

Symposium Polyelectrolytes (SYPE)

jointly organized by
 Section Biological Physik (BP),
 Section Chemical and Polymer Physics (CPP), and
 Section Dynamics and Statistical Physics (DY)

Regine von Klitzing
 Stranski-Laboratorium Berlin
 klitzing@chem.tu-berlin.de

PD Dr. Andreas Fery
 MPI of Colloids and Interfaces Golm
 andreas.fery@mpikg.mpg.de

Ralf Everaers
 Laboratoire de Physique, ENS Lyon
 ralf.everaers@ens-lyon.fr

Overview of Invited Talks and Sessions

(lecture rooms H1, H37 and Poster B)

Invited Talks

SYPE 2.1	Thu	14:00–14:30	H37	Coulomb and Flory: Fathers of SONS. Polyelectrolytes in Self Organized Nano Systems — ●MARTIEN COHEN STUART
SYPE 2.7	Thu	16:00–16:30	H37	Bundling Phenomena in Semiflexible Polyelectrolytes — ●CHRISTIAN HOLM, MEHMET SAYAR, BERK HESS
SYPE 3.1	Fri	10:30–11:00	H1	Behaviour of polyelectrolyte solutions under confinement — ●DOMINIQUE LANGEVIN, CÉSAR MARQUEZ, HEINIG PETER, DAN QU
SYPE 3.4	Fri	11:30–12:00	H1	Polymers at Surfaces: Sticking and Gliding — ●ROLAND NETZ

Sessions

SYPE 1.1–1.12	Wed	16:00–18:30	Poster B	Polyelectrolytes Poster
SYPE 2.1–2.9	Thu	14:00–17:00	H37	Polyelectrolytes I
SYPE 3.1–3.6	Fri	10:30–12:30	H1	Polyelectrolytes II

SYPE 1: Polyelectrolytes Poster

Time: Wednesday 16:00–18:30

Location: Poster B

SYPE 1.1 Wed 16:00 Poster B

Hollow Polyelectrolyte Multilayer Tubes: Preparation and mechanical characterisation — ●RENATE MÜLLER¹, LARS DÄHNE², and FERY ANDREAS¹ — ¹Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Wissenschaftspark Golm, 14424 Potsdam — ²Capsulation NanoScience AG, Volmerstr. 7b, 12489 Berlin

Tubelike hollow structures are of considerable interest for material science, as they can serve as channels for microfluidics, can be easily assembled to meshes for filtration/ sensing or serve as scaffolds for growing tissue, since they provide a high stability in combination with a low weight. Also possible is an encapsulation of chemicals inside the tubes.

Here we present a new route for the preparation of tubes with micrometer sized dimensions by using the well-known Layer-by-Layer technique [1], which enables us to control the wall thickness within few nm and depending on the composition of the multilayer either ending up in stable tubes or a bubble necklace like structure [2]. We characterised the tubes with Fluorescence Microscopy and CLSM, the wall thickness was determined by AFM imaging. The walls' permeability was also studied. The tubes mechanical properties were determined with the AFM colloidal probe technique [3], which were found to be dependent on the AFM probing position and yielded a Young's Modulus of 200 MPa.

1. Decher G. Science 1997; 277 (5330): 1232-1237./ 2. Mueller R, et al. Polymer 2006: submitted./ 3. Fery A, et al. New Journal of Physics 2004; 6: 18-31.

SYPE 1.2 Wed 16:00 Poster B

Preparation and characterization of nanocomposite films with switch effect — ●W. WANG¹, A. LASCHEWSKY², and P. MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik - Department E13, James-Franck-Str. 1, D-85747 Garching, Germany — ²Potsdam Universität, Mathematisch-Naturwissenschaftliche Fakultät, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam-Golm, Germany

Nanostructures based on polymeric materials are of growing interest for numerous applications in electric and optic areas. The goal of this study is the production and characterization of nano-structured thin films with switch effect from encasing inorganic-organic hybrid materials. The central emphasis is to prepare the films with good thermal-mechanical and chemical characteristics. The basis of the production is a sol-gel template based synthesis of ceramic metallic oxide nanoparticles, with which amphiphile diblockpolymer is used as matrix. In the first step, the polymer matrix - poly(styrene-block-N-isopropylacrylamide), which is synthesized by RAFT polymerization, is deposited on the pre-cleaned, oxide covered silicon (100) substrates as well as glass slides by the spin coating technique. As the performance is strongly influenced by the morphology of the films, atomic force microscopy (AFM) is routinely used to monitor the surfaces of polymer films giving rise to a real-space visualization of the surface topography. A meaningful statistical analysis of film thickness and roughness is advantageously performed with conventional X-ray reflectivity measurement.

SYPE 1.3 Wed 16:00 Poster B

Experiments with single colloids — ●KEGLER KATI¹, GUTSCHE CHRISTOF¹, SALOMO MATHIAS², and KREMER FRIEDRICH¹ — ¹PAF, Exp. Physik 1, Universität Leipzig, Linnestr.5, 04103 Leipzig — ²Biophysik, Universität Leipzig, 04103 Leipzig

In rheological experiments the flow resistance of single blank or DNA-grafted colloids is determined by Optical tweezers and compared. The degree of swelling of the grafted DNA is adjusted by exchanging the ion concentration of the surrounding medium. For all examined flow velocities one observes an interesting deviation from Stokes law which can be traced back to a shear-dependent conformational change of the brush layer. The ratio of the effective hydrodynamic radii of DNA-grafted and blank colloids shows a pronounced dependence on the flow velocity, but as well on the length of the grafted DNA and the ionic strength of the solvent. The experimental findings are in qualitative agreement with hydrodynamic simulations based on an elastically-jointed chain model. Optical tweezers are employed to measure the forces of interaction between single DNA-grafted colloids. Parameters to be varied are the length of the DNA, the grafting density and the ionic concentration of

the surrounding medium. From the measured force-separation dependence an interaction-length at a given force is deduced. It shows in the mushroom regime a scaling with the grafting density which levels off for brushes. For the latter the transition from an osmotic to a salted brush can be traced in detail by varying the ionic concentration in accordance with meanfield theories.

SYPE 1.4 Wed 16:00 Poster B

Conductivity spectra of polyphosphazene based polyelectrolyte multilayers — ●YAHYA AKGÖL¹, CHRISTIAN HOFMANN¹, YUNUS KARATAS², CORNELIA CRAMER¹, HANS-DIETER WIEMHÖFER², and MONIKA SCHÖNHOF¹ — ¹Institut für Physikalische Chemie und SFB 458, WWU Münster, Germany — ²Institut für Anorganische und Analytische Chemie und SFB 458, WWU Münster, Germany

Polyphosphazenes are promising materials for application as polymer electrolytes with a high ion conductivity due to their flexible backbone. Here, polyelectrolyte multilayers are built up from ionically modified polyphosphazenes by layer-by-layer assembly of a cationic and an anionic polyphosphazene (PAZ+ and PAZ-). In comparison, multilayers of poly (sodium 4-styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) are investigated. Frequency-dependent conductivity spectra are taken in sandwich geometry at controlled relative humidity. Conductivity spectra of ion conducting materials generally display a dc plateau at low frequencies and a dispersive regime at higher frequencies. Dc conductivity values, which can be attributed to long range ionic transport, are on the order of 10_{-10} Scm⁻¹ to 10_{-7} Scm⁻¹ and strongly depend on relative humidity. For PAZ+/PAZ- multilayers the dc conductivity is consistently larger by one decade as compared to PSS/PAH layers. The dispersive regime shows a frequency-dependence, which is deviating from the typical behaviour found in most ion conducting materials.

SYPE 1.5 Wed 16:00 Poster B

Effective charge of polyelectrolytes as a function of the solvent permittivity — ●UTE BÖHME and ULRICH SCHELER — Leibniz Institute for Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

One important issue in polyelectrolyte research is the determination of the effective charge, the charge which is capable of interacting with other molecules or solid surfaces. Due to counterion condensation the nominal charge is significantly reduced, depending on the nominal charge density of the polyelectrolyte, potential additional salt ions, the pH and the dielectric properties of the solvent. The effective charge of polyelectrolytes in organic solvents with varying dielectric constants has been derived from a combination of electrophoretic mobility and diffusion coefficient [1], both obtained from PFG NMR experiments. Decreasing permittivity of the solvent results in a drastically reduced effective charge and in changing conformation of the polyelectrolytes simultaneously.

[1] U. Scheler, in H.S. Nalva (ed.) *Handbook of Polyelectrolytes and their applications*, American Scientific Publishers (2002)

SYPE 1.6 Wed 16:00 Poster B

Diffusion and binding of phenol in sub-micron polyelectrolyte capsule dispersions measured using PFG-NMR — ●RÜDRA PROSAD CHOUDHURY and MONIKA SCHÖNHOF — Institute of Physical Chemistry and Graduate School of Chemistry, WWU Münster, Germany

The distribution and dynamics of phenol molecules in colloidal dispersions of sub micron hollow polymeric capsules is investigated by pulsed field gradient NMR (PFG-NMR). The capsules are prepared by self-assembly of polyelectrolytes onto silica particles, followed by dissolution of the silica core in HF. Here, diffusion echo decays are single exponentials, proving the fast exchange of phenol between a free site and a capsule-bound site. However, apparent diffusion coefficients extracted from the echo decays depend on the diffusion time, which is typically not the case for the fast exchange limit. We attribute this to the presence of a particular regime, where apparent diffusion coefficients are observed, which are influenced by an ultrafast spin relaxation in the bound site. Indeed, relaxation rates of phenol are strongly enhanced in the presence of capsules, indicating binding to the capsule wall rather than encapsulation in the interior. We present

an analysis in terms of a combined diffusion-relaxation model, where exchange times can be determined from diffusion and spin relaxation experiments even in this particular regime, where the exchange is fast. Based on the ultrafast relaxation in the bound site, the apparent diffusion coefficients become sensitive to the diffusion time. The results show an increase of exchange rates with phenol concentration.

SYPE 1.7 Wed 16:00 Poster B

The Influence of Secondary Interactions during the Formation of Polyelectrolyte Multilayers: Layer Thickness, Bound Water and Layer Interpenetration — ●MANESH GOPINADHAN¹, OXANA IVANOVA¹, HEIKO AHRENS¹, JENS-UWE GÜNTHER¹, ROLAND STEITZ², and CHRISTIANE A. HELM¹ — ¹Institut für Physik, Ernst-Moritz-Arndt Universität, F.-L.-Jahn-Str. 16, D-17487 Greifswald, Germany — ²Hahn-Meitner Institut, Glienicker Strasse 100, D-14109 Berlin, Germany

With X-ray and neutron reflectivity the structure and composition of polyelectrolyte multilayers from poly (allyl amine) (PAH) and poly (styrene sulfonate) (PSS) is studied as function of preparation conditions (salt concentration and solution temperature). The onset of a temperature effect occurs at 0.05 M NaCl (Debye length less than 1 nm). At 1 M salt, the film thickness increases by a factor of three on heating the deposition solution from 5 to 60°C. The PAH/PSS bilayer thickness is independent of the kind of salt (NaCl or KCl) yet its composition is different (more bound water for NaCl). At low T, the internal roughness is 33% of the bilayer thickness, it increases to 60% at high T. The roughening is accompanied by a total loss of bound water. At which temperature the roughening starts is a function of the kind of salt (50°C for NaCl and 35 °C for KCl). The strong temperature dependence and the eventual loss of bound water molecules can be attributed to the hydrophobic force. However, there is an isotope effect since the loss of bound water is less pronounced in the deuterated layers.

SYPE 1.8 Wed 16:00 Poster B

Deposition and nanostructure of poly(ethyleneimine)/poly(acrylic acid) multilayers in dependence of polyelectrolyte concentration — ●MARTIN MÜLLER, BERND KESSLER, and WUYE OUYANG — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden

Polyelectrolyte (PEL) multilayers (PEM) of poly(ethyleneimine)/poly(acrylic acid) (PEI/PAC) were reproducibly deposited in an automated flow cell and studied in dependence of the adsorption step z and PEL concentration cPEL by in-situ ATR-FTIR spectroscopy and AFM. Quantitative information on the deposited amount and PEL composition was provided based on the integrated areas of characteristic IR bands of either PEI or PAC. Varying cPEL between 0.001 M and 0.1 M resulted in a maximum PEM deposited amount for moderate cPEL. Evidence for the release of outermost located PEI upon PAC immersion (even step) and of outermost PAC upon PEI immersion (odd step) was obtained. AFM images on the surface deposits for PEM-10 revealed smaller structural features for low and high cPEL and larger ones for moderate cPEL. The found cPEL dependent deposition and morphological features are suggested to be determined by a competition of two types of electrostatic attraction: between the outermost PEL and the underlying PEM zone (PEM formation and stability) (i) and between the outermost PEL and the immersed one (PEM rupture and solution complexation) (ii) mediated by Debye length and PEL supply. Applications are related to both charged and nanostructured surfaces for selective drug or protein interaction.

SYPE 1.9 Wed 16:00 Poster B

Layer-by-layer Polyelectrolyte films containing magnetite nanoparticles: Construction and magnetic properties — ●MARJOLEIN NEELEMAN and ANDREAS FERY — Max-Planck-Institut für Kolloid und Grenzflächenforschung, Am Mühlenberg 1 14424 Potsdam

Magnetic ultrathin membranes are of interest for various applications ranging from data storage to the biomedical field. We have investigated the construction of such membranes using the well-established electrostatic layer-by-layer deposition. This method allows to build up nanoscale surface coatings by alternating adsorption of poly(allylamine hydrochloride) (PAH) and magnetite nanoparticles from aqueous solutions. We have characterized the dependence of the structure of these coatings on deposition parameters like salt concentration of the adsorption solution using atomic force microscopy and X-ray reflectivity. We find that depending on the deposition conditions both linear film

growth and exponential film growth can be observed for this system. Finally, hollow magnetic capsules were produced by coating dissolvable core particles with multilayers and subsequently dissolving the particles under conditions that do not destroy the multilayer. With a magnetic balance the magnetic moment of the resulting microcapsules was studied. We find an almost linear increase of the magnetic moment with the number of bilayers applied to the cores, which demonstrates that our method allows producing membranes of well defined magnetization.

SYPE 1.10 Wed 16:00 Poster B

Molecular weight dependence of PEO permeation through the walls of hollow polyelectrolyte capsules — ●RUDRA PRASAD CHOUDHURY¹, PETRIK GALVOSAS², and MONIKA SCHÖNHOF¹ — ¹Institute of Physical Chemistry and Graduate School of Chemistry, WWU Münster, Germany — ²Faculty of Physics and Earth Sciences, University of Leipzig, Germany

The exchange dynamics of polyethylene oxide (PEO) in colloidal dispersions of hollow polymeric capsules is studied by pulsed field gradient (PFG)-NMR and diffusion-relaxation correlation spectroscopy. The capsules are prepared by self-assembly of polyanions and polycations onto silica particles, followed by dissolution of the silica core in HF. In PFG-NMR two echo decay components with diffusion coefficients corresponding to free PEO and capsules, respectively, are found. In addition, relaxation-diffusion correlation spectra reveal two peaks with different diffusion coefficients, but almost identical relaxation times. This implies the presence of mobile PEO chains in the capsule interior. From variations of the diffusion time, the exchange behaviour is analysed by a two-site exchange model of free and encapsulated PEO. Exchange times and permeation rates through the capsule wall are extracted for different molecular weight. Permeation rates are decreasing with increasing molecular weight of PEO. While for short chains (Mw < 10000 Da) the dependence on Mw is strongly pronounced, another, less pronounced dependence is found for larger Mw. This suggests a transition between two different mechanisms of permeation as the molecular weight is increased.

SYPE 1.11 Wed 16:00 Poster B

Measurement of long-ranged steric forces between polyelectrolyte covered surfaces — ●STEPHAN BLOCK and CHRISTIANE HELM — Institut für Physik, Ernst-Moritz-Arndt Universität, F.-L.-Jahn-Str. 16, D-17487 Greifswald, Germany

Colloidal Probe Technique (CPT) is used to investigate the distance dependent interaction force between polyelectrolyte coated surfaces in salt solutions between 0.1 mM and 1 M, with the polyelectrolyte layers adsorbed from 1 M NaCl solution. As polyelectrolytes poly(allylamine) hydrochloride (PAH), Poly-L-Lysine (PLL) and poly (styrene sulfonate) (PSS) are used, the latter on Si surfaces which are positively charged by silanization.

The repulsive surface forces are more long-ranged with decreasing salt concentration and their decay length always exceed the Debye length. It can be described by the theory of Alexander and de Gennes for interacting surfaces covered with neutral anchored polymers. Apparently, the polyelectrolyte layer is swollen and loops and tails of the adsorbed polyelectrolyte layer dangle into the solution.

There is no approach-separation hysteresis and no influence of the history of the experiment, ie if the salt concentration is increased or decreased by several orders of magnitude. The situation is very different from the well-known flat polyelectrolyte adsorption layers obtained from salt free solutions, where the interaction force is purely electrostatic.

SYPE 1.12 Wed 16:00 Poster B

Direct evidence of Layer-by-Layer assembly of polyelectrolyte multilayers on soft and porous temperature sensitive PNIPAM-microgel using fluorescence correlation spectroscopy — ●JOHN ERIK WONG¹, WALTER RICHTERING¹, and ANDRÉ LASCHEWSKY² — ¹RWTH Aachen University — ²Potsdam University

We describe the Layer-by-Layer assembly of polyelectrolyte multilayers on soft and porous temperature-sensitive poly(N-isopropylacrylamide) (PNIPAM) microgel. Microgels are not hard and rigid but rather soft and porous particles and polyelectrolytes can not only interdigitate with each other during multilayer formation but also interpenetrate with the microgel. Because of this difference, there could be concerns about the feasibility of the Layer-by-Layer technique on these systems. The argument being that the layer being deposited is stripping the underlying layer instead of anchoring to the latter, and common methods

of characterizing film growth on particles such as zeta-potentials will still show *successful* charge reversal.

To address this issue, we used two differently labeled-polyelectrolytes during the deposition. Due to the small size of the microgel (400 nm) studied, we cannot distinguish between polyelectrolytes adsorbed on

or in the microgel. However with fluorescent correlation spectroscopy we can clearly distinguish between free labeled-polyelectrolytes and those that are bound to the microgel. Dual-color correlation confirms the presence of both polyelectrolytes bound to the same particle while fluorescence imaging (on a dry sample) provides the visual proof.

SYPE 2: Polyelectrolytes I

Time: Thursday 14:00–17:00

Location: H37

Invited Talk

SYPE 2.1 Thu 14:00 H37
Coulomb and Flory: Fathers of SONS. Polyelectrolytes in Self Organized Nano Systems — ●MARTIEN COHEN STUART — Laboratory of Physical Chemistry and Colloid Science, Wageningen University, P.O. Box 8038, 6700 EK Wageningen, The Netherlands

Supramolecular chemistry exploits the many non-covalent interactions between molecules to create novel and functional structures. A most versatile interaction is the electrostatic force that emerges between ions and polyions. We have seen an enormous activity in recent years to fabricate novel materials using pairs of oppositely charged macromolecules; in particular, fabrication of thin films consisting of polyelectrolyte complexes by controlled deposition in alternating fashion has captured the imagination of many chemists and physicists. The debate concerning the description of these systems in terms of fundamental physical laws and chemical properties is going on.

In the present contribution we exploit the same tendency of oppositely charged chains to form a condensed phase, but we add new features, with the aim to make new complex and functional nanoparticles. The new feature is a 'stop mechanism' that suppresses growth of a macroscopic phase so that only small particles result. Connecting a neutral, water soluble to at least one of the polyelectrolytes participating in complexation, one will get micellar particles, which we call 'Complex Coacervate Core Micelles (C3M's), and which have been denoted as 'Poly Ion Complexes' (PIC's) or 'Block Ionomer Complexes' (BIC's) by others.

SYPE 2.2 Thu 14:30 H37
Pore size distribution in polyelectrolyte multilayers determined by cryoporometry — ●FABIÁN VACA CHÀVEZ and MONIKA SCHÖNHOF — Institut für Physikalische Chemie, WWU Münster, Germany

Permeability and porosity of polyelectrolyte multilayers (PEM) are properties of major interest, as they are crucial for applications in encapsulation, controlled release and membrane separation. In the current work the first pore size distribution of PEM in samples consisting of silica particles coated with poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS) is presented. To this end, the Nuclear Magnetic Resonance (NMR) cryoporometry technique was applied. NMR cryoporometry has been successfully applied to various porous systems and, in our approach, we consider polyelectrolyte multilayers as a porous material, where the hydration water can freeze in dependence on the size of water pores. The proton NMR signal of liquid water is analyzed assuming a log normal distribution of motional correlation times. From our results, it is possible to determine the size of water sites in the layers to around 1 nm. In addition, a slight variation with the number of layers is found. The average pore size agrees with cut-off sizes found in permeation experiments.

SYPE 2.3 Thu 14:45 H37
Adsorption of Light and Heavy Water Vapours in Polyelectrolyte Multilayer Films — CHRISTOPHE DELAJON¹, ●THOMAS GUTBERLET², HELMUTH MÖHWALD¹, and RUMEN KRASTEVA¹ — ¹Max-Planck-Institute of Colloids and Interfaces, Wissenschaftspark Golm, 14424 Potsdam, Germany — ²Paul Scherrer Institute, 5232 Villigen, Switzerland

We studied the swelling and the uptake of water (H₂O or D₂O) vapours in polyelectrolyte (PE) multilayer (PEM) samples deposited on solid support (Si wafers) as a function of the isotope nature of the vapour and the charge of the last polymer layer. The samples were prepared with deuterated poly(sodium 4-styrenesulfonate) (dPSS) and poly(allylamine hydrochloride) (PAH). Two types of samples were studied. The sample with a structure Si/PEI/(dPSS/PAH)₆/dPSS was negatively charged. A positively charged sample was PAH terminated and had the structure Si/PEI/(dPSS/PAH)₆. The film thickness

and density were estimated from neutron reflectometry experiments and the results were complemented with in-situ QCM measurements. The swelling of PEM in H₂O and D₂O vapours is the same, but the amount of sorbed water depends on the used water isotope. It is about twice as large in the case of D₂O compared to H₂O. We attribute the effect to the strength of the hydrogen and deuterium bonds formed between the water molecules and the PEM matrix. We also show that the amount of sorbed water depends on the nature of the last layer which builds the PEM.

SYPE 2.4 Thu 15:00 H37
Elasticity testing of freestanding polyelectrolyte membranes with different charge density — ●INGO DÖNCH, MARC NOLTE, and ANDREAS FERY — Max-Planck-Institut für Kolloid und Grenzflächenforschung, Am Mühlenberg 1, 14424 Potsdam

To build micro scale applications like a sensor or pressure sensitive valve new ways have to enter. It looks realistic to scale sensors down by using known polyelectrolyte membranes. After finding a new way to transfer polyelectrolyte multilayer films stress free to a patterned substrate, it is possible to test different properties of PE-membranes in variable environment, for changing radii. With the existing knowledge of PE-membranes, it is possible to scale down sensors for such applications. The work is primarily specializing in investigating the micromechanical response of the PE-membranes made from PDADMAC/PSS, in these we use PDADMAC with different charge density. The behavior of the resulting membrane patches is dependent only on the thickness of the membrane and the radius of the covered hole. It can be described with simple continuum mechanical models. We generate an osmotic pressure between bulk and the cavities which lead to a bending of the freestanding part of the membrane. This compliance of a fluorescent labeled film can be measured with a confocal microscope. Since the thickness of the multilayer can be precisely controlled in the nanometer range, the compliance of the membrane can also be varied over orders of magnitude. The PE-membranes are also semi-permeable, which makes them sensitive to osmotic pressure differences. Thus they are promising components for future micro-scale membrane sensors.

SYPE 2.5 Thu 15:15 H37
Self-assembly of thermoresponsive polyelectrolyte microgels on polyelectrolyte coated surfaces — STEPHAN SCHMIDT¹, ●THOMAS HELLWEG², and REGINE VON KLITZING² — ¹MPI KGF, Wissenschaftspark Golm, 14424 Potsdam, Germany — ²TU Berlin, Stranski-Lab., Strasse des 17. Juni 124, 10623 Berlin, Germany

PNIPAM-co-poly(acrylic acid) microgels are deposited on poly(ethylene imine) coated silicon wafers using the well known layer-by-layer approach. The obtained surface coverage strongly depends on the degree of charge of the microgels, which is controlled via the pH-value of the used buffer. At intermediate pH (approx. 6) a coverage of about 40 % is obtained and the formation of island structures can be observed. However, placing these surfaces in a similar buffer a second time leads to a complete rearrangement of the structure. Highly ordered surface patterns are obtained. The process is studied in situ using confocal microscopy. In addition ellipsometry and AFM measurements are performed to characterize the prepared surfaces.

SYPE 2.6 Thu 15:30 H37
growth of polyelectrolyte complex nanoparticles: experimental and simulation studies — ●VITALIY STARCHENKO^{1,2}, MARTIN MÜLLER¹, and NIKOLAI LEOVKA² — ¹Leibniz-Institut für Polymerforschung, Dresden, Deutschland — ²Ovcharenko-Institute of Biocolloidal Chemistry, Kiev, Ukraine

Formation of polyelectrolyte complex (PEC) nanoparticles is of large fundamental interest and has application potential in e.g.

biomedicine (drug/protein carrier) and water treatment (flocculation). Monodisperse particles were prepared by mixing cationic poly(diallyldimethylammonium chloride) (PDADMAC) and anionic poly(styrenesulfonate) (PSS) at nonstoichiometric monomer charge ratios followed by consecutive centrifugation, which was characterized by dynamic light scattering (DLS). Using this concept small primary particles of low aggregation number have been suggested to merge to larger secondary particles by attractive dispersive forces, while the colloidal stability and the final particle size is determined by electrostatic repulsion in line with the DLVO theory. To check for the role of the Debye length, we report herein on ionic strength dependence of the particle size. In conformity with theoretical assumptions a model based on Smoluchowski theory, which includes a colloidal potential according to DLVO theory, was developed. This model can be used exclusively for simulation of the coagulation process of particles on the colloid level. Hence, additionally the influence of polyelectrolyte molecular weight on the particle size was studied to figure out the Debye length dependent contribution on the macromolecular conformation level.

15 min. break

Invited Talk SYPE 2.7 Thu 16:00 H37

Bundling Phenomena in Semiflexible Polyelectrolytes — ●CHRISTIAN HOLM^{1,3}, MEHMET SAYAR², and BERK HESS³ — ¹Frankfurt Institute for Advanced Studies, Johann Wolfgang Goethe - Universität, Frankfurt, Germany — ²Koc University, College of Engineering, Istanbul, Turkey — ³Max-Planck-Institut für Polymerforschung, Mainz, Germany

We present the results of extensive computer simulations performed on solutions of monodisperse charged rod-like polyelectrolytes. In the first part of the talk we investigate the bundle formation of DNA-like semiflexible generic polyelectrolytes. DNA is known to aggregate in the presence of multivalent cationic condensing agents into toroidal and bundle like structures. We study a coarse-grained semiflexible bead-spring model in the presence of trivalent counterions, using a combination of parallel tempering and hybrid Monte Carlo techniques. Our results show that for small values of the electrostatic interaction the solution mostly consists of dispersed single rods. In the second part of the talk we investigate the bundle formation in solution of hydrophobically modified sulfonated poly(p-phenylene) oligomers (PPP) via atomistic simulations in the presence of Na and divalent Ca counterions. We show that the basic packing of the PPP oligomers does not change upon increase of the counterion valency, but the interaction among bundles goes from repulsive to attractive.

SYPE 2.8 Thu 16:30 H37

Bundle Formation in Polyelectrolyte Brushes — ●JENS-UWE

GÜNTHER¹, HEIKO AHRENS¹, STEPHAN FÖRSTER², and CHRISTIANE HELM¹ — ¹Institut für Physik, Ernst-Moritz-Arndt Universität, F.-L.-Jahn-Str. 16, D-17487 Greifswald, Germany — ²Institut für Physikalische Chemie, Universität Hamburg, Bundesstr. 45, D-20146 Hamburg, Germany

Bundle formation in the vertically oriented chains of poly(styrene sulfonate) (PSS) within polyelectrolyte brushes is studied with grazing incidence diffraction as function of grafting density and ion concentration. The brush thickness determined with X-ray reflectivity amounts to 30-50% of the contour length. As predicted theoretically, bundle formation can be induced by adding divalent ions, ie CaCl₂. However, at 0.5 Molar monomer concentration and without added salt, already bundles are observed. Then, a bundle consists of two chains and is 5 nm long. On the addition of up to 1 M CsCl in the subphase the aggregation number increases up to 20 whereas the bundle length approaches a limiting value, 2 nm. We suggest that the bundle formation is determined by a balance between long-ranged electrostatic repulsion, whose range and amplitude is decreased on salt addition, and a short-ranged attraction.

SYPE 2.9 Thu 16:45 H37

Collapse of highly charged polyelectrolytes by dipole-dipole interactions — ●ANDREY CHERSTVY and ROLAND WINKLER — IFF, Forschungszentrum Jülich, D-52425 Jülich, Germany

Although collapse of highly charged polyelectrolytes (pe) was considered in a number of theoretical [1,2] and simulation [3-5] studies, some questions about effect of added salt and scaling relations for compact state remain open. We consider the influence of electrostatic (el) and dipole-dipole (dd) interactions on properties of flexible highly charged pes [6]. The dd interactions of pe segments are due to condensed counterions. We sum screened el and dd interactions along pe assuming that Gaussian statistics is weakly perturbed [7]. Attractive averaged dd interactions used are akin to Keesom energy. For weakly charged pe (below Manning limit), pes are swelled due to el repulsion of monomers. As condensation of counterions sets in, attractive dd interactions start to counteract el repulsion and trigger chain compaction into globules. We study onset on collapse as a function of chain length and salt conc. Scaling relations for size of the globule depending on pe charge density are obtained, with and without excluded volume interactions. We treat also the persistence length of dipolar chain and scaling relations for dense aggregates.

[1] H. Schiessel et al., MM 31 7953 (1998). [2] A.G. Cherstvy et al., JPCB 106 13362 (2002). [3] R.G. Winkler et al., PRL 80 3731 (1998). [4] R.G. Winkler et al., PRE 66 021802 (2002). [5] R.G. Winkler New J. Phys. 6 11 (2004). [6] A.G. Cherstvy and R.G. Winkler, in preparation. [7] S. Lifson et al. JPolSci XI 409 (1953).

SYPE 3: Polyelectrolytes II

Time: Friday 10:30–12:30

Location: H1

Invited Talk SYPE 3.1 Fri 10:30 H1

Behaviour of polyelectrolyte solutions under confinement — ●DOMINIQUE LANGEVIN¹, CÉSAR MARQUEZ², HEINIG PETER³, and DAN QU⁴ — ¹Laboratoire de Physique des Solides, Université Paris-Sud, Batiment 510, 91405 Orsay — ²Laboratoire de Physique des Solides, Université Paris-Sud, Batiment 510, 91405 Orsay — ³Laboratoire de Physique des Solides, Université Paris-Sud, Batiment 510, 91405 Orsay — ⁴Laboratoire de Physique des Solides, Université Paris-Sud, Batiment 510, 91405 Orsay

We have studied free horizontal liquid films made with semidilute polyelectrolyte solutions and stabilised by minute amounts of surfactants. A stratification phenomenon is observed during film thinning, with a step size close to the mesh size of the polymer network: dark domains nucleate and expand, the outer polymer layer dewetting a thinner film. The kinetics of dark spot expansion is not simply related to bulk viscosity and becomes slower or faster when the film thickness decreases, depending of the surface conditions (presence or absence of a mixed polyelectrolyte surfactant surface layer). Other domain shape dynamics have been analysed and related to a local viscosity in stratifying foam films.

SYPE 3.2 Fri 11:00 H1

Polyelectrolyte complexes and effective charge — UTE BÖHME BÖHME and ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden, e.V., Hohe Str. 6, D-01069 Dresden

Condensation of counterions onto polyelectrolytes is directly monitored in diffusion and electrophoresis NMR. From a combination of both experiments the effective charge per molecule is determined. The diffusion coefficient and electrophoretic mobility measured for counterions or small ligands is the population-weighted average of the values for the free and the bound state, the later corresponding to that of the polymer. Knowing both values, the bound fraction of counterions is calculated, from which with the effective charge the molecular weight of the polymer is determined model free. Binding of ligands and the formation of polyelectrolyte complexes is investigated with an emphasis on weak binding and the equilibrium states. Examples shown include flexible polyelectrolyte like PDADMAC and PSS and rigid-rod poly(aramides).

SYPE 3.3 Fri 11:15 H1

A new method to determine ionic mobilities in polymer electrolytes at low charge carrier density — ●PETER KOHN, KLAUS SCHÖTER, and THOMAS THURN-ALBRECHT — Department of Physics, Martin Luther University Halle-Wittenberg, Germany

Apart from mechanical properties the conductivity and its dependence on various parameters like temperature, number of charge carriers, etc., is the decisive quantity for applications of ionically conducting materials. As for other conducting systems the conductivity is determined by the product of the mobility and the number density of the free charge carriers. A basic understanding therefore requires the knowledge of at least one of these quantities in addition to the conductivity.

We present an electrical method that allows an independent determination of the charge carrier density and the mobility of the ions in polymer electrolytes with low density of charge carriers. The number density of free ions is obtained by polarization experiments with high DC-voltages and the ion-mobility can be determined from the transient current after a subsequent voltage reversal.

For an exemplary application we studied polymethylmethacrylate (PMMA) doped with small amounts of a lithium salt (LiCF_3SO_3). A comparison of the values obtained for the ion mobility and the charge carrier density with the conductivity shows good agreement for all salt concentrations studied.

Invited Talk

SYPE 3.4 Fri 11:30 H1

Polymers at Surfaces: Sticking and Gliding — ●ROLAND NETZ — Physics Department, TU Munich, 85748 Garching, Germany

Recently, peptides and different polyelectrolytes were pulled off from various low-dielectric and high-dielectric surfaces with the AFM, leading to a number of interesting observations: i) Surprisingly, the electrostatic contribution to the adsorption energy is always quite small, even for highly charged surfaces. The dominant solvation attraction can be quantitatively explained with classical MD simulations including explicit water. ii) Charge regulation of polymers at the surfaces is important and has to be taken into account for the quantitative modeling of adsorption energies. iii) Uncharged, hydrophobic surfaces appear negatively charged and give rise to sizable electrostatic adsorption energies. This finding is related to the water structure at hydrophobic substrates which involves an oriented first water layer and specific ion adsorption. iv) The friction coefficient of bound polymers is very low on hydrophobic substrates, which is traced back to the presence of a vacuum layer between substrate and water, which forms a lubricating cushion on which the polymers glide.

SYPE 3.5 Fri 12:00 H1

The force on DNA in a nanopore — ●U. F. KEYSER^{1,2}, S. VAN DORP¹, R. M. M. SMEETS¹, D. KRAPP¹, N. H. DEKKER¹, and C. DEKKER¹ — ¹Kavli Institute of Nanoscience, Delft University of Tech-

nology, The Netherlands — ²Institut für Experimentelle Physik I, Universität Leipzig, Germany

Among the variety of roles for nanopores in biology, an important one is enabling transport of polyelectrolytes like DNA or RNA, for example in gene transfer between bacteria and transport of RNA through the nuclear membrane. Recently, this has inspired the use of protein and solid-state nanopores as single-molecule sensors for the detection and structural analysis of DNA and RNA by voltage-driven translocation [1]. The magnitude of the force involved is of fundamental importance in understanding and exploiting this translocation mechanism, yet so far it has remained unknown. Here, we demonstrate the first measurements of the force on a single DNA molecule in a solid-state nanopore by combining optical tweezers with ionic-current detection [2]. The opposing force exerted by the optical tweezers can be used to slow down and even arrest the translocation of the DNA molecules [3]. We obtain a value of 0.24 ± 0.02 pN mV⁻¹ for the force on a single DNA molecule, independent of salt concentration from 0.02 to 1M KCl. [1] R. M. M. Smeets, U. F. Keyser, et al. Nano Letters 6 (2006) [2] U. F. Keyser et al., Rev. Sci. Instr. 77, 105105 (2006) [3] U. F. Keyser et al., Nature Physics 2, 473 (2006)

SYPE 3.6 Fri 12:15 H1

Forces of interaction between DNA -grafted colloids : an optical tweezers measurement — ●FRIEDRICH KREMER¹, KATI KEGLER¹, CHRISTOF GUTSCHE¹, and MATHIAS SALOMO² — ¹PAF, Exp. Physik 1, Universität Leipzig, Linnéstr. 5, 04103 Leipzig — ²Biophysik, Universität Leipzig, Linnéstr. 5, 04103 Leipzig

Optical tweezers are employed to measure the forces of interaction between single DNA-grafted colloids. Parameters to be varied are the length of the DNA (1000 base pairs (bp) to 6000 bp), the grafting density (1.84×10^{-4} chains/nm² to 1.97×10^{-5} chains/nm²) and the ionic concentration (10^{-5} M to 10 mM NaCl) of the surrounding medium. From the measured force-separation dependence an interaction-length at a given force (2pN) is deduced. It shows in the mushroom-regime a scaling with the grafting density which levels off for brushes. For the latter the transition from an osmotic to a salted brush can be traced in detail by varying the ionic concentration in accordance with meanfield theories. Further experiments are carried out to measure the influence of the valency of the added salt. Special emphasis is given to the interaction between one DNA-grafted and one blank colloid. The results are discussed with respect to the different brush regimes.

[1] K. Kegler, M. Salomo, and F. Kremer, in Press Phys. Rev. Lett.