by surface complexation model and is in accordance with predictions of the Multi-site Complexation Model (MUSIC). In such a case electrokinetic streaming potential measurements of the particular crystal plane provides the clear isoelectric point and higher values of the zeta potential with respect to measured inner surface potentials (Figure 1.). This unexpected behavior could be explained by considering pH dependent charging of the interfacial water layer affecting electrokinetic behavior but not the surface potential. Additionally the surface and zeta-potential measurements on AgCl and AgBr single crystals and colloid particles show that the zeta-potential exhibits pH-dependence, while the surface potential does not.

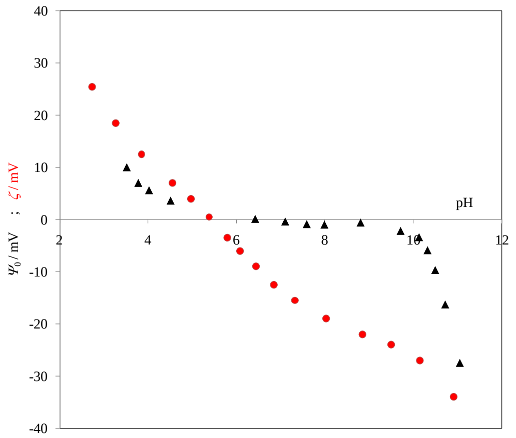

Fig. 1 Surface potential of sapphire: Ψ_0 (▲ 10^{-3} mol dm^{-3} KCl)
Electrokinetic potential of sapphire: ζ (● 10^{-3} mol dm^{-3} KCl)

Remediation of Triclosan in Soil through Electrokinetics

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This work discusses the efficiency of the electrokinetic process (EK) applied to soil matrices aiming triclosan remediation.

Two soils were used in this study: S1 (Valadares, Vale de Milhaços, 0–15 cm depth) and S2 (Paul de Magos, Salvaterra de Magos, Portugal, 0–20 cm depth). Soil S1 (sandy) was used as a support medium and S2 (silty loam) as the contaminated matrix. Four experiments were carried out without pH control at 0, 10 and 20 mA; and with pH control (anolyte, pH > 13) at 10 mA.

After the EK treatment, contaminant was mainly mobilized towards the cathode end due to electroosmosis, this fact being more expressive when pH was controlled. The octanol–water distribution of triclosan depends on the pH of the environmental matrix to which it is exposed, and, as the hydroxyl groups (–OH) in the molecule are capable of deprotonation, it promotes its water solubility. Triclosan has a pKa of 7.9 and at the end of experiment with pH control, soil pH near the cathode was 9.36, consequently triclosan will be predominantly in its ionised form. This resulted in a higher solubility and faster mobilization to the cathode end. In the last 24 h of the EK experiment, triclosan presented a mobilization rate of c.a. 1.2 $\mu g\ min^{-1}$.

The mass balance performed showed that the amount of triclosan not detected in the cell was similar to the quantity that may suffer photo and electrodegradation (approx. 60%).

In all experiments, the percentage of contaminant that remained in both soils was approximately 30, with no statistical differences between treatments.

Remediation of triclosan seems to be feasible through an integrated approach with different remediation/removal mechanisms (EK transport, electro- and photodegradation). The results here presented are of valuable knowledge for the remediation of organic contaminants similar to triclosan using the EK process.

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Flocculating Properties of an Extracellular Biopolymer Produced by Bacterial Strain *Rhodoccocus*

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At present, flocculants are widely applied in different industrial processes such as wastewater treatment, drinking water purification and downstream processes in biotechnology. Microbial-produced flocculants are a kind of newly developed flocculants. These natural occurring and environment-friendly flocculants have received increasingly scientific and technical attention because they are biodegradable and nontoxic. Over the past decades, some microorganisms, including algae, bacteria, actinomyces and fungi, have been reported to produce bioflocculants. Bioflocculants are kinds of extracellular biopolymer containing glycoprotein, polysaccharide, protein, cellulose, lipid, glycolipid and nucleic acid [1].

The mechanisms of flocculation in biological systems has been extensively investigated, however are not fully understand. In general, bioflocculants cause aggregation of cells and particles by bridging and charge neutralization. Most bioflocculants and suspended particles are negatively charged. Hence, cations can neutralize negatively charged functional groups of both bioflocculant molecules and suspended particles, which increased the adsorption of biopolymer on suspended particles and may mediate bridging between solid particles and the bioflocculant molecules [2,3].

The influence of bioflocculant produced by bacterial strains belonging to family Nocardiaceae on the behavior of kaolin dispersions was studied in the presence of calcium ions at different pH. Kaolin suspension acted as a model to explore the flocculating mechanism. Flocculating activity was investigated by means of zeta potential, mean diameter and light transmittance measurements.

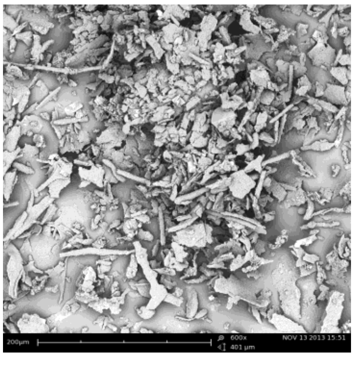

Fig. 1 Extracellular polysaccharides produced by bacterial strains *Rhodoccocus* belonging to *Actinomycetales*.

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Electrophoretic and Electro-Optical Research of Montmorillonite Nanoplates

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The montmorillonite (MM) is clay mineral with the form of plates consisting of nanoplates which crystal structure is comprised by central alumina and two lateral silicon monolayers. The MM-plates are negatively charged due to isomorphic substitution of Al^{III} with Mg^{II} in the Al-monolayer and of Si^{IV} with Al^{III} in the two Si-monolayers. So originated negative charge is pH-independent; the plate edges obtain pH-dependent positive or negative charge (due to association of H^+ or OH^-) when MM is suspended in aqueous medium.

The aim of our work is to find the quantity and distribution of the substituted atoms and on this base to construct a model of MM nanoplate. For this purpose we applied the methods of microelectrophoresis to determine the surface charge density and the electric light scattering to find out the lateral asymmetry of the substituting Al^{III} atoms. The novelty in our work is the combination of electrokinetic and electro-optical methods which allows obtaining information of both charge density and its asymmetrical distribution.

Our results for the pH-dependence of the electrophoretic mobility show out that the isoelectric point is at pH 7.3. The charge density at this pH (where the plate edges are not charged) gives the density of all substituted atoms. The difference between the so determined charge and the Mg^{II} heteroatoms (measured by emission atom spectroscopy) is equal to the surface density of the substituting Al^{III} atoms.

The dispersion curve of the electro-optical effect (EOE) shows out a low-frequency behaviour which traditionally is interrelated as a permanent dipole moment but the form of EOE at applying of a rectangular electric impulse or reversed two impulses disproves this interpretation. So, we accept that the substituting Al^{III} atoms are distributed symmetrically in the two Si-monolayers and have constructed a model of MM nanoplate which takes into account the charge density and the quantity of Mg^{II} atoms in the central Al-monolayer.

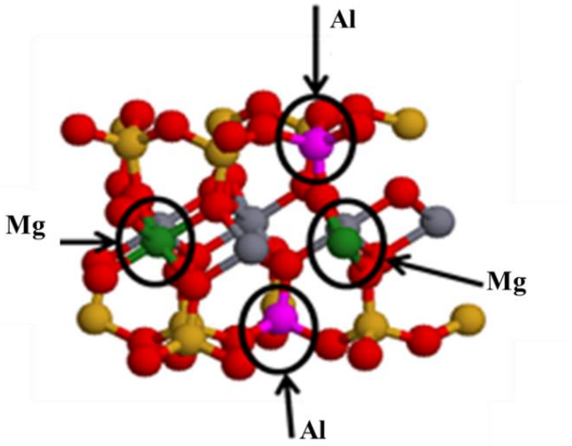

Fig. 1. Model of MM-montmorillonite nanoplate. The atoms are coloured in: red (O), gray (Al), yellow (Si), green (substituting Mg in the Al-monolayer), and pink (substituting Al in the two Si-monolayers).

Electrophoretic mobility of alumina particles with adsorbed carboxymethyl cellulose

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Continuing investigation of the electric properties of colloid particles with adsorbed polyelectrolyte [1, 2] in the present work we study the electrophoretic mobility at different surface concentration and charge density of the polymer chains. As a polyelectrolyte was chosen carboxymethyl cellulose (CMC) which charge can be altered by pH of the medium due to dissociation of the COOH (carboxylic) groups [3]. As colloid particles with amphoteric surface was chosen aluminum oxide (γ-Al_2O_3). The applied method was microelectrophoresis in dark light field allowing measuring the mobility of free single particles with submicron size. The measurements are done at pH 4.5 and pH 6.0 where the particles are positively charged with equal surface charge density and CMC chains are negatively charged but with different linear charge density.

The polymer concentration dependence of the electrophoretic mobility shows out that the particle total charge changes its sign from positive to negative at CMC adsorption. Before reaching the isoelectric point (IEP) the total charge decreases faster at pH 6.0 according to the higher chain charge (at pH 4.5 and pH 6.0 the degree of dissociation is $\alpha \approx 0.5$ and 1.0, respectively) but after IEP the CMC concentration dependence shows that the total charge at pH 6.0 is less than that at pH 4.5. That means that the adsorbed polymer chains introduce smaller charge to the particles although they are stronger charged. This fact is a new observation which we explain with two known phenomena.

The first is the counterion condensation on a polyelectrolyte chain which appears when the linear charge density exceeds some critical level; as a result the adsorbed CMC chains add to the surface smaller effective charge than their own. The application of the Manning's theory to the used CMC shows out that at pH 4.5 there is no condensation but at pH 6.0 about 37% of the chain charges are neutralized forming group-ion pairs [$COO^{-}Na^{+}$] [3]. Nevertheless the linear charge density is higher at pH 6.0 than at pH 4.5 and that do not allow explaining the smaller electrophoretic mobility of recharged particles if we use the counterion condensation phenomenon.

The smaller total charge at pH 6.0 can be explained with the smaller number of adsorbed CMC chains after IEP taking into account that the long free CMC chains have a random coil conformation in solution and their radius of gyration increases with the charge density due to the electrostatic expansion [3]. Being adsorbed on the particle surface each chain covers area which is higher at pH 6.0 than at pH 4.5 and that hinder the adsorption of additional chains on the locally free particle surface.

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Pore Network Model of Electrokinetic Transport through charged porous media

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We introduce a method for the numerical determination of the steady-state response of complex charged porous media to pressure, salt concentration and electric potential gradients. The macroscopic fluxes of solvent, salt and charge are computed within the framework of a Pore Network Model (PNM) [1], which describes the pore structure of the samples as networks of pores connected to each other by channels. The PNM approach is used to capture the couplings between solvent and ionic flows which arise from the charge of the solid surfaces. The microscopic transport coefficients on the channel scale, taken here of a simple analytical form obtained previously by solving the Poisson-Nernst-Planck and Stokes equations in a cylindrical channel [2], are upscaled for a given network by imposing conservation laws for each pores, when macroscopic gradients are applied to the sample. The complex pore structure of the material is captured by the distribution of channel diameters. We investigate the combined effects of this complex geometry, the surface charge and the salt concentration on the macroscopic transport coefficients. The upscaled numerical model preserves the Onsager relations between the latter, as expected [3]. The calculated macroscopic coefficients behave qualitatively like their microscopic counterparts, except for the permeability (see Fig. 1) and the electro-osmotic coupling coefficient when the electrokinetic effects are strong. Quantitatively, the electrokinetic couplings increase the difference between the macroscopic coefficients and the microscopic ones for a single channel of average diameter.

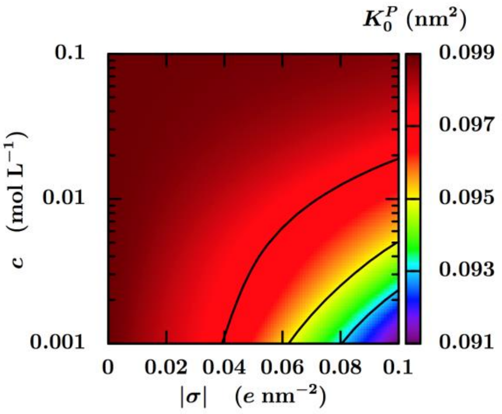

Fig. 1 Macroscopic permeability K_0^P (in nm^2) as a function of the salt concentration c in the reservoirs in equilibrium with the charged porous material, and of the surface charge density σ of the channels.

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Optical Trapping Electrophoresis of Conjugated Microparticles for Drug Delivery and Biomolecule Detection

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Functionalized colloidal particles are being extensively used for drug delivery and biomolecule detection. In these applications, the surface properties of a colloidal particle are chemically modified using a suitable biopolymer, giving specific characteristics to the system. This surface modification results in the variation of electrical properties of the particles. Knowledge of these electrical properties is essential to determine the suitability of a colloid for a specific problem.

We use a novel technique called optical trapping electrophoresis (OTE) to examine the effect of this surface modification on the electrical properties of the particles. In OTE, a single colloidal particle is confined by a tightly focussed laser while being subjected to an externally applied AC field. This allows for a mobility measurement from which the zeta potential of this particle can be calculated. Furthermore we compare the results of this single-particle technique with those obtained by using commercial Malvern Zetasizer.

We studied carboxylated polystyrene particles bioconjugated with chitosan and gelatin in deionised water (DI) and a Dulbecco's phosphate buffered saline (DPBS). After each step of the surface modification process the zeta potential of the particles was measured using the aforementioned methods. For the particles immersed in DPBS, we found an excellent agreement between the zeta potential measurements acquired with OTE and with the commercial Malvern Zetasizer.

Light Beam Modulation Using Nematic Defect Lines

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Liquid crystals are important materials in modern optics and photonics due to their birefringence and the possibility of external control. Of special importance for photonics are distortions of nematic order at the micrometer and even sub-micrometer scale, which can be naturally generated by nematic defects and colloids [1,2]. Recently, it was shown that nematic singularities can induce singularities also in the light field by propagating light along nematic defects [3].

In this work, we model the propagation of light along various nematic defect structures using the Finite-difference time-domain (FDTD) method [4]. The FDTD modelling approach is custom developed, capable of calculating the time-evolution of full electric and magnetic fields by applying the first two Maxwell's equations on a discrete time and space lattice. Using the numerical method, we model the propagation of light along nematic defect lines with different winding numbers. Interestingly, we find that at distinct birefringence and defect line length, the polarization of light obtains a defect with twice the winding number of the liquid crystal defects lines, combining the topological invariants of the two fields. Additionally, defect lines can be used to shape the intensity profile of a short laser pulse and even split the pulse into multiple modes. Finally, we show that modulation of both light intensity and polarization is possible by propagating light along nematic defect lines, further allowing for controllable tuning of the flow-of-light with parameters like temperature and external electrical fields.

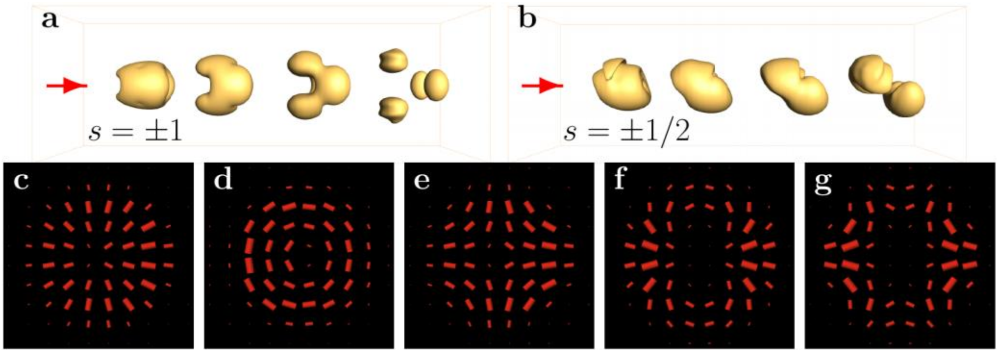

Fig. 1 Intensity and polarization profiles obtained by shining a short laser pulse (a,b) or continuous laser light (c-g) along nematic disclination lines with different winding numbers.

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Travelling Wave Electrophoresis for Microfluidic Separations

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Travelling Wave Electrophoresis (TWE) is a newly developing technique for microfluidic separations. Periodic arrays of electrodes are used to create a travelling electric field down a microchannel to transport, concentrate, and separate charged species. It allows for tunable real-time switching between separative and non-separative transport. This is achieved by the various species being trapped, partially trapped, or failing to be trapped by the travelling electric wave. The advantages the technique shows over capillary electrophoresis will impact the fields of proteomics, molecular biology, cell biology, genetics, materials synthesis, and lab-on-a-chip devices for in-the-field analysis [1].

Through use of COMSOL v.4.4 finite element modeling we analyze the dependence of band dispersion and separation on various system parameters such as the molecular concentration, species mobility, system dimensions, and wave speed. The Poisson-Nernst-Planck system of equations is used to solve for the states of the continuous ion concentrations and the electrostatic potential over time. A microchannel with periodic boundary conditions on the ends contains an array of electrodes each with a low frequency AC potential with a quarter period difference from one electrode to the next. Our simulations confirm experiments performed by Timperman et al which have successfully demonstrated separation of simple mixtures [2].

Fig. 1 An example of the device producing a travelling electric wave through the microchannel.

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Enzyme Concentration Measurements with Optical Tweezing Electrophoresis

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The demand for quantitative detection of enzymes arises in many applications such as diagnostics, therapeutics and water quality monitoring. Typically only minute concentrations of the target enzyme are available, along with several other biomolecules. Hence a method to determine concentration of this enzyme needs to be sensitive and specific.

We propose a novel way to determine this enzyme concentration, based on optical tweezing electrophoresis (OTE). This method measures the electrophoretic mobility of a single microparticle that is able to bind specifically with the target enzyme because of an antibody coating. A tightly focused laser beam is used to confine this particle. Additionally, an applied AC electric field makes the particle oscillate with an amplitude proportional to its electrophoretic mobility. Hence, by accurately measuring the particle position in time, we can extract its mobility. Since a binding of the target enzyme changes electrophoretic mobility of the particle, we are thus able to quantify the number of enzyme bindings on the particle and hence the concentration of the target enzyme present in the solution.

This work uses biotinylated polystyrene particles to determine the concentration of avidin in a solution. We show that OTE can be used for concentration monitoring of enzymes. Moreover, we can clearly discriminate between specific and non-specific binding. Also, the results are compared with standard PALS zeta potential measurements.

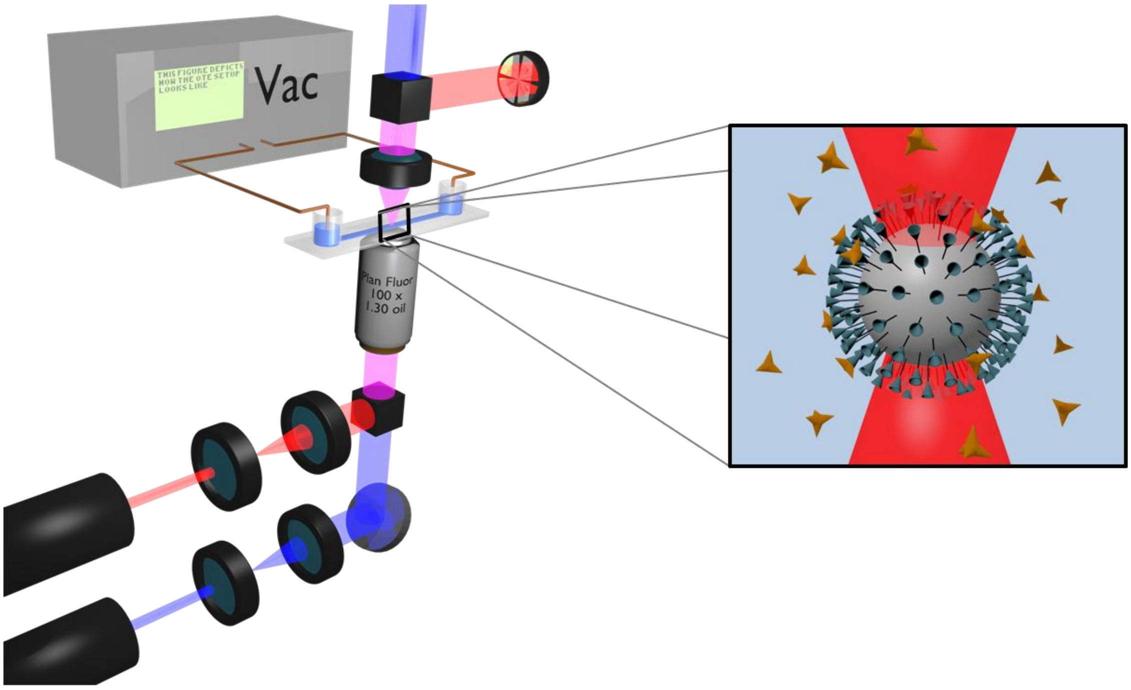

Fig. 1: Schematic representation of Optical Tweezing Electrophoresis.

Transient Electrokinetic Flow in a Fibrous Porous Medium

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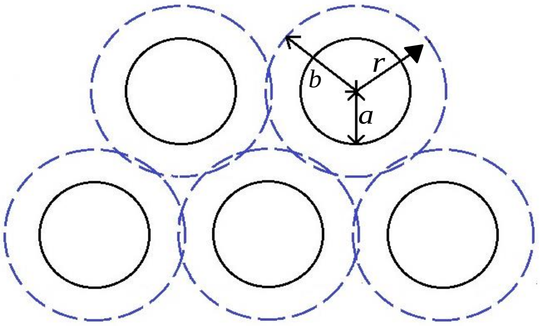
The transient response of an electrolytic solution of viscosity η, kinematic viscosity ν, and dielectric permittivity ε in a fibrous porous medium constituted by a homogeneous array of parallel charged circular cylinders of radius a to the step application of an electric field E and a pressure gradient P in the axial direction is analyzed through the use of a unit cell model. By solving the Poisson-Boltzmann equation and modified Navier-Stokes equation applicable to the system, the electric potential distribution $\psi(r)$ and time-evolving velocity profile $u(r,t)$ in the fluid phase are determined for arbitrary values of the electric double layer thickness $1/\kappa$ and the zeta potential ζ associated with the dielectric cylinders. Results for the flow rate, the electroosmotic velocity, and the effective electric conductivity of the fluid are obtained as functions of the elapsed time t and the porosity $1-\varphi$ [$= 1-(a/b)^2$] of the fibrous medium. The effects of the relevant dimensionless parameters (κa, $\zeta e/kT$, φ, $\nu t/a^2$) on the transient starting electrokinetic flow in the fiber array are significant and interesting. For a fibrous medium with smaller porosity, a much shorter elapsed time is needed for the fluid velocity and the electric current density to be within a certain percentage of their steady-state values.



$$u(r,t) = u_\infty(r) - u_{\mathrm{t}}(r,t)$$

$$u_\infty = \frac{P}{4\eta}(2b^2 \ln\frac{r}{a} + a^2 - r^2) - \frac{\varepsilon E}{\eta}[\zeta - \psi(r)]$$

$$u_{\mathrm{t}} = \sum_{n=1}^{\infty} C_n W_{0n}(r)\exp(-\beta_n^2 \nu t)$$

Fig. 1 Geometrical sketch of the unit cell model for a fibrous porous medium constructed by a uniform assemblage of parallel circular cylinders.

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Electro-Thermal Micro-Pumps: Exploiting Structural Polarizations at Smeared Interfaces

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We present various designs for new AC electro-thermal micro-pumps (ETµPs) which exploit AC electro-kinetic forces acting in the volume of a fluid in the presence of a temperature gradient.[1,2] The temperature gradient is induced by local Joule heating or separate heating elements. It creates conductivity and permittivity gradients in the pump medium. In the presence of such gradients, an external AC electric field influences smeared spatial charges in the bulk of polarizable media. When there is also a symmetry break, the field-charge interaction results in an effective volumetric force resulting in medium pumping, which can only be observed when the heating gradients and an AC pump field were applied simultaneously.[1-4] Different ETµP chip designs were processed on glass carriers by micro-systems technology (Fig. 1). The AC-field electrodes and an optional DC-heating element consisted either of bare or passivated 100 nm thick platinum structures, which were arranged in differently sized channel geometries in the 10 to 100 µm ranges. The pump-channel walls and cover were made from polymer and thin-glass, respectively. Measurements of the velocity of the pump flow were consistent with finite-element method (FEM) simulations and an analytical model for passivated and non-passivated ETµPs using an equivalent-circuit diagram.[5,6] The advantages of the ETµP principle are the absence of moving parts, the opportunity to passivate all the pump structures, homogeneous pump channel-cross sections reducing the risk of the channel clogging by debris, force plateaus in broad frequency ranges as well as a reversal of the pump direction in dependence on the driving frequency. The operating frequencies ranging from kHz to GHz avoid electrolytic processes and electrode deterioration. The integration of additional inductances allows for an increase of the pump velocity at low AC-field voltages at resonance conditions. The usable conductivity of the pumping medium ranges from extremely low to above physiological values. A further miniaturization of the pumps is also viewed as quite feasible.

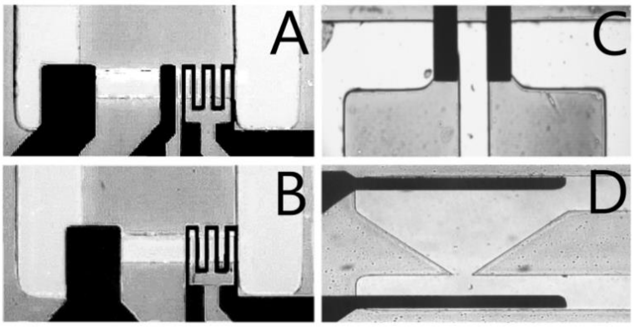

Fig. 1: Microscopic images of different ETµP designs (dark: platinum structures; light gray: polymer-wall structures; light areas: fluid channels). A and B are indirectly (separate ground-field electrode) and directly heated ETµPs with meander-heating elements, respectively. C and D have only field electrodes. A symmetry break is introduced by a T- (C) or a funnel-shaped pump channel (D).

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Electro-Osmotic Flow of Semidilute Polyelectrolyte Solutions

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We investigate electro-osmosis in aqueous solutions of polyelectrolytes using mean-field equations[1]. A solution of positively charged polyelectrolytes is confined between two negatively charged planar surfaces, and an electric field is applied parallel to the surfaces. When electrostatic attraction between the polymer and the surface is strong, the polymers adhere to the surface, forming a highly viscous adsorption layer that greatly suppresses the electro-osmosis. Conversely, electro-osmosis is enhanced by depleting the polymers from the surfaces. We also found that the electro-osmotic flow is invertible when the electrostatic potential decays to its bulk value with the opposite sign. These behaviors are well explained by a simple mathematical form of the electro-osmotic coefficient. Furthermore we mention the result is related to the electrophoresis of charged colloids.

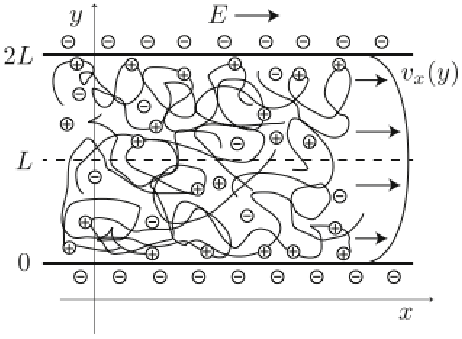

Fig. 1 The schematic picture of our system.

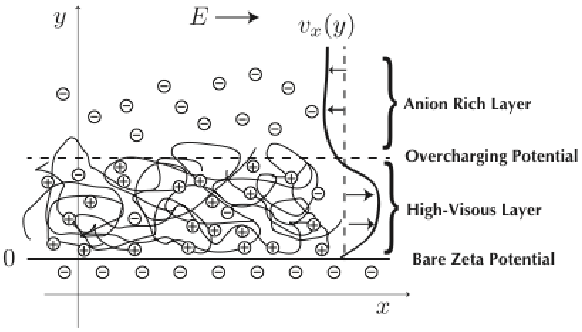

Fig. 2 The details of surfaces when surface charge is inveted.

$$V = L_{11}P + L_{12}E,$$
$$J = L_{21}P + L_{22}E.$$

$$L_{12} \approx \frac{\eta_{\mathrm{b}}}{\eta_{\mathrm{S}}} L_{12}^{\mathrm{b}} + \left(1 - \frac{\eta_{\mathrm{b}}}{\eta_{\mathrm{S}}}\right) L_{12}^{\mathrm{M}},$$

V is volume flux density through the slit, *J* is the electric current density, *P* is the pressure difference, *E* is the electric field, L_{ij}'s are the kinetic coefficients, especially, L_{12} is the electro-osmotic coefficient. At the situation where the adsorptive polyelectrolytes invert the sign of the surface charge, the electro-osmotic coefficient is determined by above equation. η_b and η_S are the viscosity at the bilk and near the surface. L_{12}^b and L_{12}^M are the bare coefficient and the coefficient estimated by overcharging potential.

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Electroacoustics of Nanoparticle Doped Hydrogels

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The Electrokinetic Sonic Amplitude (ESA) is an effect that has been used widely to ascertain particle size and zeta-potential in concentrated colloids. However, the ESA spectrum encodes more than the particle size and zeta-potential when the particles are dispersed in a polymeric gel. This study experimentally examines the electroacoustic response of nanoparticles dispersed in polyacrylamide hydrogels, systematically varying the particle size and hydrogel elasticity. These experiments were undertaken at frequencies from 1 to about 20 MHz. As expected by theory (Wang & Hill, 2009), the magnitude and phase of the dynamic electrophoretic mobility are influenced by hydrogel elasticity. For large particles (~100 nm diameter), the mobility decreases monotonically with increasing gel modulus, whereas for small particles (~30 nm diameter), the mobility becomes independent of the gel modulus when dispersed in sufficiently weak gels (<1 kPa). This has previously been attributed to the particles being smaller than the hydrogel mesh size (Bhosale *et al.*, 2011). Here, analysis of the phase reveals that the dynamic mobility becomes independent of the gel stiffness at high frequencies; this reflects the dynamics being controlled by viscous stresses. At low frequencies, the gel elasticity controls the dynamics, with the phase being highly sensitive to the gel elasticity.

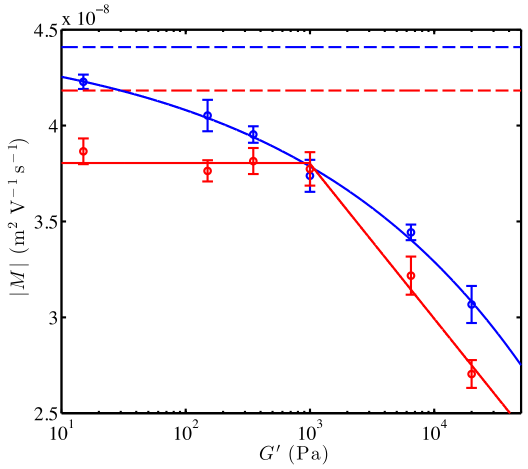

Fig. 1 Dynamic electrophoretic mobility magnitude (at 14 MHz) of 100 (blue) and 30 (red) nm diameter particles dispersed in a hydrogel versus the gel storage modulus; dashed lines identify particle mobilities when in pure interstitial electrolyte.

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A Critical Review of the Electrospray Mechanisms.

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Electrospray ionization (ESI) is a widely adopted soft ionization method for mass spectroscopy (MS). In spite of the unequivocal success of the technique, its mechanisms are difficult to be analytically modelled or observed, because the process is characterized by non-equilibrium conditions. The common belief is that the formation of gas-phase ions takes place at the apex of the Taylor cone via electrophoretic charging. The charge balance requires that a conversion of ions to electrons should occur at the metal-liquid interface of the injector needle. We have detected that the above description is based on unproved assumptions which are not consistent with the correct evaluation of the problem. Some experiments probe that the emitted droplets are not charged, even in cases where the liquid consists of a solution of ionic species. This conclusion appears to be valid as long as no corona discharge at the needle is observed, which is a condition easily fulfilled at atmospheric pressure. Further work is required to clearly understand how ionization occurs in in ESI-MS.

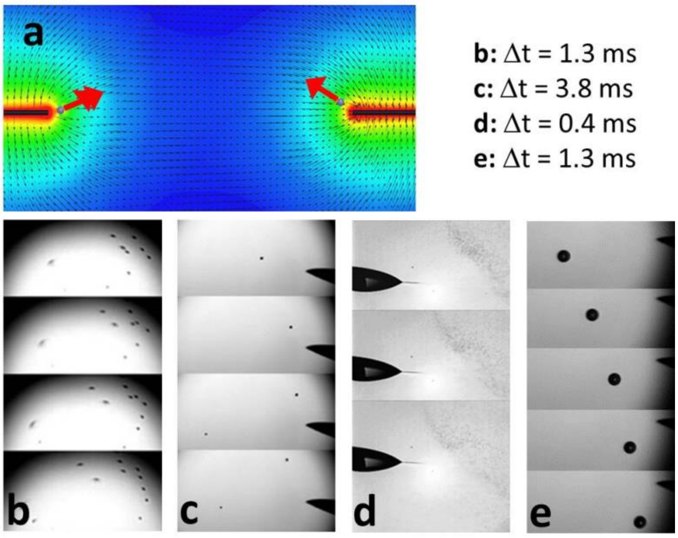

Fig. 1 Droplet motions (from left to right) under symmetric field conditions. Panel a: electric field and E-vectors as obtained by finite elements calculations. The red arrows indicate the direction of the force acting on probe water drops in some selected positions. Panel b-e: sequences of frames extracted form high speed movies (20000 frames/s). The time elapsed between adjacent photograms is reported in the legend. Time increases in downward direction. Panel b: water droplets. Injector at -6.6 kV, extractor at ground. Injector-extractor distance 2 cm. Flow rate: 4 μl/s. The images are centered at 1 cm from the injector tip. Panel c: water droplets. The experimental conditions are the same of panel b. The images are centered at the extractor. Panel d: ethanol stable jet. Injector-extractor distance: 2.7 cm. Flux: 1 μl/s. Injector a -3.9 kV; extractor at ground. Panel e: NaCl aqueous solution. Injector-extractor distance: 1 cm. Injector at 2kV, extractor at ground. Flux: 4μl/s

Electrical Switching of Droplets in Segmented Flow

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Droplet switching operations find application in miniaturized biotechnology, cell cultivation and screening programs as well as for future applications in miniaturized and automated diagnostics and in particular for automated experiments in ultraminiaturized combinatorial chemistry and combinatorial screenings in multidimensional parameter spaces [1].

In droplet-based microfluidics, two immiscible phases combine to form a segmented flow of discrete segments. This contribution describes how aqueous droplets separated by tetradecane can be switched into either output branch of the y-shaped microchannel [2]. Non-galvanic electrical switching was achieved by applying a potential to copper electrodes inserted into a moulded polycarbonate chip, so that an electric field was applied perpendicular to flow through the channel. Image-based triggering facilitated reproducible and reliable switching operations. Model experiments demonstrate that the motion of droplets is initiated only by the response to the change of polarity of the electrical field and not by the static electrical field itself. The transient buildup of electrostatic charge at the water-oil interface is the likely cause of the observed electrokinetic phenomenon.

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Electroacoustic versus Electrophoretic Measurements on Dispersions of Nanocolloids

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A key aspect of colloidal particles is that they often bear an electrical charge that controls their interactions with the surrounding medium. Properly characterizing this charge is then of prime importance for understanding numerous phenomena such as coagulation/flocculation or heavy metal and natural organic matter adsorption in environmental systems. In the case of nanoparticle's dispersions, the main technique applied is laser Doppler electrophoresis, while conductivity or electroacoustics are seldom used [1].

In the present study we show the advantages of electroacoustics over electrophoresis for charged systems with diameters between 1 and 20 nm using model systems. Our home made electroacoustic device provides the electrical potential produced by an ultrasonic wave at 1MHz for a sample of 4 ml. It has been recently validated on polyoxometallates for which the measurements agree with the theoretical signal [2] calculated without adjusting parameters. With this electroacoustic device, the mobility of silica nanoparticles (diameter 12 nm) dispersed in water can be determined down to 0.05% in weight, although this electroacosutic technique is usually claimed to operate above 1% in weight. In these dilute silica dispersions, laser Doppler electrophoresis is considered the most suitable technique, however the measured signal appears too noisy or even too low to extract reliable mobilities.

These results open new possibilities for understanding the behaviour of such small nanocolloids, for example electrostatically stabilized iron nanooxides in polar organic solvents as DMSO and DMSO-water mixtures, for which preliminary results will be presented.

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Surface Energy Analysis (SEA) Study of Hyaluronan Powders

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Results of inverse gas chromatography adsorption/desorption experiments of selected probes on sodium hyaluronate powder material are presented. It was found that a dominating was a dispersive surface energy part thus indicating low polarity character of the studied HA powder. For 0 % coverage 30 mJ/m^2 total surface energy was found. There was found a relatively high inhomogeneity of the surface structure of the studied polymer powder. A total surface energy distribution was ranging from 10 to 34 mJ/m^2 with maximum at 18.5 mJ/m^2. It was similarly as in the previous case of surface energy profile controlled by dispersive part. By measuring free energy profiles dependencies for selected probe molecules of different polarity there was found approximately seven-fold higher energy content (15 kJ/mol) in comparison to dichloromethane (2 kJ/mol). There were determined work of cohesion and work of adhesion (water) on HA surface.

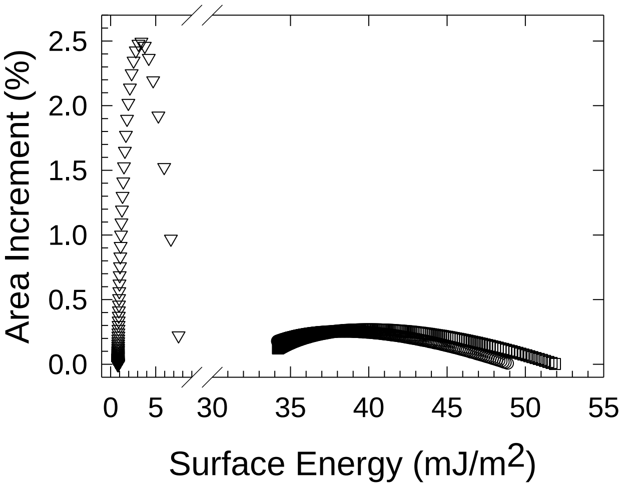

Fig. 5. Total surface energy and its components distribution plot of freeze-dried HA powder. Circle – dispersive part of the surface energy, triangle down – acido-basic part of surface energy, square – total surface energy.

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Low Frequency Complex Impedance Measurements of Na-Montmorillonite Suspensions

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The accurate knowledge of the textural and electrochemical properties of clay suspensions is of great importance for many applications in soil and environmental chemistry involving the use of clay-rich porous media. These applications concern, for example, the understanding of the reactive transport properties of bentonites and argillites for the long-term prediction of the diffusivity of ionic species around radioactive waste repositories[1]. Na-montmorillonite suspensions are characterized by an anisotropic surface charge distribution: a permanent high surface charge of their basal planes and a pH and salinity dependent surface charge of their edge planes. Current complex impedance measurements of charged suspensions are limited at low frequencies (typically < 1 kHz) by the electrochemical polarization of the current and potential electrodes and by the phase accuracy of the impedancemeter. A new four electrodes sample holder (separate current injection and potential electrodes, Fig. 1a) and a very high accuracy impedancemeter[2] are proposed to improve the low-frequency complex impedance measurements of charged Na-montmorillonite suspensions. Low-frequency ([0.1 Hz 45 kHz]) complex impedance measurements, at various clay volume fractions (0.1, 0.2, 0.4, 0.6, and 2%), pH (5, 7, 9) and salinities (NaCl, from 10^{-4} to $5x10^{-2}$ mol L^{-1}), were done to elucidate the textural and electrochemical properties of Na-montmorillonite suspensions. Our results show that the electrochemical polarization of the electrical double layer around the Na-montmorillonite particles can also be observed at low frequency and high salinity (Fig. 2a). Nevertheless, our measurements are also disturbed by the electromagnetic coupling due to the short triaxial cables, which connect the electrodes to the impedancemeter.

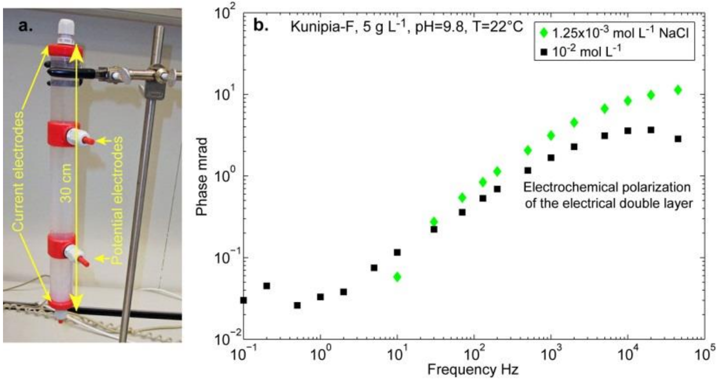

Fig. 1. **a.** The four electrodes sample holder for the complex impedance measurements and **b.** the recorded phase of Na-montmorillonite suspensions

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New Insights into the Streaming Potential Analysis of Solids

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The electrokinetic effects of streaming potential and streaming current for the assessment of the electrokinetic or zeta potential at the interface between a macroscopic solid and an aqueous solution have been known and employed for more than a century. The streaming potential is thus expected to offer a mature method for surface charge characterization. However, recent literature tells us that there are a lot of open questions still to be resolved. Yaroshchuk and Ribitsch have assumed an impact of porosity of a solid material on the streaming potential and thus on the magnitude of the zeta potential [1]. Experimental prove for this assumption and the effect of porosity on the streaming current, which was unexpected until then, was presented only recently [2]. The modified Helmholtz-Smoluchowski equation for porous material surface analysis was applied to thin-film composite polymer membranes [3] which revealed another artefact in the streaming potential measurement: the impact of undeveloped flow conditions [4].

In this contribution we discuss the physical background for the streaming potential and streaming current inside pores and present an experimental method for the separation of their outer and inner surface contributions to the zeta potential of porous material. This method is comprised of the measurement of streaming current at different distances between adjacent sample surfaces. Fig. 1 shows an example for the linear dependence of streaming current with the height of the rectangular capillary between flat sheet membranes. Depending on the sample dimensions we obtain a certain threshold in this so-called gap height and a deviation in the linearity of the streaming current-distance dependence. Above this threshold distance the liquid flow becomes only partially developed which suppresses the streaming current and streaming potential. Using distances between sample surfaces above this threshold will lead to an overestimation of the contribution of streaming current inside pores.

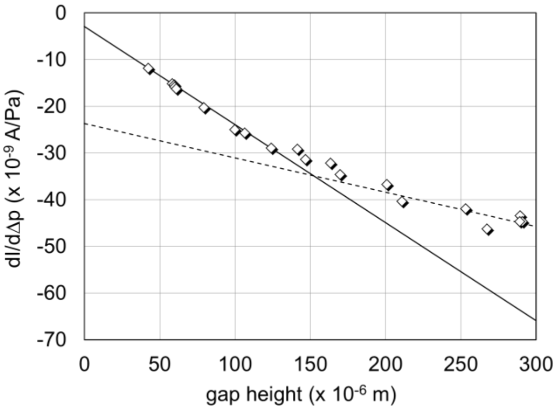

Fig. 1 Streaming current coefficient for a thin-film composite polymer membrane for nanofiltration at different distance between sample surfaces (PBS, 0.002 mol/l, pH 7.4).

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Electrical Properties of Polyelectrolyte/Nanoparticle Hybrid Films on Anisometric Colloids Studied by Electro-Optics

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In this study, electro-optics is applied for the first time for investigation of suspension stability and electrical properties of colloidal particles covered with hybrid multilayer film. The polyelectrolyte/nanoparticle hybrid film is prepared onto ellipsoidal β-FeOOH particles through a subsequent layer-by-layer adsorption of anionic poly(sodium 4-styrene sulfonate), cationic poly(diallyldimethylammonium chloride), and silica nanoparticles. The formation of each layer is done with fine control of the adsorption process in order to produce stable and well defined system. The adsorbed amounts of the highly charged PSS and PDADMAC have been measured by UV-VIS spectroscopy, whereas the amount of the adsorbed silica nanoparticles was calculated from the thickness of the adsorbed layers. The comparison of the electrical polarizability of the PSS and PADMAC coated particles allowed us to calculate the charge balance in this bi-layer as positive. The relaxation frequency of the kilohertz electro-optical effect was found to depend on the charge density of each adsorbed component, which means that the polarization of the excess charge in the outermost layer dominate the behavior of the entire composite film.

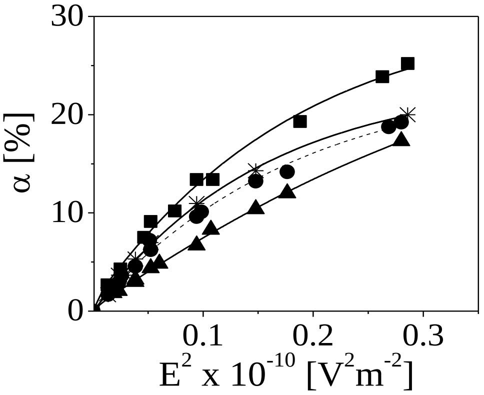

Fig. 1. Dependence of the electro-optical effect as a function of the quadratic of electric field strength at low energy of orientation for bare β-FeOOH particles (*) and for particles with adsorbed layer from NaPSS (●), PDADMAC (■) and silica nanoparticles (▲). The frequency of the applied electric field is 1 KHz.

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Pore Size Monitoring of MF/UF Membranes During Filtration Processes by Streaming Potential Measurement

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In membrane filtration processes the selection of pore size of membrane is the most important factor because the separation (transmission and rejection) performances depend on the pore size. However, the separation performances can be altered during the filtration by accumulation of retained materials on membrane surface via pore constriction, pore blocking or cake layer formation, which are generally called as fouling. For these unsteady phenomena the techniques of the pore size monitoring have been desired. We have focused on the streaming potential across the membrane because the streaming potential reflects the pore size in addition to the surface charge density. The techniques of the pore size determination for clean membrane[1] and fouling status monitoring during the fouling processes [2,3] were developed. In this study the development of the pore size monitoring method for MF/UF membrane filtration systems by streaming potential measurement was conducted. The apparent pore size was determined from streaming potential assuming a constant surface charge density of pore surface. Bovin serum albumin (BSA) was used as a fouling material. The apparent pore size can be monitored by the developed technique and it decreased during the filtration reflecting the change in configuration of membrane pore structure by accumulation of BSA. These results showed that the apparent pore size monitored during the filtration can be a qualitative index for the fouling phenomena.

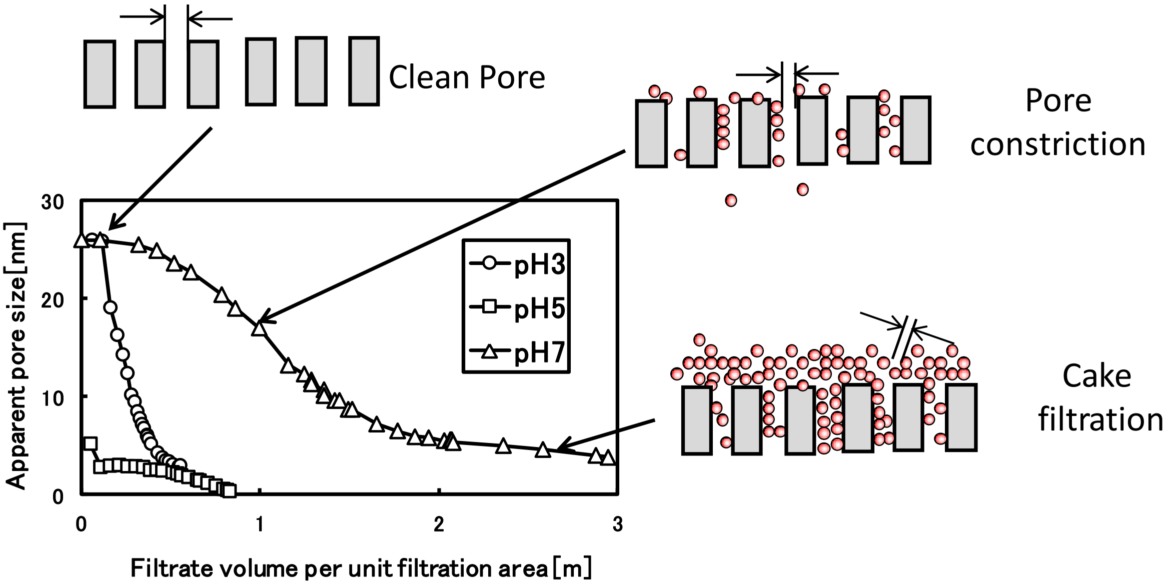

Fig. 1 Pore size monitoring during the filtration of BSA with MF membrane (pore size 0.1 μ m).

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Alternating Zeta-Potential Pattern to Eliminate Electro-Osmotic Flow

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Optical trapping electrophoresis is a technique to accurately determine the zeta-potential of a single colloidal particle. An IR optical laser traps a particle and an AC electric field induces oscillatory movement. The amplitude of the movement is measured with a quadrant photodiode. In nonpolar liquids, this technique can measure with unit charge resolution, revealing accurate charging dynamics of a particle [1]. However, in polar liquids, such as water, electro-osmosis strongly disturbs the measurement.

Up to now, electro-osmosis has been reduced in two ways; by decreasing the zeta-potential of the channel surface and by increasing the frequency of the electric field. The first does lower the velocity of the flow, but the necessary capillary force would vanish under a perfectly zero zeta-potential. Increasing the electrical frequency yields a smaller amplitude of movement.

A novel approach to counteract this flow, is to pattern the microfluidic with long strips of alternating polarity. Each strip tries to direct a flow in the opposite direction with respect to its neighbors. This system creates vortex-like flows near the channels surface, which has been applied for mixing purposes [2]. In a wide channel (>10 times pattern period), this flow does not couple to the bulk. Fig. 1 compares the flow profile of a cross section of a classical channel with a patterned channel. The flow velocity in the center of the patterned channel is uniform and is 150 times lower than in the classic channel.

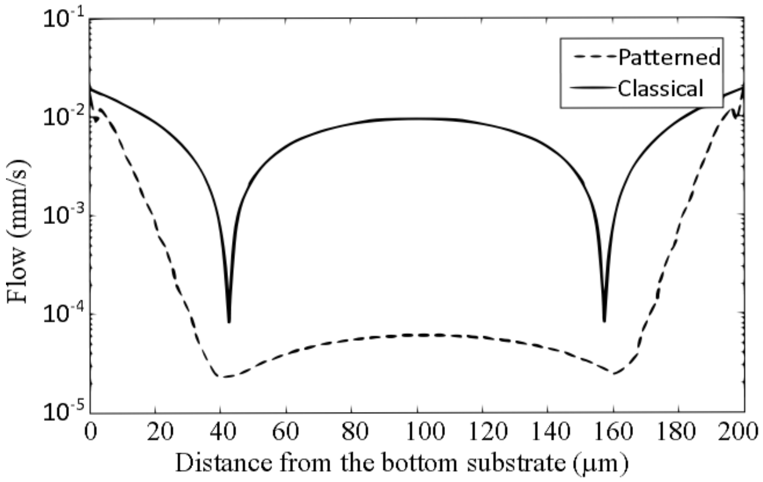

Fig.1. Simulation of the flow profile of a vertical cross-section of a classical channel (full line) and a patterned channel (dashed line).

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Fourier-Bessel Based Image Analysis for Multi-Parameter Particle Characterization

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Currently used methods to characterize colloidal particles all have their advantages and limitations. Ensemble based methods based on dynamic light scattering, Coulter counter and disc centrifugation are fast and cost-efficient but they lack the resolution and versatility to measure multiple parameters. Single particle based methods such as holographic microscopy are more versatile but also slower and more complicated. We demonstrate a particle characterization method based on decomposition of conventional microscopy images in Fourier-Bessel (FB) components [1]. White light scattered from a single particle is captured with a high magnification (100x) objective on a camera. By decomposing these images in a finite FB series we can link the FB components to the size, refractive index, shape and 3-dimensional position and orientation of the particle. This approach can be situated in accuracy and speed in between holographic microscopy where images are fitted to the Lorenz-Mie scattering theory[2] and methods which extract just the intensity centroid or a few higher order intensity moments [3]. In Fig. 1 the size resolution of about 1% for spherical polystyrene (PS) particles is demonstrated. In Fig. 2 the size and refractive index of PS and poly(methyl methacrylate) (PMMA) particles is determined simultaneously for individual particles with refractive index (RI) resolution for particles of d=1000nm around 0.0025. We conclude that the analysis using FB image decomposition can be used simultaneous characterization of the size, refractive index, 3D position and orientation of single colloidal particles.

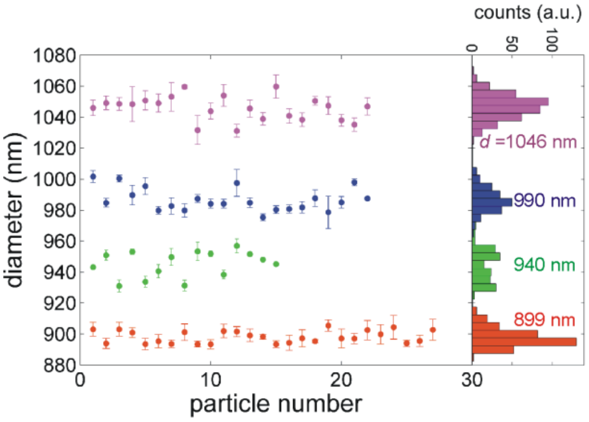

Fig. 1 Diameters obtained for different PS particles and overal size histogram for monodisperse samples with mean diameter d=899 nm, 940 nm, 990 nm and 1046 nm. Typical attained accuracy is ±5 nm (≈1%).

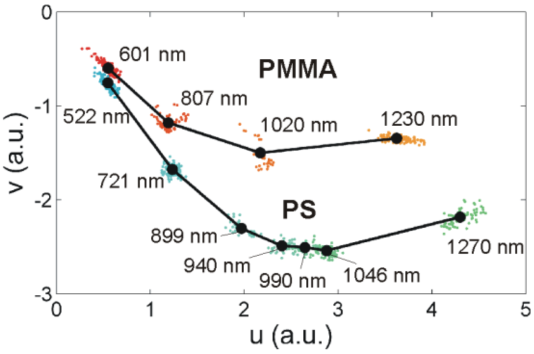

Fig. 2 The use of linear combinations of FB coefficients u and v shows that the RI and diameter can be resolved simultaneously for different PS and PMMA samples. The RI resolution for particles of d=1000nm is around 0.0025

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Impinging Jet Study of the Deposition of Colloidal Particles on Synthetic Polymer (Zeonor)

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Adsorbtion, deposition and removal of colloidal particles and bioparticles on a solid/liquid interface is of a high scientific and industrial importance, e.g. for better understanding of filtration processes, water treatment, microfluidic devices construction, paper making, biofouling of membranes and artificial organs etc. For detailed and exact understanding of the latter mentioned phenomena well defined hydrodynamic and physicochemical conditions during experiments are required. These conditions are met in Impinging Jet technique [1]. In our study, Impinging Jet deposition experiments were performed on microscopic glass and on synthetic polymer (Zeonor) original and by micro-embossing modified substrates with well defined topology as confirmed by AFM, SEM and TEM. Deposition experiments were performed at ambient temperature and at selected flow regimes (Re = 10). As a particles deposited the PS 1.1 μm diameter particles (Sigma-Aldrich) were used having negative charge of -40 mV as observed by zeta potential experiments. There was found gradual increase of total number of deposited particles with time reaching steady state number. Obtained kinetic curves were fitted to the theoretical blocking model, where characteristic time required to reach the steady state (blocking time) as well as steady state number of deposited particles were calculated.

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Electrokinetic Properties of Primary Particles of the Deagglomerated Detonation Nanodiamond in Aqueous KCl Solutions

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Electrokinetic properties of detonation nanodiamond (DND) particles in aqueous electrolyte solutions are among most important characteristics, inherently connected with its surface chemistry and specific to DND processing. An important feature of nanodiamond particles produced by detonation synthesis is that they form nanoporous fractal agglomerates consisting of 4 nm primary crystalline diamond grains. Recently several methods for deagglomeration were suggested and used for preparation of the monodispersed hydrosols containing the isolated primary DND particles.

The current presentation includes the results of an integrated investigation of electrical surface properties (surface charge density σ_0, electrkinetic potential ζ and surface conductivity K_s) of monodisperse primary DND particles prepared by Ioffe Institute method of the DND deagglomeration [1] in aqueous KCl solutions.

The electrophoretic mobility *u*e of the deagglomerated particles at an effective volume fraction p = 0.001 in hydrosols containing 0.0001 - 0.01 M KCl at pH = 3.5 - 10.5 was measured using the technique of laser Doppler electrophoresis. For conversion of *u*e into ζ - potential values an analytical expression developed by Ohshima [2] for electrophoresis of the monolithic particles with arbitrary values of ζ - potential and the Debye length / particle radius ratio was used. The acid - base titration of DND hydrosols containing 0.0001 - 0.01 M KCl as a background electrolyte was used to obtain the dependency of the particle surface charge density σ_0 on pH. The surface conductivity of monolithic DND particles in hydrosols containing 0.0001 - 0.01 M KCl at pH = 3 and 5 was determined from the dependence of the hydrosol conductivity K on the particle volume fraction p = 0 - 0.001 using Street's expression [3]. It was found that the effective particle conductivity is one or two orders of magnitude higher than the conductivity of electrolyte solutions. The reason for this phenomenon is the presence on the diamond surfaces of hydrogen-terminated (hydrocarbon) groups $–CH_n$ (n = 1,2,3). Early it was found [4] that in this case diamond exhibits the pronounced surface conductance due to electron transfer from the diamond valence band to the electrolyte solution and formation of a two-dimensional hole layer near the diamond surface.

A model of a double electrical layer at the interface of such diamond particles and electrolyte solution is discussed taking into account presence of holes in the diamond near its surface.

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Visualization of Reverse Micelles Containing Water

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Research of the optical and electrical properties of mixtures of nonpolar liquid with surfactant is essential for understanding applications such as electrophoretic displays and liquid toner printing. In this work, we present a study of a mixture of the surfactant poly-isobutylene succinimide (PIBS), the nonpolar solvent n-dodecane (DDC) and water. In a nonpolar solvent such as dodecane, the surfactant molecules form inverse micelles. When no water is present, the micelle diameter is around 10-15 nm. Visualization of such small objects is a big challenge.

It is known that polar molecules such as water molecules prefer the polar interior of the inverse micelles. Therefore adding water to the DDC+PIBS solution leads to an increase of the micelle size. The size of the swollen micelles increases with the amount of added water and is on average 200 nm. A commercial water based luminescent dye (CF488) is also added to visualize the micelles. As a result, swollen micelles can be investigated with luminescence microscopy. The Brownian motion and the field-driven motion in an electrical field of individual micelles can then be observed. Using this technique the size, diffusion constant, charge and mobility of individual micelles can be determined.

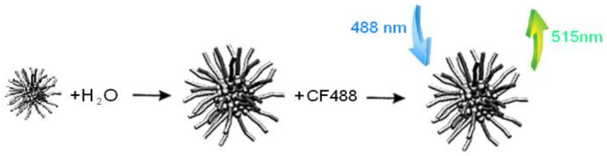

Fig. 1. Sample preparation

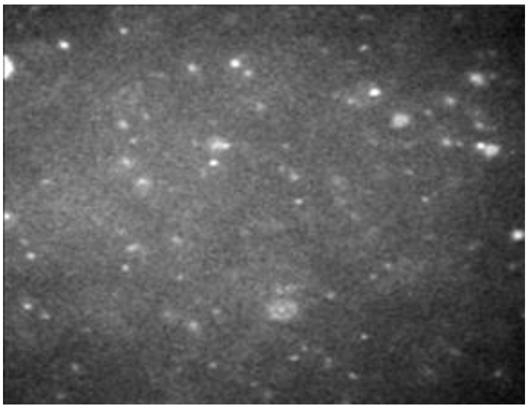

Fig. 2 . OLOA+water+CF488 micelles in DDC (λ_{ex}=488nm, λ_{em}=515nm)

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Highly Charged and Salt Free Nonpolar Colloids

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The low dielectric constant which defines nonpolar media results in long ranged electrostatic interactions, with interesting ramifications for colloids. In particular the phenomenon of counterion condensation, an important facet of some aqueous polyelectrolytes such as DNA [1], is also important in nonpolar systems. For a polymer charged above a critical value, counterions are predicted to condense into a tightly bound layer on the polymer, with a diffuse phase of surrounding counterions. While well established for aqueous polyelectrolyte systems, spherical colloids have never shown this behaviour due to geometric dependent entropic considerations.

By using spherical particles containing a covalently bound ionic liquid and dispersed in dodecane, a highly charged, salt free and unique system is prepared with which the aforementioned phenomena can be studied. Prior results on this counterion only system have shown strong evidence for a condensation effect dependent on particle volume fraction [2]. In this poster, pair potentials measured with the aid of blinking optical tweezers [3] will be presented. The results will be discussed in the context of more traditional aqueous potentials as well as more complex systems such as Pickering Emulsions.

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Characterization of Size Inverse Micelles in Nonpolar Liquids Using Transient Current Measurements

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The increased interest in surfactants in nonpolar liquids in the last decade has led to the need for adequate characterization techniques. The transient current measurement method is used to characterize charge carriers in nonpolar liquids. This method allows to obtain both the concentration and mobility of charge carriers [1, 2]. In this work, we use this method to study five different surfactants in dodecane: OLOA11k, Solsperse13940, Span80, Span85 and AOT. For some surfactants, the steady-state currents are low and the analysis of the transient current is straightforward (OLOA11k, Solsperse13940). For the surfactants with smaller sizes and as a result higher steady-state currents (Span 80) the accuracy of interpretation can be increased by optimizing the device thicknesses and the applied voltages. For the surfactants with even higher steady-state currents and smaller sizes (AOT and Span85) the contribution of bulk and surface generation is minimized by additionally covering the electrode with an insulating layer. In this way, the concentration and mobility of the inverse micelles for these surfactants can also be determined (Figure 1). The calculated hydrodynamic radius of some inverse micelles, based on Stokes' law, is in good agreement with values reported in literature.

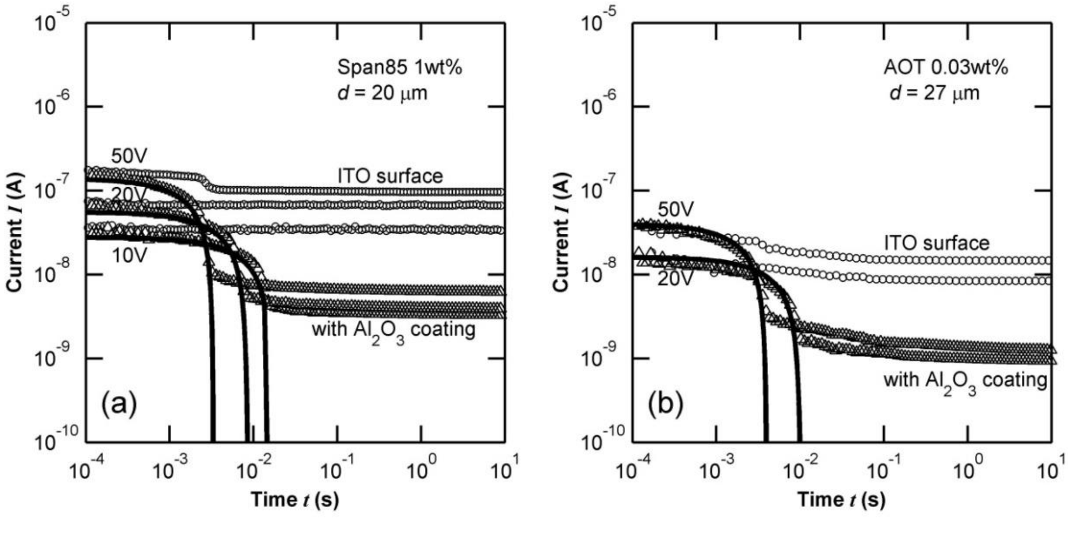

Fig. 1 Transient current measurements for (a) Span85 and (b) AOT in dodecane systems for cells with bare ITO electrodes (○), with Al_2O_3 coating electrodes (Δ), and 1D simulation (solid lines) in cells with S=1cm^2, with given thickness *d* and surfactant concentration and applied voltage.

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Switching Charged Inverse Micelles in Non-Polar Liquids

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Non-polar liquids with added surfactant are relevant for applications such as electrophoretic ink displays and liquid toner printing. The electrical behavior of such surfactant containing non-polar liquids is governed by the presence of charged inverse micelles. For surfactants like PIBS and Solsperse the switching from $0 \to V$ and from $V \to 0$ has been studied using transient current measurements[1,2,3]. The main contributions to these currents are due to drift and diffusion of charged inverse micelles. Now the transition from $V_1 \to -V$ which is relevant for the switching of colloidal particles is investigated with the surfactant Solsperse in dodecane. The first part of the measured currents upon switching voltages from $V_1 \to -V$ are in good agreement with simulations of the Nernst-Planck-Poisson equations (see Fig. 1). For the lowest voltages V it can be seen that the shape of the currents originates from dynamic space-charge effects related to switching of the charged inverse micelles. For increasing voltages V this current evolves to a constant current until the charges arrive at the opposite electrodes. However, it is observed that a peak in the measured currents occurs earlier than expected due to electrohydrodynamic effects which speeds up the switching of charged micelles. At some voltages a second peak appears which is related to previously accumulated charges at the electrodes that are switching with some delay.

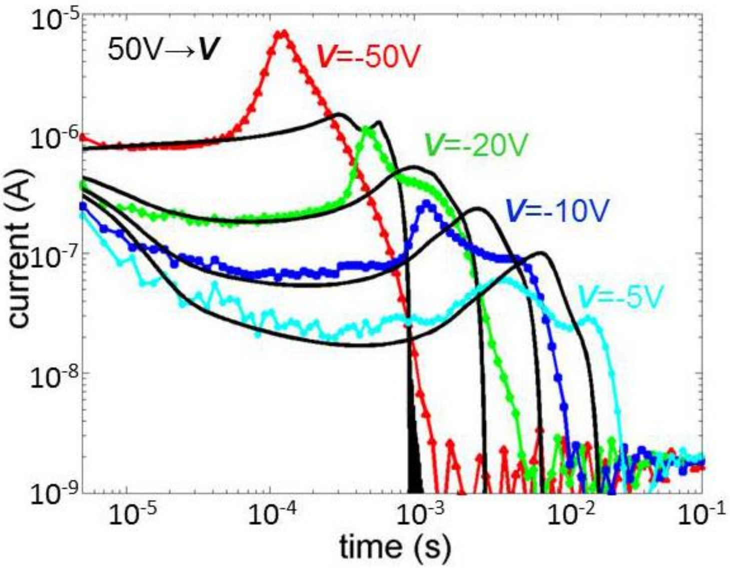

Fig.1 Transient current measurement for voltages going from 50V to V=-5, -10, -20 and -50V. The measurements (colored dots) and simulations (black lines) shows a good agreement at short times and low voltages. For increasing voltages a peak in the current occurs earlier than expected due to electrohydrodynamic effects.

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Image Analysis for Studying Electrokinetics in Nonpolar Liquids

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We have developed a Fourier-Bessel (FB) decomposition method of microscopy images which allows to investigate properties of individual colloidal particles (see Fig.1). The method allows to determine the size, refractive index, 3-dimensional position and electrophoretic mobility of individual colloidal microspheres based on a simple calibration procedure. Using this method the electrophoretic mobility of single, optically trapped colloidal particles is measured while gradually depleting the co-ions and counterions in the liquid around the particle by applying a dc voltage[1,2]. This is achieved in a nonpolar liquid, where charged reverse micelles act as co-ions and counterions. By increasing the dc voltage, the mobility first increases when the concentrations of co-ions and counterions near the particle start to decrease. At sufficiently high dc voltage (around 2 V), the mobility reaches a saturation value when the co-ions and counterions are fully separated. The increase in mobility is larger when the equilibrium ionic strength is higher. Similarly, the dynamics of the particle mobility when the double layer is stripped off with a dc voltage and when the double layer is restored when setting the voltage zero are investigated (see Fig. 2). This method is useful for studying the electrophoretic retardation effect and charging mechanisms for nonpolar colloids, and it sheds light on previously unexplained particle acceleration in electronic ink devices[3].

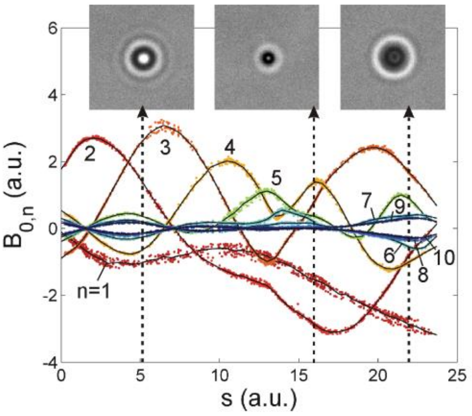

Fig. 1. The optical fingerprint of a 899nm PS particle in water consisting of 10 FB-coefficients $B_{0,n}$ with n=1,…,10 as a function of the position s along the piecewise linear curve S fitted at the scattered multi-dimensional coefficients.

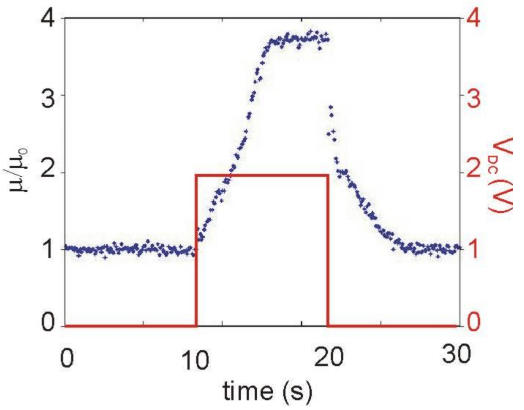

Fig. 2 Measurement of the dynamics of the particle mobility when stripping off the double layer with a dc voltage and when the mobility relaxes to the equilibrium mobility when the voltage is set to zero.

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Influence of DPPC Layers and PLA_2 on Surface Properties of Silica Particles

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Different lipid/particles assemblies composed of the particles core surrounded by a lipid shell have attracted attention mainly because of their biomedical and biotechnological applications, e.g. in biological sensors and drug delivery system.

From the other hand respirable silica causes damge of phagocytic cells in the lung and hence is considered to be responsible for silicosis [1]. However, molecular mechanism of this disease is still not fully understood. It is assumed that silicosis is caused by the destruction of cell membranes via the interaction of silica with biomembranes. According to Chunbo et al. [2] silica particles interact with the phosphate moiety of the headgroup of DPPC via hydrogen bonds. Moreover they found that aluminium ions reduces cytotoxicity of silica via competing with silanols for phosphate sites in cell walls.

It is also claimed that to reduce dust toxicity it is coated by lung surfactant (mostly DPPC). Moreover subsequent enzyme action restoring cytotoxicity for crystalline quartz [3].

The effect of phospholipid DPPC (1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine) and phospholipase A_2 (PLA_2) in the presence of calcium ions on surface properties of silica particles was investigated by means of zeta potential, mean diameter and light transmittance. Silica particles were precoated with the monolayer (ML) or the bilayer (BL) of the phospholopid from the chloroform solution (SiO_2/DPPC) or coated by DPPC adsorption (SiO_2 + DPPC) from the aqueous solution containing calcium ions. It was found that Ca^{2+} ions presence improved remarkably neutral phospholipid (DPPC) adsorption to the silica surface. The obtained silica suspensions were found to be stable probably due to steric stabilization.

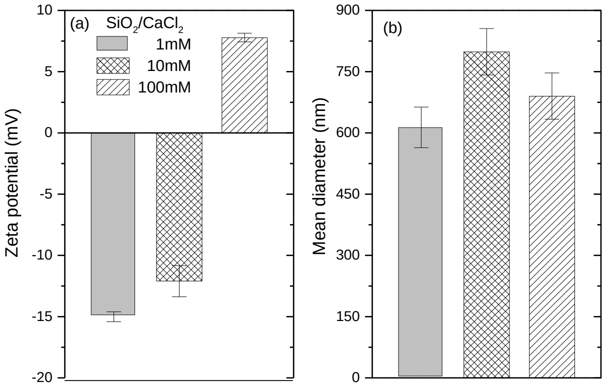

Fig. 1 Zeta potential (a) and mean diameter (b) changes of silica particles dispersed in $CaCl_2$ solutions as a function of concentration.

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Ionization, Molecular Architecture and Biointeractions of StarPEG-Heparin Hydrogels

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Materials mimicking the exogenous signals of extracellular matrices to control cell fate decisions are instrumental for tissue engineering [1,2]. Biohybrid hydrogels containing glycosaminoglycans (GAGs) are particularly promising for that purpose due to the effective binding, protection and sustained release of numerous growth factors [3]. Growth factor binding to GAGs can be attributed to the sulfation pattern of these molecules and is, thus, largely determined by electrostatic interactions between ionized sulfate groups along the GAGs and oppositely charged protein domains. Unraveling details of ionization, structure and biomolecular interactions within such networks therefore defines an important analytical challenge that requires the extension of current methodologies.

To analyze the charge and structure of biohybrid hydrogels, we developed and applied a mean-field approach for the numerical evaluation of surface conductivity data [4]. Data obtained for a poly(ethylene glycol)-heparin system [5] will be exemplarily used to demonstrate how *electrostatic fingerprints* of these materials sensitively display the composition and structure of the polymer network. It will be shown how the density of ionizable groups, heparin concentration and cross-linking degree of such hydrogels can be derived by comparing experimental surface conductivity and swelling data with simulation results. In addition, we present a concept and results for the application of the methodology [4] for the detection of biomolecular interactions in GAG hydrogels.

Acknowledgement

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Electro-Orientation of a Metal Nanowire Subjected to Thermal Fluctuations

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The electro-orientation of electrically polarized metal nanowires suspended in an electrolyte is studied for small voltages. Nanowire rotation is originated by both the electrical torque on the induced dipole and by induced-charge electroosmotic flow around the particle. At low frequencies of the applied ac field, induced-charge electroosmotic rotation dominates while induced dipole torque rotation dominates at high frequencies. The alignment of a Brownian nanowire in an ac field with a given direction is not complete due to thermal (fluctuating) torques. We measured the orientation distribution for different frequencies of the applied ac field, see Figure 1. Electro-orientation at low frequencies is weaker than at high frequencies. Also, the angular standard deviation and the rotational rate are calculated from the measured fluctuating angle around equilibrium direction as a function of time. Good agreement with theoretical predictions is found and the results are in accordance with previous experiments of deterministic electro-orientation of metal nanowires [1]. The experimental results indicate that the electrical torque on a nanowire near an insulating wall is reduced with respect to the bulk.

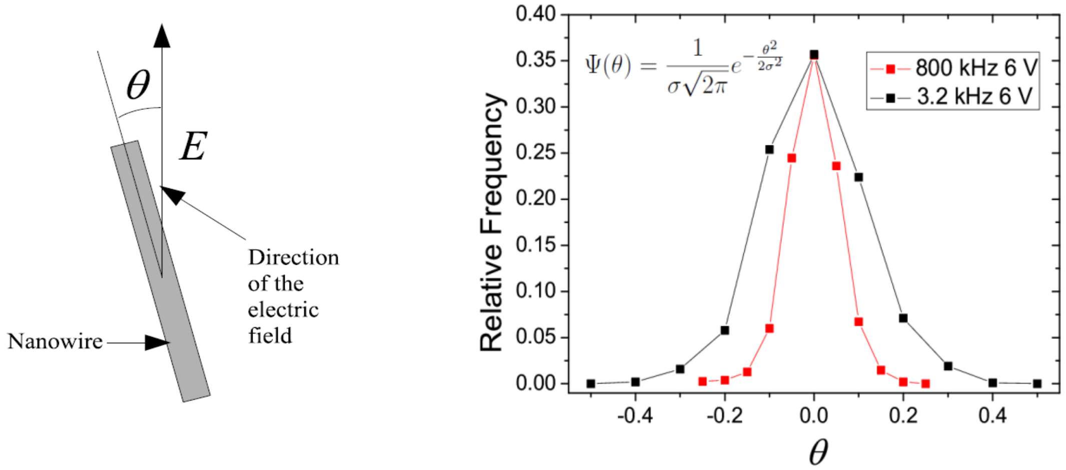

Fig. 1. The distribution of angles is shown for two values of the frequency of the applied field. For small values of the angle, probability is given by a normal distribution.

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Monte Carlo Simulation of Thermo-Responsive Charged Nanogels in the Presence of Salt

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Temperature-sensitive micro- and nanogels have gained considerable attention during the last decades because they undergo reversible and rapid volume phase transitions in response to changes of temperature as well as to other stimuli such as ionic strength. Thus, temperature-triggered uptake and release of drugs or chemicals are possible. Furthermore, their small size allows them to overcome some biological barriers. Our ability to control these processes resides in a better understanding of the swelling behaviour of these smart nanoparticles, which has been generally studied through the classical formalism for macroscopic gels. However, this approach completely ignores the electric double layer (EDL) around the nanogel, which implies serious shortcomings. On the one hand, it cannot provide information about particle properties that depend on this inhomogeneous distribution of charge. In this work, two thermo-shrinking charged nanogels in the presence of 1:1 and 3:1 electrolytes have been explicitly simulated through the bead-spring model of polyelectrolyte [1]. Concerning swollen nanogels, we have studied the sizes of both systems when trivalent cations are present. It should be also stressed that the electrostatic repulsion, completely neglected in the classical theory of swelling, seems to play an important role according to our results. The presence of salt can often have influence on the thermal response of nanogels, such as the shift of the transition temperature of slightly ionized polyelectrolyte networks. The effect of additional electrolyte is also noticeable for moderately ionized nanogels, whose shrinkage in the presence of trivalent cations cannot be exclusively attributed to hydrophobic forces. Regarding the surface electrostatic potential, it should be pointed out that the thermosensitivity in size determines to some extent the sensitivity of this property to temperature changes. In any case, the surface electrostatic potential displays a rich behaviour when temperature varies, which is conditioned by the interplay between size and charge. The modified PB cell model proposed here is able to capture such rich behavior.

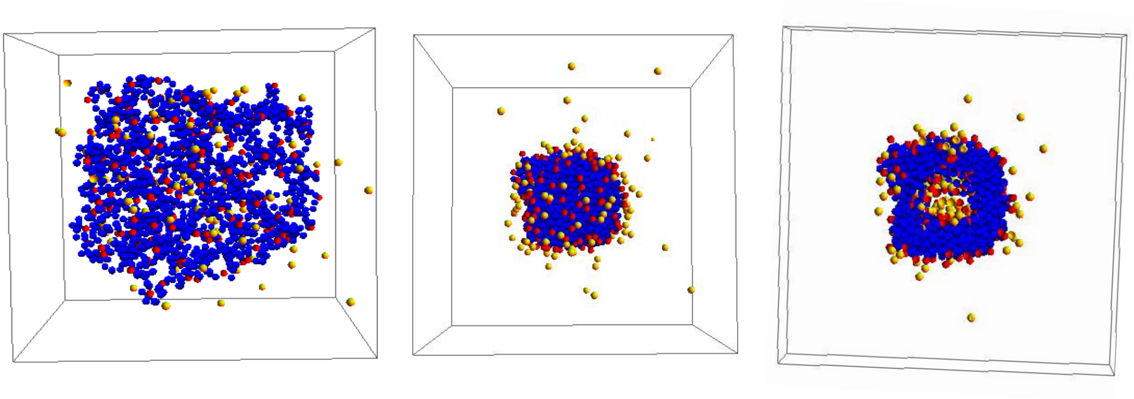

Fig. 1 Monte Carlo simulation of the nanogel structure upon increasing temperature (from left to right).

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Electrophoretic Mobilities in Mixed Electrolytes: Effect of Ionic Strength in Concentrated Buffer Solutions. Modeling within the Mean Spherical Approximation.

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In electrophoresis experiments, solutions can be naturally concentrated, by their origin, or in order to improve the resolution of electrophoresis peaks by addition of a supporting electrolyte. The exact position of the electrophoresis peaks can be strongly affected by the presence of this supporting electrolyte. Theoretical models currenty used in this field (extended Debye Onsager Bjerrum models) are limited to the 0.01M to 0.1M range, at least for the non ideality in transport. However progress in the transport theories, have been made in the last decade, for self and mutual diffusion, individual or global conductivity [1]. Those models allow to describe quantitatively the evolution of those transport coefficients for concentrations of the order of 1 to 2 M even for small electrolyte mixtures [2] and are also convenient to describe highly charged species in solutions such as micelles formed in ionic surfactants [3], or humic acid solutions [4]. We present a model leading to explicit expressions for the individual electrophoretic mobilities of ions and of the electrical conductivity of a weak electrolyte solution containing several simple ionic species.

On the other hand, the characterization of highly charged ions requires to take into account the formation of the different chemical complexes between the different ions in solution, in particular when the charge of the ions is dependent of the pH of a buffer solution. Applications of the mean spherical approximation (MSA) theory have allowed to describe osmotic and activity coefficients of real electrolyte solutions for high concentrations [5,6]. It is then possible to consider the modelisation of highly charged ions in solutions with both transport and equilibrium non idealities, as well as speciation phenomena (complex formation). We present a theoretical description of the electrophoresis and ionic conductivity, arising from physical theories of liquids and solutions.The strengths and weaknesses of this approach are compared with those of theories commonly used to describe the colloidal solutions.

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How Good are Theories of Electrolyte Transport? Answers from Mesoscopic Simulations

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The theoretical descriptions of structural and dynamic properties of charged particles in aqueous solution fall in different categories: theories of simple electrolytes, theories of polyelectrolytes and theories of colloids. For particles of nanometric size, it's not obvious to choose between these different theoretical descriptions, although it is of paramount importance for the understanding of transport properties in industrial, geological or biological systems that contain charged nanoparticles.

In this work, we propose to determine until which size and charge a spherical particle can still be considered as a simple electrolyte from the theoretical point of view. Our precise goal is to use mesoscopic simulation techniques to assess the limitations of an advanced electrolyte transport theory developed in our group [1-2]. We first compared the transport coefficients of charged nanoparticles for two different mesoscopic simulation techniques: Brownian Dynamics (BD) with hydrodynamic interactions, which can be used for relatively dilute solutions, and hybrid molecular dynamics /Stochastic Rotation Dynamics (SRD), which can be used for very dense solutions [3].

After studying the mesoscopic simulations, we could extract reference results for charged solutions with particle size ranging from 0.5 nm to 5 nm and particle valency ranging from 1 to 100. We compared the results of the simulations with the predictions of our transport theory for various transport coefficients (diffusion coefficients, conductivity, electrophoretic mobility, vibration potential), and we could then evaluate for all these systems the level of validity of the theory.

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Modelling the Induced Polarization of Bentonite-Sand Mixtures

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Spectral induced polarization (SIP) has become an increasingly popular geophysical method for hydrogeological and environmental applications. These applications include for instance the non-intrusive characterization of the textural and interfacial physicochemical properties of bentonites used as permeability barriers in landfills or to store various types of contaminants including radioactive wastes. Bentonites are mainly constituted of smectites, which have very high specific surface areas (SSA) and cation exchange capacities (CEC). Therefore, these minerals have very high electromigration and polarization current densities responsible for very high in phase and quadrature conductivities, respectively. In addition, in diluted water, the diffuse layer of smectitesoccupies a large fraction of the pore space and may be therefore considered as part of the pore space. In our approach, complex electrical conductivities of saturated unconsolidated bentonite and bentonite-sand mixtures are modeled at different salinities (NaCl) of the bulk pore water. Our predictions are successfully compared to experimental data [1]. Our surface conductivity model depends on the surface sites densities of adsorbed ions in the Stern and diffuse layers, which are calculated by coupling a Donnan equilibrium model [2] with a surface complexion model of the basal planes. We assume the DC contribution of the diffuse and Stern layers as well as the electrochemical polarization of the Stern layer coating the grains with different sizes.The macroscopic SIP model is based on the differential effective medium theory and considers the complex surface conductivity of the sand and smectite grains and the complex conductivity of the pore space. Nevertheless, our SIP model can’t predict the quadrature conductivity spectra observed at very low frequencies ($< 10^{-1}$ Hz). The missing polarization mechanism may correspond to membrane polarization and there is an effort to be done to incorporate this contribution in a unified model.

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A Program for the Fitting of Debye, Cole-Cole, Cole-Davidson, and Havriliak-Negami Dispersions to Dielectric Data

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The description and interpretation of dielectric spectroscopy data usually requires the use of analytical functions. These expressions, arising from theoretical or empirical models, include unknown parameters that must be determined by means of a fitting procedure. If the model expression depends non-linearly on at least one of the unknown parameters, an iterative procedure becomes necessary to determine the best parameter set. This is not a trivial task and much effort has been spent to find the best way to accomplish it.

While the theoretical approach based on the Levenberg-Marquardt algorithm [1] is well known, no freely available program specifically adapted to the dielectric spectroscopy problem exists to the best of our knowledge. Moreover, even the more general commercial packages usually fail on some of the following aspects:
(1) allow to keep temporarily fixed some of the parameters,
(2) allow to freely specify the uncertainty values for each data point,
(3) check that parameter values fall within prescribed bounds during the fitting process,
(4) allow to fit either the real, or the imaginary, or simultaneously both parts of the complex permittivity.

A program that satisfies all these requirements and allows fitting any superposition of the most frequently used dispersion functions: Debye, Cole-Cole, Cole-Davidson, and Havriliak-Negami, plus a conductivity term to measured dielectric spectroscopy data is presented. It is based on the theory, not the implementation, given in [1], which has been adapted to the dielectric dispersion problem including data input from file, output of results to file, and the coding of the above mentioned dispersion functions. It is available on request from the author.

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Assessment of the Validity Range of the Standard Linear Perturbation Models of Electrophoresis with High Electric Field Calculations

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Very recently, the synthesis and experimental study of a new class of highly charged polymer particles has been described, which spontaneously charge in non-aqueous low-polarity solvents [1,2]. These suspensions are an example of what is known as salt-free systems. The study of suspensions of charged colloidal particles in a salt-free medium is nowadays increasing [3]. The term salt-free does not mean that there are not ions present in the suspension because those ions coming from the charging process of the colloidal particles, which are known as "added counterions", will always dissolve into the supporting medium. This fact implies that the electric double layers that surround the colloidal particles in non-aqueous suspensions are constituted by one single ionic species.

For those systems, there is a non-linear singular relationship between the surface potential and the surface charge density. While for low surface charge density this relation is roughly linear, above a critical value of the surface charge density, the surface potential increases very slowly. This phenomenon is related to the counterion condensation effect, *i.e.*, the generation of a compact layer of counterions that develops very close to the particles surface, and can considerably affect the macroscopical physical behavior, such as the electrokinetics, the rheology, etc., of these suspensions. Striking non-linear effects in the presence of high electric fields, as the unbinding of counterions from the condensation regions, have been observed in electrophoresis experiments [1,2].

In this work we have performed some initial calculations with the finite element method for solving the full time-dependent non-linear governing equations inside a unit Wigner-Seitz cell. In the theoretical study of the electrophoretic mobility against the applied electric field, we have successfully reproduced the numerical results of the standard linear perturbation model in the limit of low applied electric fields and test its range of validity. From this starting point we have explored the electrophoretic behavior as the electric field is increased.

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ZnO Nanowire Arrays Grown by Electrophoretic Deposition Technique from Colloidal Suspensions of ZnO nanoparticles

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In the present work electrophoretic deposition (EPD) [1], which involves the guided drift and deposition of charged particles in a colloidal suspension under the influence of a suitable electric field, is used to produce ordered ZnO nanowire arrays on silicon substrates, which were covered with Au nano-clusters deposited by sputtering [2] at room temperature.

The ZnO nanostructures were grown from a low concentration colloidal suspension of ZnO nanoparticles in 2-propanol [3]. The size of the nanoparticles obtained in the colloidal suspension was estimated from absorbance and photoluminescence measurements [4, 5], which yielded an average diameter of 5 nm with a narrow size distribution. Physical and chemical properties of the resulting colloidal suspension were measured, such as conductivity, pH, zeta potential, density, and viscosity, in order to calculate relevant parameters for the EPD technique.

A careful design of the EPD cell was performed in order to find the best way to obtain homogeneous and reproducible deposits. This allowed the engineering of the directionality and intensity of the applied electric field, which is one of the main parameters determining the effectiveness of the EPD method in producing complex nanostructures with controlled thickness and morphology. The effect of process parameters on the obtained nanostructures properties such as deposition time, intensity and distribution of the electric field, as well as the addition of different zinc nitrate concentrations to the colloidal suspensions, were studied and discussed.

Scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy, and photoluminescence measurements were performed in order to determine the quality of the ZnO nanostructures obtained by EPD.

The growth of ZnO semiconductor nanowires is of great industrial interest because ZnO is a wide band gap (3.37 eV) n-type semiconductor with photoconductive properties and high excitonic binding energy, which make it potentially useful for the design of photonic devices, such as UV photo detectors, solar cells, laser and optical memories. ZnO nanostructures have also been proposed as suitable nanomaterials for sensors, actuators and nano-enabled synthetic biology [6].

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Extended Coarse-Grain Methods for Coulomb Soup

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Theoretical understanding of transport properties of "Coulomb Soup" *i.e.* colloidal particles dissolved in electrolyte solution is extremely difficult even if a simple model is used for colloidal particles. This is because the motion of colloidal particles, the concentrations of small mobile ions, the long-range Coulomb potential, and the solvent velocity are coupled with each other through essentially nonlinear equations [1].

In order to discuss the transport properties in these systems, improvements in the simulator were then needed to include the effect of the solvent in multi-scale environments (Fig. 1). First, the solvent model was made to include the solvation effect of polymers and counter- and co-ions. In the framework of dissipative particle dynamics, the polarizability of a set of solvent molecules was described as oscillators [2]. The solvent flow was then included by calculating the Brownian particles by Langevin dynamics and the solvent flows by the Lattice Boltzmann method [3]. In this method, the dynamics of a huge amount of small ions were enabled by treating each Brownian particle as a point described by a Stokes-source. These methods essentially treat ions as particles. In order to treat macroscopic phenomena, a multiphysical simulator based on continuum equations of ion solvent flow and electric fields was created. The distributions of small ions are treated by the Nernst-Planck equations to determine transitional and non-bulk ion distribution [4]. Whereas these methods are under testing, the Coulomb systems such as a friction of polyelectrolytes brush that is a model of synovial joint [5], asymmetric ion transport in soggy sand system that is additives for electrolyte solutions for batteries, are being able to be treated.

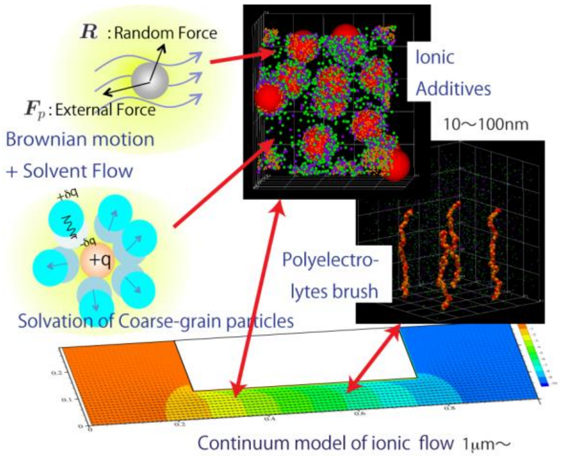

Fig. 1 Molecular simulations for ionic systems.

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Colloidal Dynamics in Simultaneous Electric and Optical Potentials

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Electro osmotic flow is a common method used in microfluidic devices to establish a flow field. Colloidal particles can be manipulated with this flow field so that they undergo a biased Brownian motion. In addition, one- or two-dimensional potentials are imposed on the colloidal particles by the use of holographic tweezers [1].

The dynamics of non-interacting particles in one- or two-dimensional potential energy landscapes without a biased Brownian motion could already be studied [2,3]. The addition of the electro osmotic flow now allows the effect of steady and time-dependent driving forces on the motion of the particles through the energy landscape to be examined.

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Influence of the Finite Size and Effective Permittivity of Ions on the Equilibrium Double Layer around Colloidal Particles in Aqueous Electrolyte Solution

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The existence of an electric double layer around dispersed colloidal particles has a crucial effect on a wide variety of equilibrium and nonequilibrium phenomena in colloid science. This is the reason for the great importance of theoretical studies tending to improve the representation of the electric double layer structure.

The Poisson–Boltzmann (PB) equation is the most acknowledged and widely used description of the electrical double layer, due in part to its conceptual and mathematical simplicity. The PB equation is obtained by the inclusion of a series of simplifying assumptions: finite sizes of ions are neglected, non-coulombic interactions between ions and the particle surface are disregarded, the permittivity of the medium is assumed to be constant, incomplete dissociation of the electrolyte is ignored, etc. Many attempts have been made in the last two decades to modify the classic PB equation so that the ionic interactions can be accounted for. They are all based on the assumption that the density of each ion type cannot surpass anywhere a finite value $c_i^{\max}$. Because of this, the counterion density close to a charged interface cannot attain unrealistically high values, improving on the results predicted by the PB equation. However, the correction of the modified PB equation only appears at high surface charges and for high bulk electrolyte concentrations.

In recent papers [1,2], we presented an extension of the modified PB equation considering that ions can be modeled as insulating spheres with a permittivity different from that of the surrounding medium. This leads to an additional increase of the surface potential with respect to the PB solution, which has a similar magnitude to that obtained considering only steric effects.

While these developments make it already possible to fit experimental data near highly charged interfaces using effective ionic radii that are comparable to their hydrated values, there is still one aspect of the model that should be addressed. In all our preceding studies, we used a Bikerman type expression for the excess electrochemical potential μ_i^{ex}. While this is the first and simplest equation that allows introducing the ion-ion interactions into the PB equation, later studies have produced more precise expressions. In the present work, we also use the Carnahan-Starling equation in order to determine the equilibrium electric double layer structure for a symmetric binary electrolyte solution with equal size counterions and co-ions taking into account all of the above-mentioned effects.

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