

IGRTG 1524 Annual Meeting 03.–06.10. 2011			
Date	Time	Speaker	Chair
03.10.	08:00	<i>Bus departure NCSU, EB1 building</i>	
	08:45	<i>Bus departure Hilton Homewood Suites hotel</i>	
	12:00	<i>Arrival/Check in New Bern, lunch</i>	
	14:00	<b>Keith Gubbins</b> Introduction and Welcome remarks	
	14:10	<b>Martin Schoen</b> Where we are standing and where we might be headed in theory	Lipowsky
	14:55	<b>Hyung-Jun Koo</b> A new class of aqueous soft matter based photovoltaic devices	
	15:15	<b>Ying Liu</b> Self-folding of polymer sheets triggered by local light absorption	
	15:35	<b>Michael Dickey</b> A micromoldable metal for soft, stretchable and biomimetic electronics	
	16:05	<i>coffee break</i>	
	16:30	<b>Carol Hall/Keith Gubbins</b> Theory, US	Spontak
	17:15	<b>Tahereh Rouhi</b> Pattern formation in multicomponent membranes	
	17:35	<b>Ju-Hee So</b> Towards soft matter circuits: quasi-liquid diodes and memristors	
	17:55	<b>Emily Curtis</b> Multiscale modeling for phospholipid bilayer simulations	
	18:15	<b>Orlin Velev/Jan Genzer</b> <i>Soft matter assembly at surfaces and in external fields (-19:00h)</i>	
19:30	<i>dinner</i>		

## Introduction and Welcome remarks

Keith Gubbins

*Notes:*

**Where we are standing and where we might be headed in theory**

Martin Schoen

*German groups perspective talk – Theory*

***Notes:***

## A New Class of Aqueous Soft Matter Based Photovoltaic Devices

Hyung-Jun Koo<sup>1</sup>, Suk Tai Chang<sup>2</sup>, Rajesh R. Naik<sup>3</sup> and Orlin D. Velev<sup>1</sup>

<sup>1</sup>*NC State University, Department of Chemical and Biomolecular Engineering*

<sup>2</sup>*School of Chemical Engineering and Materials Science, Chung-Ang University, Rep. of Korea*

<sup>3</sup>*Materials and Manufacturing Directorate, Air Force Research Lab., Wright-Patterson AFB*

This presentation describes a new class of biomimetic photovoltaic systems, inspired by the materials and structures found in natural leaves. For our first approach inspired by hydrated, soft materials of leaves, photovoltaic devices based on aqueous soft gel will be presented [1]. Agarose gel, used as a biomimetic medium of the devices, contains 98% of water and 2% of polysaccharides derived from natural seaweed. Two photosensitive ions, DAS<sup>-</sup> and [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, were used as photoactive molecules embedded in a matrix of water-based agarose. The provisional mechanism of the operation of the hydrogel photovoltaics (HGPs) suggests that the dye ions cooperatively work and contribute to the photocurrent generating process both on the surface of the working electrode and in the bulk of the gel. To reduce the cost of HGPs without efficiency loss, we found an efficient replacement of the expensive Pt counter electrode with inexpensive copper coated with carbon materials. Biologically derived photoactive molecules, such as Chlorophyll and Photosystem II, were successfully operated in the aqueous gel media of HGPs. For the second strategy, we will discuss how channels can be embedded in such gel photovoltaic systems to mimic the microvascular network of leaf venation. The channel structures could enable efficient and continuous supply of the reagents necessary for photovoltaic operation. We developed modeling tools to numerically estimate the rapidity and efficiency of the reagent supply through the various gel-network structures, thereby optimizing the channel design embedded in hydrogel cells. The concept of the channel embedded PV systems has been demonstrated in the dye-sensitized solar cell devices (DSSCs), where dyes and electrolytes can be continuously supplied. Such gel based and microvascular channel embedded PV concepts could allow constructing biomimetic photovoltaic systems with unprecedented functionality.

[1] H.-J. Koo *et al.*, *J. Mater. Chem.* (2011), 21, 72

### **Notes:**

## Self-folding of polymer sheets triggered by local light absorption

Ying Liu, Julie K. Boyles, Jan Genzer, Michael D. Dickey

*NC State University, Department of Chemical and Biomolecular Engineering*

In the presentation, we will describe a simple approach to self-folding that uses localized light absorption on a pre-stressed polymer sheet. Self-folding is a deterministic assembly process that causes a predefined 2D template to fold into a desired 3D structure with high fidelity.<sup>[1]</sup> Self-folding takes advantage of the multitude of available 2D patterning techniques (e.g., lithography, inkjet printing, screen printing). Self-folding is useful for packaging, actuation, and sensing.

Our approach to self-folding applies printing patterns of ink on a pre-stressed polymer sheet. The pre-stressed polymer sheets (Shrinky-Dinks) are commercially available as a craft toy. The black ink (i.e., the hinge) is patterned using a desktop printer on either side of the optically transparent sheets. Hinges absorb selectively the light to locally heat the underlying polymer and causes the polymer to shrink. The 2D patterned polymer sheets can fold into complex 3D structures (e.g., cubes, tetrahedrons) within seconds.

Most approaches to self-folding use hinges (i.e., regions of a substrate that fold) that have unique chemical composition from the bulk, which requires complicated photolithography or other multiple fabrication steps.<sup>[1]</sup> Our approach is appealing since it uses inexpensive materials and simple patterning techniques to form complex structures.

We study experimentally the impact of the hinge geometry, line width and the support temperature of the 2D pattern on folding. Modeling of the temperature profile inside the polymer films also captures effectively the folding trends measured experimentally based on the predicted time when the folding starts.

References:

<sup>[1]</sup>T.G. Leong, A.M. Zarafshar, D.H. Gracias, *Small*, **2010**, 6, 792.

**Notes:**

## A Micromoldable Metal for Soft, Stretchable and Biomimetic Electronics

Michael Dickey

*NC State University, Department of Chemical and Biomolecular Engineering*

This talk will describe efforts in our research group to create electronic devices with new properties and architectures by harnessing interfacial phenomena, microfabrication, and the unique properties of a moldable liquid metal. Conventional electronics are typically fabricated from rigid materials (e.g., silicon for transistors, copper for antennas). New materials are being explored as candidates for flexible/stretchable/soft electronics because of the novel applications that emerge from their mechanical properties. Examples include flexible displays, implantable devices, electronic textiles, and soft robots. This talk will discuss the underlying fundamental science motivating two active areas of research in our group:

- Ultra-stretchable wires, sensors, antennas, and microelectrodes created by injecting a gallium-based metal alloy into elastomeric microchannels. The metal is a liquid at room temperature with low-viscosity (water-like) and can be micromolded due to a thin, oxide skin that forms rapidly on its surface. The properties of the metal will be discussed as well as methods to shape the metal to form ultra-stretchable electronic components.
- Soft, biomimetic memory (“memristor-like”) devices composed of hydrogels and moldable metal. These memory devices are composed entirely of soft materials and operate based on the ability to control the thickness of an interfacial oxide between the metal and gel. This system is brain-like in the sense that it is soft, 3-D, operates in an aqueous environment using ionic conductance, and has characteristics that mimic synapse formation.

**Notes:**

## **Perspective on theory studies at NCSU**

Carol Hall/Keith Gubbins

*US groups perspective talk – Theory*

***Notes:***

## Pattern formation in multicomponent membranes

Tahereh Rouhi

*Max Planck Institute of Colloids and Interfaces, Potsdam*

Part 1: Adhesion induced phase separation in multi-component membrane

Biomimetic membranes with several molecular components exhibit two-phase coexistence regions and patterns of intramembrane domains. We considered a lattice gas model and performed analytical calculations and Monte Carlo simulations to reach the phase diagram of the adhesion-induced phase separation in multicomponent membranes.

Part 2: Characterization of the Phagocytosis force implied by Macrophages

Macrophages are white blood cells produced by the differentiation of monocytes in tissue. Their role is to phagocyte the pathogens and stimulate lymphocytes and other immune cells to respond to pathogens. We have studied the force and kinetics of phagocytosis by human Macrophages. To this aim, we used the human opsonized Red blood cell. The force calculation is based on blood cell's shape deformation and elastic properties.

**Notes:**



## Towards Soft Matter Circuits: Quasi-Liquid Diodes and Memristors

Ju-Hee So, Hyung-Jun Koo, Michael D. Dickey, and Orlin D. Velev

*NC State University, Department of Chemical and Biomolecular Engineering*

New types of electronic devices and circuits based on soft materials have potential applications in bio-electronic circuits, artificial neural networks, and brain-machine interfaces. We will present a new class of diodes and memristors composed entirely of soft, liquid-based materials formed by combining a moldable liquid metal and hydrogel doped with polyelectrolytes. The electronic functionality of these devices originates from the ability to control the electronic and ionic transport at the interface between the metal and the hydrogel. The metal is a eutectic alloy of gallium and indium (75 % Ga, 25 % In). At room temperature it is a low viscosity liquid with a high conductivity ( $\sigma = 3.4 \times 10^4 \text{ S/cm}$ ). Its surface is coated with a thin, native skin of gallium oxide, which is a wide band-gap semiconductor. The oxide skin passivates the liquid metal; that is, the oxide does not grow thicker with time without any additional driving force. The electrical resistance through the oxide skin depends on its thickness, which can be controlled using pH and/or electrical bias to oxidize or reduce the skin. The agarose gel, which interfaces with the liquid electrodes, is composed of more than 90% water and offers a soft aqueous media into which polyelectrolytes may be doped to control the local pH. We fabricated soft and quasi-liquid electronic devices that mimic solid-state, semiconductor devices, such as diodes and memristors, by sandwiching two hydrogel films: one doped with polyacrylic acid (PAA) and one doped with polyethyleneimine (PEI, which is basic). We contacted both sides of the film stack with liquid metal electrodes. The PEI-doped hydrogel suppresses the oxidation reaction at the metal electrode interface, whereas the thickness of the metal oxide layer at the interface with the PAA-doped hydrogel can be controlled by applying an electric bias. The direction and the magnitude of the electric bias pre-applied to the electrodes controls the anisotropy of current conductance, resulting in tunable rectification ratios. The pre-programmed anisotropy is preserved for more than an hour, which enables the fabrication of memory storage devices (i.e., memristors). We will discuss the rectification characteristics of diodes and the on/off switching behavior of memristors with different geometries composed entirely of soft materials.

**Notes:**

## Multiscale Modeling for Phospholipid Bilayer Simulations

Emily Curtis

*NC State University, Department of Chemical and Biomolecular Engineering*

A multiscale modeling approach was used to develop an implicit-solvent intermediate-resolution model to simulate the behavior of the lipid, 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) in water. By reducing the DPPC representation to 14 coarse-grained sites with unique properties, treating solvent implicitly, and employing discontinuous molecular dynamics, a very fast alternative to traditional molecular dynamics, we are able to simulate the spontaneous formation of a bilayer from a random solution of 512 DPPC molecules in several hours on a fast workstation. Data used to calculate the coarse-grained model parameters was obtained by running united-atom simulations with GROMACS. Radial distribution functions were plotted for all pairs of non-bonded coarse-grained sites to estimate the hardsphere and square-well diameters. The interaction energy between each pair of non-bonded coarse-grained sites was calculated using the Boltzmann inversion scheme. The relative stiffness of each lipid is maintained by imposing pseudobonds, which limit the bond lengths to fluctuate by the same amount observed in the united atom simulations. In the model each coarse-grained site has its own realistic mass. Simulation results show that the model accurately reproduces structural properties of the DPPC bilayer including the area per lipid, bilayer thickness, bond order and mass density profiles. Current work is focused on extending the model to lipid mixtures and simulating the phase separation that occurs as a bilayer composed of DPPC and 1,2-distearoyl-*sn*-glycero-3-phospho-L-serine (DPPS) changes from an initially-homogeneous state (at neutral pH) to a phase-separated state at low pH.

**Notes:**

**Soft matter assembly at surfaces and in external fields**

Orlin Velev/Jan Genzer

*US groups perspective talk – Experiment*

***Notes:***

Date	Time	Speaker	Chair
04.10.	09:00	<b>Syamal Tallury</b> Enhanced shape memory in multi-component fibers	Discher
	09:20	<b>Raphael Michel</b> Phospholipid vesicles in contact and interacting with silica nanoparticles: from decorated vesicles to internalized particles	
	09:40	<b>Amir Bahrami</b> Interaction of vesicles with spherical particles	
	10:00	<b>Heiko Schmidle</b> Phase diagram of two-dimensional system of dipole-like colloids	
	10:20	<i>coffee break</i>	
	10:35	<b>Chloé Chevigny</b> Substrate influence on the structure and properties of polyelectrolytes multilayers	Rabe
	10:55	<b>Regine von Klitzing</b> Experimental perspectives for SSNI	
	11:40	<i>lunch</i>	
	15:00	<b>Constans Weber</b> Controlled nucleation and growth at solid surfaces	Möhwald
	15:20	<b>Liangliang Huang</b> A reactive molecular dynamics simulation of hydrogen sulfide dissociation over graphene oxide	
	15:40	<b>Erich Bain</b> Instability of SI-ATRP polyelectrolyte brushes in aqueous environments	
	16:00	<b>Züleyha Yenice</b> Assembly of nanoparticles on surface-grafted thermally responsive polyelectrolyte brushes	
	16:20	<b>Casey Galvin</b> Functional surface gradients via organosilane deposition	
	16:40	<i>coffee break</i>	
	17:00	<b>Parimal Kar</b> Replica exchange molecular dynamics simulation of NK-2 peptide in implicit solvent	Findenegg
17:20	<b>Katherine Phillips</b> Solvation structure of aqueous solutions in confinement: a simulation study		
17:40	<b>Tobias Liebig</b> Over-stretching and ripping of DNA on a surface using an AFM		
18:00	<b>Melissa Pasquinelli</b> Enhanced shape memory in multi-component fibers (-18:25 h)		
19:30	<i>dinner</i>		

## **Enhanced shape memory in multi-component fibers**

Syamal S. Tallury, Dr. Richard J. Spontak and Dr. Melissa A. Pasquinelli

*Fiber and Polymer Science Program/Textile Engineering, Chemistry, and Science, North Carolina State University*

Melt spun bi-component fibers have been produced with a polyolefin sheath and triblock copolymer core. Various ratios of the two species ranging from 25% core to 75% core were spun using SEBS triblock copolymer and PE sheath. We report novel shape memory behavior of these fibers by introducing a temporary deformed shape at room temperature. Complete and spontaneous recovery of the original shape was observed on heating the deformed fibers. These fibers were subjected to a novel tensile testing procedure wherein storage modulus as a function of strain was studied. In this talk we report the tensile behavior of these fibers under quasi-static and oscillatory modes of measurement.

***Notes:***

## Phospholipid vesicles in contact and interacting with silica nanoparticles: from decorated vesicles to internalized particles

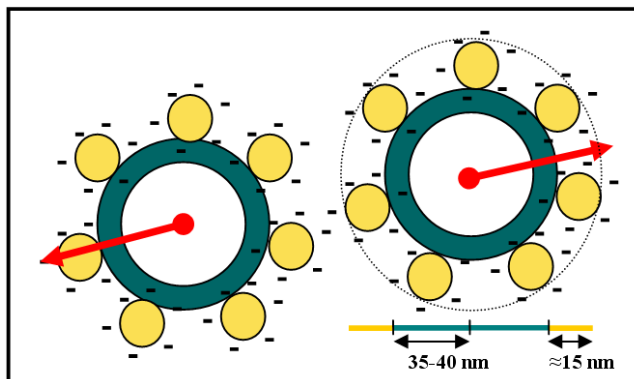
Raphael Michel

*Technische Universität Berlin, Institut für Chemie, Stranski-Laboratorium*

The interaction of bilayer vesicles with hard nanoparticles is of great relevance to the field of nanotechnology mainly because of its impact on health and safety matters, e.g. the use of drug loaded nanoparticles which then will interact with membranes for which vesicles may serve as model systems. Theories on nanoparticles/vesicles interactions predict several different scenarios, with in particular the encapsulation of the nanoparticles inside the vesicles or within the phospholipid membrane [1,2,3,4].

The phospholipids employed are DPPC and DOPC which provide a good model for regions of biomembrane where charge neutrality exists and furthermore are respectively below and above the chain melting temperature at room temperature. Unilamellar vesicles are prepared by extrusion of aqueous phospholipid dispersions. The final radius of the vesicles is around 40 nm. A commercial colloidal suspension of negatively charged silica nanoparticle in water is used with particle size around 15 nm (diameter).

Recently, we have studied systems containing different concentrations of phospholipid vesicles and silica nanoparticles by means of Dynamic Light Scattering, Zeta Potential Measurements, Cryogenic Transmission Electron Microscopy and Small Angle Neutron Scattering. These investigations resulted in the observation of a synergistic effect of silica nanoparticles and phospholipid vesicles involving the appearance of charges on the vesicle surface. In fact, once in solution, the silica particles appear to adsorb quickly on the vesicles surface leading to the formation of decorated vesicle structures (Fig. 1).



Once stored above the chain melting temperature, these structures evolve: the bilayer spreads on the nanoparticle surface leading to the internalization and encapsulation of the particle within the vesicle.

On the contrary, once cooled down below the chain melting temperature, these structures remain the same and stabilize the whole system through the repulsive interaction introduced by the adsorbed nanoparticles (Fig.1).

These results are not only of importance with respect to the fundamental interaction between vesicles and nanoparticles (as it is for instance of key importance with respect to health aspects) but also with respect to using silica particles as formulation aids for phospholipid dispersions.

[1] Noguchi, H., Takasu, M., *Biophysical Journal* 83 (2002)

[2] Ginzburg, V.V., Balijepalli, S., *Nano Lett.*, Vol. 7, No. 12 (2007)

[3] Tieleman, D.P., Marrink, S.J., Berendsen, H.J.C., *Biochim. et Biophys. Acta* 1331 (1997)

[4] Lipowsky R., Döbereiner, H.G., *Europhysics Letter*, (1998)

**Notes:**

## Interaction of vesicles with spherical particles

Amir Bahrami

*Max Planck Institute of Colloids and Interfaces, Potsdam*

We study the interactions of vesicle membranes with spherical rigid particles, which represent rigid protein molecules and colloids. Adhesion of a particle modifies the shape and physical behavior of the host vesicle. We use simulations to study the wrapping transition of the particle and its effect on the vesicle shape. When several particles adhere to a vesicle, they affect the wrapping degree and adhesion area of each other. We study the effect of more than one particle on the vesicle shape and try to understand the interactions induced by the vesicle membrane between adhered particles.

***Notes:***

## Phase diagram of two-dimensional system of dipole-like colloids.

Heiko Schmidle

*Technische Universität Berlin, Institut für Theoretische Physik*

Based on Discontinuous Molecular Dynamics (DMD) simulations we present a phase diagram of two-dimensional nano-particles with dipole-like short-ranged interactions. Similar to systems with true, long-ranged dipolar interactions the present system undergoes a transition from an isotropic fluid phase into a polymer-like fluid, characterized by an association of most particles into clusters. Further decrease of the temperature leads to a percolated system, which, moreover, displays dynamical properties reminiscent of a gel. Specifically, we find a plateau in the mean-squared displacement and a non-gaussian behavior of the self-part of the van-Hove correlation function. In the high-density region we observe crystallization from the isotropic fluid into a solid phase with hexagonal order. Surprisingly, the crystallization is accompanied by a global parallel ordering of the dipole moments, i.e., a ferroelectric phase. This behavior is in marked contrast to what is found in 2D systems with long-ranged dipolar interactions.

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## Substrate influence on the structure and properties of polyelectrolytes multilayers

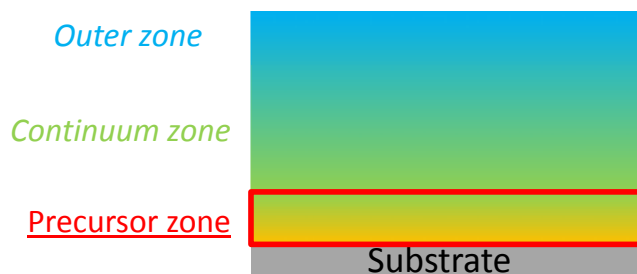
Chloé Chevigny

*Technische Universität Berlin, Institut für Chemie, Stranski-Laboratorium*

Polyelectrolytes Multilayers (PEM), made by the Layer-by-Layer (LbL) deposition technique, are a very versatile and interesting tool for many technical applications. Since their development 20 years ago, there has been an exponential increase of works in this topic, allowing a better comprehension of their structures and properties, and resulting in many applications such as sensor coatings or drug delivery systems. However, in order to better understand the functionalities of these systems and find new applications, fundamental studies are always needed.

We focus on the properties profile across the film and on the effect of the solid substrate: over which length scale the substrate affects the film properties, and from which distance does the film reach bulk properties? For this project several surfaces types are studied: silicon and gold (resp. negatively and positively charged), with or without a first protective layer of PolyEthyleneImine PEI. The structure, as well as the water-swelling properties of the multilayers in the substrate-influence zone, are determined via a combination of ellipsometry, X-rays and neutron reflectivity. The substrate is found to have an important influence. First on internal structure: the thickness of the layers close to substrate, and the interdigitation between them, were determined and proven to be different from the bulk structure. The density of the packing (loosely or densely packed layers) is also inhomogeneous. Secondly on specific properties of this area of the multilayers: water swelling capacity is dramatically changed near the substrate.

Lately, specific counter anions effects were also investigated as a function of distance from substrate.



*The “3-zones-model” for polyelectrolyte multilayers [1]: in addition to a continuous zone at the center where properties are kept constant, exist an “outer zone” influenced by external medium and a “precursor zone” influenced by the substrate. We focus on the latter one.*

[1] G. Ladam, P. Schaad, J.C. Voegel, P. Schaaf, G. Decher, F. Cuisinier, Langmuir 2000, 16, 1249-55 .

**Notes:**

## **Experimental perspectives for SSNI**

Regine von Klitzing

*Technische Universität Berlin, Institut für Chemie, Stranski-Laboratorium*

***Notes:***

## Controlled nucleation and growth at solid surfaces

Constans Weber

*Max Planck Institute of Colloids and Interfaces, Potsdam*

Classical nucleation theory distinguishes between heterogeneous and homogeneous nucleation that occur depending on the conditions. Whereas homogeneous nucleation occurs in the bulk phase heterogeneous nucleation takes place at an interface. Even though the influence of geometrical modifications at solid surfaces on heterogeneous nucleation was theoretically discussed studies up to now only addressed global properties (e.g. roughness) but did not focus on the actual nucleation site. Hence this is investigated exemplarily for C60 aggregates on SiO<sub>2</sub>. This system is broadly studied and well understood [1, 2]. In order to use spin-coating as an easy adjustable and reproducible deposition technique, we carefully investigated the evaporation process and modeled the developing concentration profiles. Figure 1a shows the obtained concentration profiles during spin-coating. The results allow for deliberately choosing in a precisely controlled way the position of the nucleation in the evaporating film [3] and to include only particles stemming from the SiO<sub>2</sub> interface. Atomic force microscopy is used for both, surface modification on a nanometer scale and investigation. Figure 1b shows AFM images of a nano-structured SiO<sub>2</sub> wafer before and after spin-coating deposition of C60.

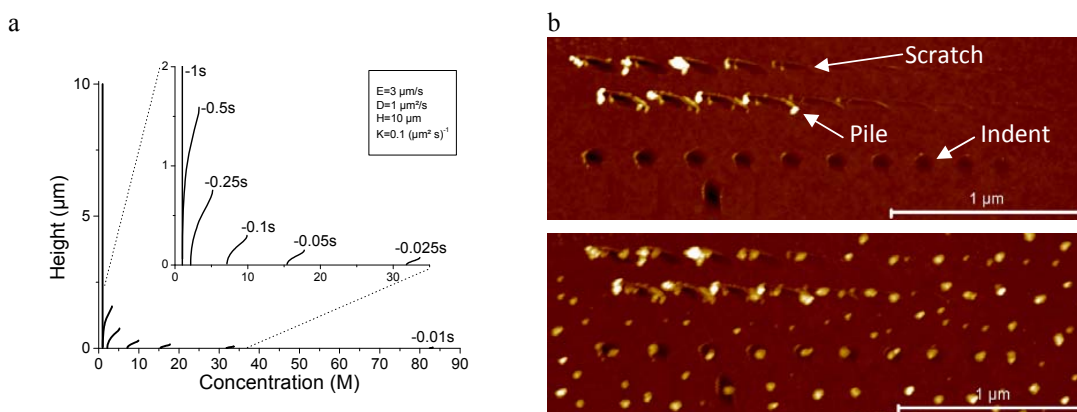


Figure 1 (a) Concentration profiles in film during spin coating and (b) AFM images showing nanometer structured SiO<sub>2</sub> surface before and after spin-coating deposition of C60.

- 1 „Impact of Negative Line Tension on the Shape of Nanometer-Size Sessile Droplets”, John Berg, Constans Weber and Hans Riegler – PRL 105, 076103 (2010)
- 2 “Line tension of nanometer size sessile droplets of fullerenes on various planar surfaces” Constans Weber, John Berga and Hans Riegler – manuscript in preparation
- 3 “Spatio-temporal concentration distribution of nonvolatile solutes within films of volatile solvents during spin coating”, Constans Weber, Andreas Vetter, John Berg and Hans Riegler , to be submitted

**Notes:**

## **A Reactive Molecular Dynamics Simulation of Hydrogen Sulfide Dissociation Over Graphene Oxide**

Liangliang Huang

*NC State University, Department of Chemical and Biomolecular Engineering*

Graphene oxide (GO) is attracting remarkable interest because it exhibits exceptional electrochemical, mechanical and optoelectronic properties, which makes it promising in batteries, field-effect transistors, nanocomposites and biomedical applications. Despite previous efforts, the catalytic potentials of GO have not been extensively explored yet. In this work we generate realistic GO structures from an annealing process and represent reactive molecular dynamics (RxMD) simulations of hydrogen sulfide dissociation over graphene oxide structures. The GO structures used in the calculations have functional groups of carboxyl, carbonyl, epoxy and hydroxyl, and defects of vacancy and large carbon-oxygen rings. We study hydrogen dissociation under different GO functional group concentrations, and compare the competitive adsorption and dissociation behaviours of hydrogen sulfide and water on GO structures.

***Notes:***

## Instability of SI-ATRP polyelectrolyte brushes in aqueous environments

Erich Bain<sup>1</sup>, Casey Galvin<sup>1</sup>, Ali E. Özçam<sup>1</sup>, Adam Henke<sup>2</sup>, Jiri Srogl<sup>2</sup>, Jan Genzer<sup>1</sup>

<sup>1</sup>*Department of Chemical & Biomolecular Engineering, NC State University*

<sup>2</sup>*Institute of Organic Chemistry & Biochemistry, Prague, Czech Republic*

Polymers grafted at interfaces are becoming increasingly attractive for a growing number of applications. These include biologically active materials featuring proteins functionalized at the surface for microarrays, antifouling layers on the surfaces of marine craft, and patterned responsive surfaces that react reversibly to external stimuli, *i.e.*, temperature, pH, solvent, or light. In order to create a densely packed film, in which the end-tethered macromolecules are forced into a stretched conformation, the “grafting from” approach is necessary. This method involves first functionalizing a surface with a layer of initiating moieties, then introducing the substrate into a monomer solution suitable for surface-initiated polymerization. “Grafting from” polymerization has enjoyed tremendous popularity in the literature in recent decades, being used routinely for such polymerization mechanisms as atom transfer radical polymerization (ATRP), reversible addition fragmentation transfer (RAFT), and free-radical polymerization (FRP). A sizeable majority of the initiators used for these surface-grafted polymerizations contain ester groups in the structure that links the initiator to the surface. Esters are known to undergo hydrolysis under acidic and basic conditions. While having a cleavable link between polymer brushes and the substrate is desirable in cases where researchers want to remove the chains for analysis, many practical applications require robust bonding to the surface and in these cases ester-based initiators are not ideal. In particular many hydrophilic or electrolytic polymer brushes are used in aqueous environments far from neutral pH, conditions for which ester-based initiators cannot be expected to deliver long-term stability. In this work we demonstrate the stability, in aqueous environments with varying pH, of polyelectrolyte brushes grafted via ester and amide containing initiators, as well as brushes grafted via an initiator containing only carbon-carbon bonds in the linking chain.

### **Notes:**

## **Assembly of nanoparticles on surface-grafted thermally responsive polyelectrolyte brushes**

Züleyha Yenice

*Stranski-Laboratorium, Institut für Chemie, Technische Universität Berlin*

The self-assembly of nanoparticles was carried out on PDMAEMA brushes with a gradient in quaternization. PDMAEMA brushes are weak polyelectrolytes and their properties are pH dependent. The brushes were converted to strong polyelectrolytes via quaternization using iodomethane. XPS analysis confirms the charge gradient along the brush. Different sizes of nanoparticles were used to see the particle interpenetration into the polyelectrolyte brushes. AFM and Ellipsometry were used to determine the distribution of particles along the gradient. The number of particles in the polymer brush/particle hybrid can be controlled by tuning the degree of quaternization.

***Notes:***

## Functional gradients via organosilane vapor deposition

Casey Galvin<sup>1</sup>, Xiaotang Du<sup>1,2</sup>, Jan Genzer<sup>1</sup>

<sup>1</sup>*Department of Chemical & Biomolecular Engineering, NC State University*

<sup>2</sup>*Zhejiang University, Hangzhou, PRC*

We have developed a versatile, facile, low-cost procedure that introduces functional groups onto solid surfaces by depositing organosilane (OS) molecules from the vapor phase. Briefly, this approach takes advantage of vapor phase diffusion of OS molecules from a reservoir to create a concentration gradient, which translates to a functional gradient on the substrate surface. This process requires no special equipment, can be carried out under ambient conditions and takes. We have produced successfully homogeneous and gradient surfaces with vinyl, primary and tertiary amine, halogen and methyl functional groups using trichlorosilanes and alkoxy silanes. We will demonstrate the versatility of these functional groups by using post-deposition modification reactions to incorporate fluorinated, zwitterionic and azide species onto surfaces.

### **Notes:**

## **Replica exchange molecular dynamics simulation of NK-2 peptide in implicit solvent**

Parimal Kar

*Max Planck Institute of Colloids and Interfaces, Potsdam*

Antimicrobial peptides are part of the innate immune defense and believed to act against invading bacteria pathogens by interacting with the bacterial membrane where they may induce pores. Understanding the antimicrobial action of these peptides requires to comprehend their membrane affinity and the effect of the membrane on the conformation of the peptides. In order to address these questions, the NK-2 peptide is studied in the solvated state using an implicit model for the solvent, together with enhanced sampling techniques such as replica exchange to overcome the notorious sampling problem associated MD simulation.

***Notes:***



## **Solvation structure of aqueous solutions in confinement: a simulation study**

Katherine A. Phillips, Jeremy C. Palmer, Keith E. Gubbins

*NC State University, Department of Chemical and Biomolecular Engineering*

Using molecular dynamics (MD) simulations, we studied the impact of confinement on the solvation of rubidium and bromide ions in aqueous solutions confined in slit-shaped pores ranging from 0.65 to 1.6 nm in size, which encompasses the range typically found in carbide derived carbons and other nanoporous electrochemical supercapacitor materials. We investigated solutions of these ions at 0.1 M, 0.5 M and 1.0 M concentrations. We determined the average number of water molecules solvating each of the ions and the structure of the solvation shell which is characterized by the ion-water radial distribution function. The effect on confinement on the dynamics was also investigated by calculating the self-diffusion coefficients of the ions. We also examined the impact of pore morphology on the hydration structure by studying the solvation of ions in an amorphous carbon structure (via Monte Carlo simulations) to determine the propensity of ions to reside in pores of specific sizes. We found a dramatic drop in the solvation number occurs when pore size was decreased below 1 nm for slit-shaped pores, while more complex geometries see only a steady decrease in solvation number as pore size decreases. Our results indicate that although materials with smaller pores have significantly increased capacitances, the diffusion of ions is hindered by the confinement, which is potentially detrimental to enhancing the power density of electrochemical supercapacitors.

**Notes:**

## Over-stretching and ripping of DNA on a surface using an AFM

Tobias Liebig

*Humboldt-Universität zu Berlin, Institut für Physik*

In order to determine the mechanical properties of DNA the standard approach is horizontal pulling experiments. Thus giving no direct information about the amount of strands involved or the angle under which the pulling takes place.

We show a novel type of pulling experiment. By fixing the ends of DNA on a surface an SFM tip can not only be used for horizontal pulling but also for imaging. It is therefore possible to pull under very defined conditions. Furthermore this setup can be used to determine the mechanical properties of a broad variety of different molecules.

***Notes:***

## **Investigation of the Properties of Polymeric Materials via Multiscale Simulations from the Nanoscale**

Melissa A. Pasquinelli

*Fiber and Polymer Science Program/Textile Engineering, Chemistry, and Science, North Carolina  
State University*

Understanding the behavior of polymer molecules, especially in confined conditions, is crucial to engineer materials with enhanced characteristics, such as mechanical strength, antimicrobial effects, or electrical conductivity. Molecular dynamics (MD) and dissipative particle dynamics (DPD) simulations provide a useful means for exploring thermodynamic details of these systems at the nanoscale, and visual-analytic tools aid in the analysis of the data. These simulation and analysis tools provide predictive capabilities that streamline the engineering design process and give insight into nanoscale systems that are challenging to characterize experimentally. We will discuss the development and use of these computational tools to investigate the characteristics of multi-component polymer fibers as well as polymers interacting with carbon nanoparticles.

***Notes:***

Date	Time	Speaker	Chair
05.10.	09:00	<b>Gal Schkolnik</b> Linking dehaloperoxidase kinetics and surface electric field using the vibrational Stark effect	Thompson
	09:20	<b>Ashlee Plummer</b> Enzyme design to convert an inhibitor into a substrate	
	09:40	<b>Jennifer Rowe</b> Electrostatic control of substrate binding in dehaloperoxidase	
	10:00	<b>Philipp Kählitz</b> Phase diagram of hard needles on a quasicrystalline substrate	
	10:20	<i>coffee break</i>	
	10:35	<b>Yun Long</b> High pressure effects in nanoporous materials	Klapp
	10:55	<b>Kyle Spinler</b> Calcium induced domain dynamics within polyanionic vesicles subject to external chemical stimuli	
	11:15	<b>Elena Blanco</b> Making patchy and core-shell zein-coated particles for pickering stabilization	
	11:35	<b>Stephanie Lam</b> Formulation and characterization of a novel class of magnetically responsive pickering foam	
	11:55	<i>lunch</i>	
	15:00	<b>Bhuvnesh Bharti</b> Random and field-directed binary supracolloidal assembly	Franzen
	15:20	<b>Mengjun Xue</b> Protein assembly in cylindrical nanopores	
	15:40	<b>Salome Pataraia</b> Purification of DC-SIGN	
	16:00	<b>Tobias Pobandt</b> Alzheimer's disease: the amyloid beta peptide and pore formation in phospholipid bilayers	
16:20	<b>David Latshaw</b> The simulation of amyloid $\beta$ in the presence of aggregation-inhibiting compounds		
16:40	<i>coffee break</i>		
17:00	<b>Gerald Rosenthal</b> Structure formation of amphiphilic Janus particles	Gubbins	
17:20	<b>Michael Melle</b> Self-assembled nematic surface-domains on Janus colloids		
17:40	<b>Jhuma Das</b> Restructuring of hydrophobic surfaces created by surfactant adsorption to negatively charged surfaces: all atom and coarse grain simulations (-18:00h)		
18:00	<b>Xiaojing Cai (-18:20h)</b> <i>Polymer Laminates interfacial modification by microgel particles &amp; block copolymers</i>		
19:30	<i>dinner</i>		

## Linking dehaloperoxidase kinetics and surface electric field using the vibrational Stark effect

Gal Schkolnik<sup>1</sup>, Junjie Zhao<sup>2</sup>, Ingo Zebger<sup>1</sup>, Diego Millo<sup>1</sup>, Peter Hildebrandt, Stefan Franzen<sup>2</sup>

<sup>1</sup> *Max-Volmer-Laboratorium, Institut für Chemie, Technische Universität Berlin*

<sup>2</sup> *North Carolina State University, Department of Chemistry*

Dehaloperoxidase-hemoglobin (DHP) is a double function protein in the marine organism *Amphitrite ornate*. It is used for oxygen storage and delivery as a globin, but also acts as a peroxidase for the oxidation of 2,4,6-tribromophenol, a marine toxin released by competing species, to the less toxic 2,4-dibromoquinone. Its peroxidase function, which depends on hydrogen peroxide activation by His55 in its closed position, has been found to be allosterically inhibited by 4-bromophenol, which enters the distal pocket and forces His55 to a peroxidase-inactive open position.<sup>1</sup> The substrate, which is deprotonated and therefore negatively charged under marine as well as physiological pH conditions, binds to DHP at an unknown site, by an unknown mechanism. An external substrate-binding site, remote from the heme pocket, has been suggested.<sup>2</sup> To shed some light on the substrate binding mechanism, single charge mutations have been created and their kinetics assayed. 4-mercaptobenzonitrile, a vibrational Stark probe attached to the enzyme's single surface cysteine, was used to determine whether changes to mutant kinetics could be attributed to changes in the protein's surface electric field.

1. Thompson, M. K., Franzen, S., Ghiladi, R.A., Reeder, B.J. and Svistunenko, D.A., **2010**, Compound ES of Dehaloperoxidase Decays via Two Alternative Pathways Depending on the Conformation of the Distal Histidine, *JACS* 132 (49): 17501-17510

2. Davis, M. F., B. G. Bobay, and S. Franzen, **2010**, Determination of Separate Inhibitor and Substrate Binding Sites in the Dehaloperoxidase-Hemoglobin from *Amphitrite ornata*. *Biochemistry* 49:1199-1206

### **Notes:**

## Enzyme design to convert an inhibitor into a substrate

Ashlee Plummer

*North Carolina State University, Department of Chemistry*

This talk will describe how an enzyme inhibitor that binds in the interior of the protein can become a substrate if it is excluded from binding in the internal site. The nature of protein cavities inside dehaloperoxidase-hemoglobin are discussed from with the aid of X-ray crystal structures and resonance Raman spectroscopy as complementary techniques. Starting with a functional description of the dual function protein crystal structures of a series of inhibitors including 4-iodo-, 4-bromo-, 4-chloro- and 4-fluorophenol have been characterized structurally and thermodynamically to reveal that existence of a specific internal protein cavity that stabilizes large halogens in the para position of the phenol ring. High-pressure Xenon X-ray structures confirm that this cavity exists. The attempts to exclude the inhibitor can be divided into two classes. Steric inhibitors that increase the bulk amino acids in the distal pocket where the inhibitor binds have been studied by means of the mutations F21V, F21Q, F21L, F24Q, :100Q and V59W. None of these mutants excluded the inhibitor. This remarkable finding strong suggests that the distal pocket is particularly well adapted for inhibitor binding. On the other hand, mutants that enlarge the pocket where the para halogen binds were made using L100T. This mutant has least inhibition of any mutant. In fact, one could say that this specific protein engineering changes the inhibitor into a substrate.

**Notes:**

## Electrostatic control of substrate binding in dehaloperoxidase

Jennifer Rowe

*North Carolina State University, Department of Chemistry*

The external substrate-binding site of the dual function protein dehaloperoxidase-hemoglobin (DHP) has been established based on functional studies and nuclear magnetic resonance (NMR). However, the substrate-binding site has not been identified despite the fact that numerous X-ray structures have been obtained with substrate soaked into the crystal. While the inhibitor 4-bromophenol easily enters crystals and occupies a pocket inside the protein, the structurally similar substrate 2,4,6-tribromophenol has not been observed in any of the X-ray crystal structures studied thus far. In order to understand the determinants of substrate binding electrostatic mutants K51A, K58A, K36A, R33Q, K87A, N61D, and a number of others have been created in order to study the local effect of altered charge on substrate binding. The surprising result is that all of these mutants that reduce the charge of the protein by approximately 1 unit give rise to a slowing of the overall rate of catalysis. The differences are sufficiently small that one cannot suggest a local effect based on these mutants. Studies of the ionic strength show that the binding is electrostatic in nature. The studies suggest that electrostatics play a central role substrate binding in enzymes. While DHP is one example, our results suggest that this is a general phenomenon.

**Notes:**

## Phase diagram of hard needles on a quasicrystalline substrate

Philipp Kählitz

*Technische Universität Berlin, Institut für Theoretische Physik*

Quasicrystals are structures with long-range positional and orientational order. However, they cannot be periodic since they possess rotational symmetries such as 5- or 10-fold axis that are forbidden for conventional crystals. In this presentation the phase diagram of hard needles with two different length scales on a decagonal substrate is shown.

***Notes:***



## High pressure effects in nanoporous materials

Yun Long<sup>+</sup>, Jeremy Palmer<sup>+</sup>, Benoit Coasne<sup>#</sup>, Małgorzata Śliwinska-Bartkowiak<sup>‡</sup> and Keith E. Gubbins<sup>+</sup>

<sup>+</sup> *NC State University, Department of Chemical and Biomolecular Engineering*

<sup>#</sup> *Université de Montpellier 2, Institut Charles Gerhardt Montpellier, France*

<sup>‡</sup> *Adam Mickiewicz University, Institute of Physics, Poland*

There is an abundance of anecdotal evidence that nanophases adsorbed within nanoporous materials exhibit high pressures as a result of the confinement. For example, phase changes and chemical reactions that only occur at high pressures in the bulk phase occur in the confined phase at bulk phase pressures that are orders of magnitude lower.<sup>1</sup> The structure of confined ice has been studied in carbon nanotubes using molecular simulation<sup>2</sup> and experiment,<sup>3</sup> and provides convincing evidence for the formation of different kinds of ice nanocrystals, including ice VIII and ice IX, phases that only occur at pressures of GPa and above in bulk water. Examples of chemical reactions that occur at low bulk pressures in nano-pores, but only at very high pressures in the bulk phase, have also been frequently observed in experiments<sup>4</sup> and molecular simulations<sup>5</sup>.

Our previous simulation studies of the pressure tensor in slit pores (pore widths from 2 to 8 molecular diameters) found that the tangential pressure can be locally very high, tens of thousands of bars, in the pore, even though the bulk phase in equilibrium with the pore is at pressures of one bar or less. Moreover, the in-pore tangential pressure is very sensitive to small changes in the bulk pressure, indicating a way to experimentally control the in-pore pressure. These very high in-pore pressures result from the strong interaction with the pore walls, which compress the confined nanophase. This leads to strong repulsive intermolecular forces in the tangential direction and large positive tangential pressures. In contrast to the simple slit-pore model, real porous materials, such as activated carbons, have highly complex structural and energetic topologies that strongly influence the behavior of confined phases. We examine the impact of these features on the in-pore pressure tensor using modified versions of the slit-pore model that include structural and energetic surface heterogeneities. We also calculate the pressure tensor in the absence of attractive solid-fluid interactions. The results indicate that the high tangential pressure arises from the strong repulsive interaction between compressed fluid molecules due to the geometric confinement of the wall, while the attractive force from the wall determines the degree of compression of the fluid molecules, and thus determines the pressure enhancement factor. Adsorption studies in a silica slit pore also indicate that the atomically detailed geometry of the wall surface has a large effect on the arrangement of in-pore fluid molecules and the pressure tensor.

**Notes:**

## Calcium induced domain dynamics within polyanionic vesicles subject to external chemical stimuli

Kyle Spinler

*Department of Chemical and Biomolecular Engineering, University of Pennsylvania*

Chemically triggered dynamics of domains within vesicular membranes is of broad relevance to biomembrane signaling processes and to possible application of phase separated vesicles. Here, we studied domain morphology and mixing kinetics upon external chemical stimuli in phase separated polymer vesicles based on calcium cross bridging of polyanionic amphiphiles. The calcium chelator EDTA was added to vesicle dispersions, and domain area shrinking was observed within minutes. The domain remixing phenomenon upon EDTA addition confirms that phase separation is due to calcium cross bridging. In addition, viscous fingering patterns and decreased domain area fraction, which indicated partially domain mixing, can be observed after increasing pH by incubating vesicles with NaOH for a period of hours. Therefore, the charge of the polyanion also controls domain formation and, surprisingly, chains that are made more negatively charged by increasing pH also tend to remix. Domain roughening, a phenomenon subject to NaOH perturbation, can be accelerated by adding additional EDTA. The kinetics of domain mixing proves to be much faster with EDTA addition (minutes to hours) than with NaOH incubation alone (hours to days), which highlights the importance of calcium cross bridging to phase separation within polyanionic vesicles. In addition, the inner and outer leaflets exhibited coupled dissolution dynamics during the leaflet asymmetric chemical stimuli. This phenomenon was observed experimentally and confirmed by coarse grain molecular dynamic simulation. Domain dynamics in spotted polymer vesicles induced by chemical stimuli improves the understanding of interactions of polyanionic vesicles and ions and suggests applications in targeted delivery.

**Notes:**

## **Making patchy and core-shell zein-coated particles for Pickering stabilization**

Elena Blanco, Stoyan K. Smoukov, and Orlin D. Velev

*NC State University, Department of Chemical and Biomolecular Engineering*

Complex colloids with chemically heterogeneous surface properties have attracted intensive attention in the soft matter field. Controlling the surface patterning of particles is both a fundamental challenge and has important practical applications, such as stabilization of foams and emulsions. We have used the heterogeneous nucleation method for the decoration of the surface of hydrophilic particles with a hydrophobic protein to achieve patchy protein coverage over the entire particle surface. In our experiments we specifically used zein protein to coat silica particles. The formation of patchy particles was visualized by TEM images. We investigated the ability of these patchy colloids to adhere to liquid-liquid or liquid-air interfaces and serve as Pickering stabilizers. We have founded large differences in the interfacial activity between spherical particles and patchy particles and this behavior was described in terms of particle wettability. The anisotropic patterned morphologies also present new fundamental questions in wettability and adsorption of particles to an interface. The amount and orientation of zein adsorbed on the silica can be controlled and used to tune the lyophilicity of these particles.

***Notes:***

## Formulation and characterization of a novel class of magnetically responsive pickering foam

Stephanie Lam<sup>‡</sup>, Elena Blanco<sup>‡</sup>, Stoyan K. Smoukov<sup>‡</sup>, Krassimir P. Velikov<sup>†</sup>, Orlin D. Velev<sup>‡</sup>

<sup>‡</sup>*Department of Chemical & Biomolecular Engineering, North Carolina State University*

<sup>†</sup>*Soft Condensed Matter, Debye Institute for Nanomaterials, Utrecht University, The Netherlands*

Soft materials which respond to external stimuli are on the leading edge of materials research. Foam and emulsion systems that can be controlled using UV light, temperature, and magnetic fields have been the focus of study of many researchers. However, magnetically responsive Pickering foams which remain stable until exposure to a gradient field have not been reported until the work presented here. The system at focus is stabilized by hydrophobically modified cellulose with magnetic responsiveness imparted through the entrapment of carbonyl iron particles in the cellulose matrix. We have shown that this system is able to remain stable for more than one week prior to exposure to a magnetic field and have evaluated the change in water fraction, collapse behavior, and foam viscoelastic properties with age. Through these studies we found the evolution of our foams to occur on a much longer time scale than surfactant stabilized foams, as would be expected. However, we also found the response of the foam to a magnetic field to be highly dependent upon the fraction of liquid in the foam films. We devised two separate mechanisms of collapse, one for wet foams and one for dry foams. We then correlated the collapse behavior to the viscoelastic properties and magnetic susceptibility of the foam, both of which are dependent on the volume fraction of liquid in the foam films. Systems such as the one presented here can find application in a range of industrial and environmental settings that require controlled defoaming.

**Notes:**

## Random and field-directed biparticle supracolloidal assembly

Bhuvnesh Bharti<sup>€</sup>, Jens Meissner<sup>€</sup>, Orlin D. Velev<sup>§</sup> and Gerhard H. Findenegg<sup>€</sup>

<sup>€</sup>*Technische Universität Berlin, Institut für Chemie, Stranski Laboratorium*

<sup>§</sup>*Department of Biomolecular and Chemical Engineering, North Carolina State University*

Interactions between oppositely charged particles play an important role in many fields of colloid and interface science. Depending on the size and size ratio of the particles involved this can give rise to phenomena like adsorption, aggregation and gelation. In this project we are studying hetero-aggregation phenomena of oppositely charged spherical (or quasi-spherical) particles at two grossly different size scales, viz., the assembly of silica nanoparticles with globular proteins (work at TUB); and assembly of micrometer-sized charged particles in an AC electric field (work at NCSU).

AC-dielectrophoresis and chaining of micrometer-sized particles: A novel approach for the formation of permanent chain structures of latex microparticles using AC-Dielectrophoresis (DEP) was developed. We studied and characterized the permanent chain structures as the function of (a) difference in the size of two kinds of particles (positive and negative), and (b) the number ratio of small and large particles. The experimental observations and complementary statistical simulations lead to assembly rules for such structures which rely on (a) and (b).

Protein-induced aggregation of silica nanoparticles: Silica nanoparticles of 20nm diameter show the formation of pH responsive hetero-aggregates with globular protein lysozyme (size ~ 4nm). Structural properties of the aggregates were studied as a function of pH at a fixed protein-to-silica concentration ratio which corresponds to a surface concentration of protein well below a complete monolayer in the complete-binding regime at pH > 6. The structure of the bridged silica aggregates was studied by sedimentation kinetics, cryo-TEM and small-angle X-ray scattering.<sup>1</sup>

<sup>1</sup> Bharti, Meissner, Findenegg, Langmuir 2011, 27, 9823.

**Notes:**

## Protein assembly in cylindrical nanopores

Mengjun Xue and Gerhard H. Findenegg

*Stranski-Laboratorium, Institut für Chemie, Technische Universität Berlin*

Ordered mesoporous silica materials have textual and structural features that make them suitable hosts for bioactive molecules. Such materials are synthesized by using surfactants or amphiphilic block copolymers as structure-directing templates. In the case of MCM-41 the pore size of the cylindrical pores can be tailored by using surfactants of appropriate chain length. In addition, the pore walls can be chemically modified in order to adjust the strength of interaction with the guest molecules. We are studying the adsorption of globular proteins (lysozyme and cytochrome c) in the pores of native and chemically modified MCM-41 and SBA-15 silica materials. It will be shown that the uptake of protein depends strongly both on the pore diameter and pH.

We have found that lysozyme can effectively block the pores of MCM-41 for smaller guest molecules (rhodamine B) at low pH, while allowing release of these molecules at higher pH. Tentatively, this is attributed to a pH dependence of the effective size of the protein molecule. Preliminary experiments show that this principle may be used for preparing mesoporous silica-based drug carrier systems with lysozyme caps for pH-responsive controlled release.

To characterize the distribution of guest molecules in the pore space of MCM-41 and SBA-15 we study the Förster resonance energy transfer (FRET) between donor and acceptor molecules, using fluorescence lifetime imaging microscopy (FLIM). Some results of these studies will be presented in the last part of this talk.

**Notes:**

## Purification of DC-SIGN

Salome Patariaia

*Max Planck Institute of Colloids and Interfaces, Potsdam*

Dendritic cells (DCs) are initiators and modulators of the immune response. While mature DCs prime T cells to complete the immune response process, immature DCs capture antigens to form major histocompatibility peptide complexes (MHCs). The immature DCs express the C-type lectin DC-SIGN (CD209) receptor, which functions as an antigen capture and cell adhesion molecule. DC-SIGN molecules form discrete nanoscale domains and are thought to play an important role in viral, bacterial and yeast binding. Therefore understanding the function and dynamics of DC-SIGN domains is of a high importance. As the biochemical composition of DC-SIGN domains is heterogeneous but not at present well-defined, we purified DC-SIGN and determined that no other molecules are co-purified through binding to DC-SIGN. To do so, we used an affinity chromatography method with DC- SIGN specific antibodies. The procedure developed for isolating DC-SIGN also enables future measurements in which the mechanism through which DC-SIGN forms clusters can be investigated in reconstitution studies.

**Notes:**

## **Alzheimer's disease: the amyloid beta peptide and pore formation in phospholipid bilayers**

Tobias Pobandt

*Max Planck Institute of Colloids and Interfaces, Potsdam*

A hallmark of the Alzheimer disease is the 39-42 amino acids long amyloid- $\beta$  peptide ( $A\beta$ ) being a cleavage product of the integral membrane amyloid precursor protein (APP). Especially small soluble oligomers of only a few peptides are known to be very neurotoxic. One possible reason for their toxicity is their ability to induce pores and ion channels in membranes. In intracellular membranes this causes the loss of calcium homeostasis and therefore cell death. To understand in more detail how and if  $A\beta_{42}$  monomers facilitate pore formation we compute free energy landscapes of nanopores using the umbrella sampling simulation method. Therefore we examine  $A\beta_{42}$  monomers attached to DPPC bilayers as well as the corresponding peptide free system. Our results suggest that  $A\beta_{42}$  monomers stabilize nanopores.

***Notes:***



## The Simulation of amyloid $\beta$ in the Presence of Aggregation-Inhibiting Compounds

David Latshaw II

*NC State University, Department of Chemical and Biomolecular Engineering*

Amyloid fibrils are found in over 40 human disorders including Alzheimer's, Parkinson's, and the prion diseases. In Alzheimer's Disease (AD), the amyloid  $\beta$  ( $A\beta$ ) peptide aggregates and forms oligomer and fibril structures in the brain causing a decline in thought processes and memory, ultimately resulting in dementia and death. The goal of the proposed work is to simulate the aggregation of  $A\beta$ , as well as the interaction of crowding molecules/inhibitors with aggregates.

Discontinuous molecular dynamics simulations will be applied to an intermediate resolution protein model based on the PRIME20 forcefield in order to explore the aggregation of  $A\beta$  peptides. A major activity will be the further development and refinement of the PRIME20 forcefield to enable a more faithful representation of protein geometry and energetics. The simulations will focus on oligomeric intermediates, fibrillar structures, kinetic pathways, macromolecular crowding, and inhibitor interactions with  $A\beta$ . The hope is that the simulations will provide information about: (1) aggregation processes that lead to the generation of toxic species, and (2) interactions with potential inhibitors that could eventually be used as drugs to combat AD.

The proposed research should advance knowledge on the aggregation not only of  $A\beta$  but also of other disease-related proteins.

**Notes:**

## Structure formation of amphiphilic Janus particles

Gerald Rosenthal

*Technische Universität Berlin, Institut für Theoretische Physik*

We apply a molecular dynamics simulation to investigate the aggregation of amphiphilic Janus-like particles in the volume system. These particles are modeled as (soft) spheres composed of a hydrophilic and hydrophobic part. Their orientation is described as a vector representing an internal degree of freedom. The solvent is treated implicitly, by applying an effective repulsion between hydrophilic sides. We determine the aggregation line and further focus on microscopic structure, cluster distributions and translational dynamics.

**Notes:**

## Self-assembled nematic surface-domains on Janus colloids

Michael Melle

*Stranski-Laboratorium, Institut für Chemie, Technische Universität Berlin*

Employing a simple model, we reproduce well-known defects induced by homogeneous colloids in nematic host with Monte Carlo simulations. Also, we simulate a new class of inhomogeneous particles, Janus particles, and find new defect structures. We have evidence that increasing the nematic strength can induce transitions between different defects.

***Notes:***

## Restructuring of Hydrophobic Surfaces Created by Surfactant Adsorption to Negatively Charged Surfaces: All Atom and Coarse Grain Simulations

Jhuma Das<sup>1</sup>, Changsun Eun<sup>1</sup>, Susan Perkin<sup>2</sup>, Max L. Berkowitz<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of North–Chapel Hill, USA*

<sup>2</sup>*Department of Chemistry, University College London, UK*

Hydrophobic surfaces created by adsorption of a monolayer of surfactants to mica in water display long-range mutual attraction. Initially, this attraction was considered to be due to hydrophobic interaction, however careful AFM analysis showed that the surfactant monolayer undergoes rearrangements and produces mobile charged patches on the surface, suggesting the nature of the long-range attraction to be electrostatic. To study possible monolayer rearrangements, we performed all-atom (AA) and coarse-grain (CG) computer simulations. Our AA model consists of a monolayer of surfactants  $\text{RN}(\text{CH}_3)_3\text{Cl}^-$  adsorbed on mica surface in water. We observe that when R has 18 carbons, the monolayer rearranges into a micelle. When R is 24, it remains a monolayer.

Since the surface dimensions of the AA model are much smaller compared to the ones in the experimental systems, we performed CG simulations. The CG model consists of a negatively charged surface with a monolayer of cationic surfactants physisorbed to it. Initially, the surfactants self-assemble into micelles, then micelles readsorb to the charged-surface to form a bilayer when immersed in water. Contrary to experiments, however, we do not observe the formation of positively and negatively charged domains, which might be due to a short time-scale (microseconds) in our simulations.

**Notes:**

## **Polymer Laminates interfacial modification by microgel particles & block copolymers**

Xiaojing Cai

*NC State University, Department of Chemical and Biomolecular Engineering*

Thin polymer films that remain stable on solid substrates hold promise for a variety of applications such as coatings, lubricants, adhesives, and biological membranes. Most of these applications require complete wettability of the substrate by the coating material. In some cases the coatings become unstable, rupture and subsequently dewet from the substrates. Indeed, controlling the film integrity of coatings is a critically important topic of both academic and industrial importance, and it requires a fundamental understanding of the mechanisms, as well as the dynamics, of the wetting/dewetting processes. Moreover, details of the destabilization mechanism can provide valuable insight into molecular-level processes involving the self-assembly and interfacial modification afforded by incorporated species such as block copolymers or nanoparticles.

***Notes:***