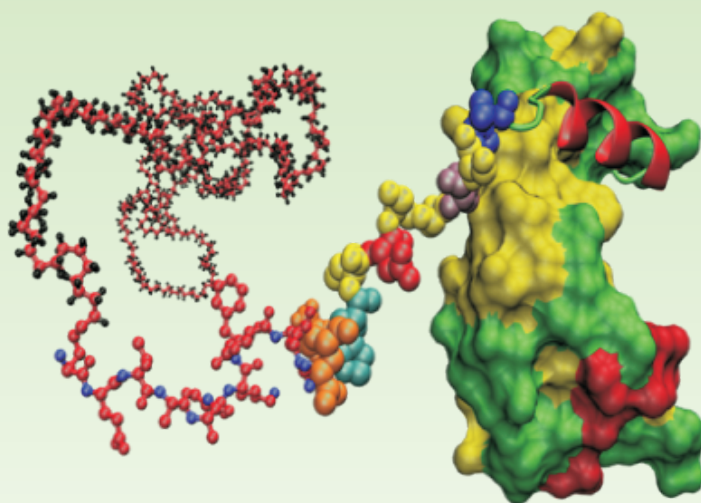


JCNS Workshop 2012

Trends and Perspectives in Neutron Scattering for Soft Matter and Biophysics



8 - 11 October 2012, Tutzing

Abstract booklet



SoftComp
SOFT MATTER COMPOSITES



www.fz-juelich.de/jcns/JCNS-Workshop2012

Dear colleagues,

Neutron scattering has proven to be a key method to get deep insight into soft matter physics, biophysics and soft matter molecular structures. A comprehensive set of techniques is used to reveal the structure and dynamics of polymers, colloids, polymer interfaces, polymer composites and glasses as well as biomolecules, biocompatible and bio-mimetic structures.

The aim of the international workshop jointly organized by the Jülich Centre for Neutron Science and the Donostia International Physics Center is to discuss the current status and the future trends and challenges of neutron scattering in this field.

The workshop will bring experts together to address the following topics:

- **Advanced Instrumentation for Soft Matter Research**
- **Physics of Life**
- **Kinetic Processes**
- **Soft Matter Materials for Energy**
- **Sustainable Polymers**
- **Functional Materials**
- **Synergies between Neutrons and Simulation**
- **Nanostructured Systems**

During the next days about 40 invited and contributed presentations will be given and exciting posters will add additional information in the mentioned topics. We would like to believe that this workshop at a gorgeous site at the Starnberger See will advance the field and we are looking forward to fruitful discussions and to a stimulating exchange of knowledge.

Scientific Organizing Committee

Dieter Richter

Juan Colmenero

The additional financial support by the SoftComp network is gratefully acknowledged.

Presentation Schedule

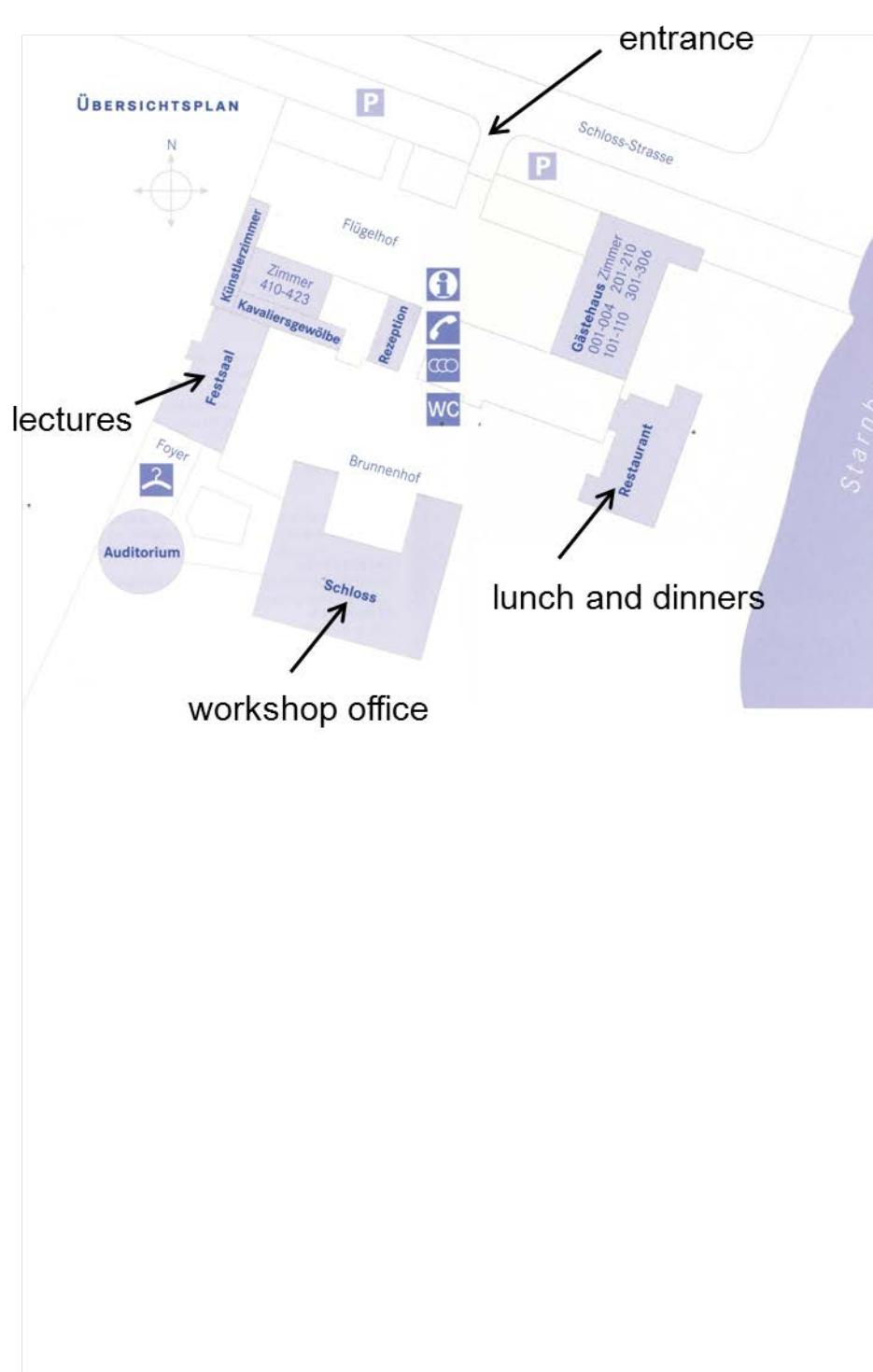
Program JCNS Workshop 2012 "Trends and Perspectives in Neutron Scattering for Soft Matter and Biophysics"

Monday, 8 October 2012		Tuesday, 9 October 2012		Wednesday, 10 October 2012		Thursday, 11 October 2012	
10:00	Registration	08:30	von Klitzing	08:30	Garcia Sakai	09:00	Grillo
		09:00	Förster	09:00	Frick	09:30	Kanaya
		09:30	Köhler	09:30	Violini	10:00	Papadakis
		09:50	Prevost	09:50	Radulescu	10:20	Jaksch
		10:10	Barroso-Bujans	10:10	Soltwedel	10:40	Coffee break
		10:30	Coffee break	10:30	Armstrong	11:10	Seto
		11:00	Ballauff	10:50	Coffee break	11:40	Bhowmik
		11:30	Kumar	11:20	Colmenero	12:00	Closing remarks
		12:00	Schwahn	11:50	Peltomäki	12:15	Lunch
12:15	Lunch	12:20	Krakovsky	12:10	Poblete		
		12:40	Jestin	12:30	Lunch		
13:15	Workshop Opening	13:00	Lunch				
13:30	Paduano						
14:00	Gradzielski	14:00	Paciaroni	14:00	Excursion		
14:30	Schönhals	14:30	Biehl		Bus tour to the Franz Marc Museum		
14:50	Pyckhout-Hintzen	15:00	Seydel				
15:10	Malo de Molina	15:20	Weik				
15:30	Coffee break	15:40	Coffee break				
16:00	Shibayama	16:10	Rheinstädter				
16:30	Urban	16:40	Sebastiani				
17:00	Koizumi	17:00	Sharp				
17:30	Frielinghaus	17:20	Poster Session				
17:50	Balog (canceled)						
18:10	Di						
18:30	Sharma (canceled)			18:30	Workshop Dinner "Griesbräu" in Murnau		
18:50	Dinner	19:30	Dinner				

as of 2012-010-04

Evangelische Akademie Tutzing

Site Map



JCNS Workshop 2012

“Trends and Perspectives in Neutron Scattering for Soft Matter and Biophysics”

October 8-11, 2012, Tutzling

Program

Monday, October 8, 2012

13:15 Opening of the workshop and welcome

Functional Materials

- 1 13:30 Luigi Paduano, University of Naples "Federico II", Naples, Italy (invited)
Nanodevices for antineoplastic diagnosis or therapy
- 2 14:00 Michael Gradzielski, Technische Universität Berlin, Berlin, Germany (invited)
Structure and dynamics of polyelectrolyte/surfactant complexes probed by SANS and NSE and their relation to the rheological properties
- 3 14:30 Andreas Schönhals, BAM Federal Institute for Materials Research and Testing, Berlin, Germany
Neutron scattering to investigate the molecular dynamics of discotic liquid crystals in the bulk and in the nanoconfined state
- 4 14:50 Wim Pyckout-Hintzen, Forschungszentrum Jülich, Jülich, Germany
Topology and dynamics in cyclic polymers: a PEG case study
- 5 15:20 Paula Malo de Molina, Technische Universität Berlin, Berlin, Germany
Structure and dynamics of mixtures of microemulsions networks with end-capped star polymers of low functionality

15:30 Coffee Break

Soft Matter Materials for Energy

- 6 16:00 Mitsuhiro Shibayama, The University of Tokyo, Chiba, Japan (invited)
Structure and gelation dynamics of tetra-PEG ion gels
- 7 16:30 Volker Urban, Oak Ridge National Laboratory, Oak Ridge, USA (invited)
Neutron scattering for energy and the environment – light harvesting biofuels
- 8 17:00 Satoshi Koizumi, Ibaraki University, Hitachi, Japan (invited)
In-situ observation of operating polymer electrolyte fuel cells (PEFC) by neutron small angle scattering – contrast variation by using deuterium gas

- 9 17:30 Henrich Frielinghaus, Jülich Centre for Neutron Science, Garching, Germany
Dynamics of microemulsions confined by a planar wall
- 10 17:50 Sandor Balog, University of Fribourg, Marly, Switzerland and Paul Scherrer Institut, Villigen, Switzerland
Small-angle neutron scattering studies of graft-copolymer electrolytes (canceled)
- 11 18:10 Zhenyu Di, Jülich Centre for Neutron Science, Garching, Germany
Phase behavior of AB/BC diblock copolymer blends
- 12 18:30 Veerendra Kumar Sharma, Bhabha Atomic Research Centre, Mumbai India
The dynamical landscape in ionic micelles (canceled)
- 18:50 Dinner

Tuesday, October 9, 2012

Nanostructured Systems

- 13 8:30 Regine von Klitzing, Technische Universität Berlin, Berlin, Germany (invited)
Stimuli sensitive polymer coatings with different film architectures
- 14 9:00 Stephan Förster, Universität Bayreuth, Bayreuth, Germany (invited)
Structure of soft lyotropic crystals and quasicrystals
- 15 9:30 Ralf Köhler, Technische Universität Berlin, Berlin, Germany
Polyelectrolyte multilayers under mechanical stress: studying changes in structure, elasticity, and swelling behavior with neutron and x-ray reflectometry
- 16 9:50 Sylvain Prevost, Technische Universität Berlin, Berlin, Germany
Equilibrium between miscible pseudo-phases for theta-shaped surfactants
- 17 10:10 Fabienne Barroso-Bujans, Materials Physics Center, San Sebastián, Spain
Structure and vibrational dynamics of poly(ethylene oxide) confined in graphite oxide by inelastic neutron spectroscopy
- 10:30 Coffee Break

Nanostructured Systems (continued)

- 18 11:00 Matthias Ballauff, Helmholtz Zentrum Berlin, Berlin, Germany (invited)
Small-angle neutron scattering – recent results on colloids and future trends
- 19 11:30 Sanat Kumar, Columbia University, New York, USA (invited)
Modeling polymer nanocomposite structure and dynamics
- 20 12:00 Dietmar Schwahn, Forschungszentrum Jülich, Jülich, Germany
SANS studies on the effect of organic matter on calcium-phosphate mineralization in order to elucidate the scaling of RO-membranes in desalination of wastewater

- 21 12:20 Ivan Krakovsky, Charles University, Prague, Czech Republic
Structural changes in epoxy-based gels induced by external stimuli investigated by small-angle neutron scattering
- 22 12:40 Jaques Jestin, Laboratoire Léon Brillouin, CEA Saclay, Gif/Yvette, France
Polymer-particle nanocomposites: influence of nanoparticles dispersion, of polymer chains conformation and of filler orientation on the macroscopic properties of materials
- 13:00 Lunch
- Physics of Life**
- 23 14:00 Alessandro Paciaroni, University of Perugia, Perugia, Italy (invited)
Elastic and quasielastic neutron scattering investigation of biomolecules in glassy environments
- 24 14:30 Ralf Biehl, Forschungszentrum Jülich, Jülich, Germany (invited)
Proteins in solution: determination of domain structure and dynamics
- 25 15:00 Tilo Seydel, Institut Laue Langevin, Grenoble, France
Protein self-diffusion in crowded solutions
- 26 15:20 Martin Weik, Institut de Biologie Structurale, Grenoble, France
Proteins need it wet. Do they?
- 15:40 Coffee Break
- 27 16:10 Maikel Rheinstädter, McMaster University, Hamilton, Canada (invited)
Frontiers in membrane biophysics
- 28 16:40 Federico Sebastiani, University of Perugia, Perugia, Italy
Collective dynamics in DNA hydration water and intracellular water in living cells
- 29 17:00 Melissa Sharp, European Spallation Source, Lund, Sweden
Domain motions in mercuric ion reductase - MerA
- 17:20 **Poster Session**
- 19:30 Dinner

Wednesday, October 10, 2012

Advanced Instrumentation for Soft Matter Research

- 30 8:30 Victoria Garcia Sakai, ISIS, Didcot, United Kingdom (invited)
Views from a soft matter neutron instrument scientist
- 31 9:00 Bernhard Frick, Institut Laue Langevin, Grenoble, France (invited),
New developments in neutron backscattering with applications in soft matter and perspectives for studies of slow dynamics
- 32 9:30 Nicolo Violini, Forschungszentrum Jülich, Jülich, Germany
Development of multi-spectral direct geometry chopper spectrometers for the future European spallation source
- 33 9:50 Aurel Radulescu, Jülich Centre for Neutron Science, Garching, Germany
KWS-2 – the high-intensity/wide Q-range small-angle neutron diffractometer with tunable resolution at the FRM II optimized for soft matter and biology
- 34 10:10 Olaf Soltwedel, Max Planck Institute for Solid State Physics, Stuttgart, Germany
NREX – neutron / x-ray contrast reflectometer
- 35 10:30 Clare Armstrong, McMaster University, Hamilton, Canada
Measurement of transient domains in biological membranes using coherence length dependent neutron diffraction
- 10:50 Coffee Break

Synergies Between Neutrons and Simulation

- 36 11:20 Juan Colmenero, Centro de Física de Materiales (CSIC, UPV/EHU) and Donostia International Physics Center, San Sebastián, Spain (invited)
Chain dynamics in un-entangled polymer blends with dynamic asymmetry. A generalized Rouse incoherent scattering function based on the GLE formalism
- 37 11:50 Matti Peltomäki, Forschungszentrum Jülich, Jülich, Germany
Scattering intensity of bicontinuous microemulsions from simulations at the mesoscale
- 38 12:10 Simon Poblete, Forschungszentrum Jülich, Jülich, Germany
Mesoscale simulations of multi-domain protein dynamics
- 12:30 Lunch
- 14:00 Excursion to the Franz Marc Museum in Kochel
- 18:30 Workshop dinner in the “Griesbräu” in Murnau

Thursday, October 11, 2012

Kinetic Processes

- 39 9:00 Isabelle Grillo, Institut Laue Langevin, Grenoble, France (invited)
Recent applications of time resolved SANS combined with a stopped-flow equipment
- 40 9:30 Toshiji Kanaya, Kyoto University, Kyoto, Japan (invited)
Flow-induced polymer crystallization – effects of molecular weight and shish-kebab formation
- 41 10:00 Christine Papadakis, Technische Universität München, Munich, Germany
Kinetics of collapse and aggregation in micellar solutions of thermoresponsive triblock copolymers – a time-resolved SANS investigation
- 42 10:20 Sebastian Jaksch, Technische Universität München, Munich, Germany
Kinetics of collapse transition of poly(2-oxazoline)s in aqueous solution
- 10:40 Coffee Break

Kinetic Processes (continued)

- 43 11:10 Hideki Seto, High Energy Accelerator Research Organization, Tsukuba Japan
Formation of a multiscale aggregate structure through spontaneous blebbing of an interface
- 44 11:40 Debsindhu Bhowmik, Donostia International Physics Center, San Sebastián, Spain
Dynamics of polymer / polymer nano-composites
- 12:00 **Closing remarks, end of the workshop**
- 12:15 Lunch

Poster Presentations

Advanced Instrumentation for Soft Matter Research

2012-1

Oxana Ivanova, Jülich Centre for Neutron Science

The Jülich neutron spin echo spectrometer (J-NSE): Dynamics with depth resolution

2012-2

Jianqi Zhang, Technische Universität München

Solvent distribution in block copolymer thin films

2012-3

Tobias Schrader, Jülich Centre for Neutron Science

In-situ light scattering during small angle neutron scattering experiments: First results and lessons learned

2012-4

Vitaly Pipich, Jülich Centre for Neutron Science

Focusing mirror VSANS diffractometer KWS-3: merging nano- and micrometer worlds

2012-5

Michaela Zamponi, Jülich Centre for Neutron Science

The high resolution neutron backscattering spectrometer SPHERES

2012-6

Stefano Pasini, Forschungszentrum Jülich

Design of a spin-echo-spectrometer for ESS

Functional Materials

2012-7

Stefan Wellert, Technische Universität Berlin

Internal structure and dynamics of microgel films at solid interfaces

2012-8

Ana Brás, Forschungszentrum Jülich

Neutron scattering of self-healing model polymers

2012-9

Konstantinos Kyriakos, Technische Universität München

Cononsolvency in aqueous solutions of P(S-b-NIPAM) diblock copolymers

Kinetic Processes

2012-10

Thomas Zinn, Forschungszentrum Jülich

Exchange kinetics in aqueous dispersions of n-alkyl-PEO polymers by TR-SANS

Nanostructured Systems**2012-11**

Margarita Krutyeva, Forschungszentrum Jülich
The influence of solid surface on the dynamics of polymer melt

2012-12

Guido Goracci, Donostia International Physics Center
Role of H-bonding on the structure and the dynamics of concentrated polymeric solutions

2012-13

Artem Feoktystov, Jülich Centre for Neutron Science
Detailed SANS contrast variation on toluene-based Co ferrofluid

2012-14

Barbara Gold, Jülich Centre for Neutron Science
Polymerdynamics in silicabased nanocomposites with attractive interaction

Sustainable Polymers**2012-15**

Shyamal Kumar Kundu, Galgotias University
Shear induced brush deformation of soft colloidal mixtures

2012-16

Nino Ruocco, Forschungszentrum Jülich
Microscopic study of branched polymer systems

2012-17

Leonardo Chiappisi, Technische Universität Berlin
On the small-angle scattering curves arising from oppositely charged polyelectrolyte surfactant mixtures: the case of chitosan - alkyl ether carboxylates

JCNS Workshop 2012

Trends and Perspectives in Neutron Scattering for Soft Matter and Biophysics

Abstracts

Status: October 04, 2012

Nanodevices for antineoplastic diagnosis or therapy

Luigi PADUANO^{1,2}, Gaetano MANGIAPIA^{1,2}, Gerardino D'ERRICO^{1,2}, Carlo IRACE³, Aurel RADULESCU⁴, Henrich FRIELINGHAUS⁴, Daniela MONTESARCHIO¹

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³ University of Naples "Federico II", Experimental Pharmacology Department, Naples, Italy

⁴ Jülich Centre for Neutron Science, Garching bei München, Germany

Amphiphilic molecules of appropriate design can form a variety of supramolecular aggregates such as micelles, vesicles and inverse bicontinuous cubic phases that may be exploited in several applications such as in medical diagnostic and therapy. The aim of this lecture is to present the update development and improvement of potential tumor-specific supramolecular contrast agents for magnetic resonance imaging (MRI) applications or chemotherapy.

In the field of tumor diagnosis nanodevices based on gadolinium complexes and peptides were prepared. [1,2] In the field of tumor therapy new classes of potential antineoplastic agents based on ruthenium amphiphilic complexes were synthesized and used to form nanoaggregates. [3,4]

Their morphology has been studied in different conditions of pH, temperature and ionic strength by means of small-angle neutron scattering, dynamic light scattering, electron paramagnetic resonance spectroscopy and electron cryomicroscopy. These aggregates are stimuli-responsive can switch from one structure to other depending on the environmental condition. Appropriate literature models were used to be fitted to SANS data with the aim to get the microstructural parameters of the nanoaggregates. In the case of bicontinuous phase a new theoretical model has been proposed to fit the SANS experimental data. [5]

Finally *in vitro* and *in vivo* tests, of these nanoaggregates on live cultures of human cancer cells were performed, demonstrating high efficiency of these tools both in diagnosis and therapy.[2,3]

- [1] M. Vaccaro, A. Accardo, D. Tesauro, G. Mangiapia, D. Loef, K. Schillen, O. Soederman; G. Morelli, L. Paduano, Luigi, *Langmuir* **22**, 6635 (2006).
- [2] M. Vaccaro, G. Mangiapia, A. Radulescu, K. Schillen, G. D'Errico, G. Morelli, L. Paduano, *Soft Matter* **5**, 2504 (2009).
- [3] L. Simeone, G. Mangiapia, G. Vitiello, C. Irace, A. Colonna, O. Ortona, D. Montesarchio, L. Paduano, *Bioconjugate Chemistry*, **23**, 758 (2012).
- [4] G. Mangiapia, G. D'Errico, L. Simeone, C. Irace, A. Radulescu, A. Di Pascale, A. Colonna, D. Montesarchio, L. Paduano, *Biomaterials*, **33**, 3770 (2012).
- [5] G. Mangiapia, M. Vaccaro, G. D'Errico, H. Frielinghaus, A. Radulescu, V. Pipich, A.M. Carnerup, L. Paduano, *Soft Matter* **7**, 10577 (2011).

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October 8, 2012, 14:00h

Functional Materials

Structure and Dynamics of Polyelectrolyte/Surfactant Complexes Probed by SANS and NSE and their Relation to the Rheological Properties

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Mixtures of oppositely charged polyelectrolyte and surfactant exhibit rich phase behaviour and high structural diversity, depending on the mixing ratio, total concentration and molecular structure of the components. The self-assembled structures formed may cover a large mesoscopic size range and have many potential applications, e.g. in cosmetics, detergency, drug delivery, and also for rheological control in formulations.

In our experiments mixtures of cationic polyelectrolyte JR400 with anionic surfactants (SDS, SDBS, SDES) were studied in the semi-dilute regime. In the range of excess polymer the addition of surfactant leads to the formation of highly viscous networks, where the viscosity increases by 3-4 orders of magnitude as compared to the pure polymer solution and the rheological properties of these systems were characterised comprehensively. The structure of the polyelectrolyte/surfactant complexes was studied by means of static and dynamic light scattering (SLS, DLS) and in further detail by means of small-angle neutron scattering (SANS). SANS with its option of contrast variation (using deuterated surfactant) delivers a detailed structural picture. Our investigations show the formation of rod-like mixed aggregates whose length increases as a function of the surfactant concentration and these rods then become increasingly interconnected, thereby explaining the enhanced viscosity.

To obtain further insight into the relations between mesoscopic structure and dynamics and the macroscopic rheological behaviour, neutron spin-echo (NSE) were done, which allow to probe the mesoscopic dynamics. Together with the DLS experiments, which probe larger length scales and can be described in terms of the mode-coupling theory, this yields a deeper insight into the complex dynamics of such complexes. Interestingly, NSE measurements show a much less pronounced effect on the dynamics as compared to DLS.

The structure and dynamics of oppositely charged polyelectrolyte/surfactant complexes in solution were correlated to the pronounced viscosity increases, where we focussed on the role of the polyelectrolyte in the complexes. These investigations are not only of fundamental interest but also relevant to the design of application formulations with tailor-made properties.

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October 8, 2012, 14:30h

Functional Materials

Neutron scattering to investigate the molecular dynamics of discotic liquid crystals in the bulk and in the nanoconfined state

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Discotic liquid crystals (DLC) consist of a flat and rigid aromatic core substituted by flexible aliphatic chains. While the former is responsible for the π -stacking, the latter increases the solubility and gives rise to a rich thermotropic behavior. DLCs are self-assembled soft matter materials. The disc-shaped molecules organize into columns that further assemble into two-dimensional arrays with a hexagonal mesophase. The alkyl chains fill the intercolumnar space giving rise to a nanophase separated state. Two different homologous systems based on triphenylene derivatives were investigated as model systems for DCLs by inelastic neutron scattering. Measurements in the bulk state and nanoconfined to the unidirectional nanopores of anodised aluminium (Pore diameter 40nm and 80 nm) were carried out where both the vibrational density of states from neutron time-of-flight spectroscopy as well as the molecular dynamics on a time scale of ca. 1 ns (elastic scans from neutron backscattering spectrometers) were considered. The influence of both the structure (length of the aliphatic chains) and the confinement will be discussed in detail. Comparison is made to x-ray diffraction investigations and to dielectric spectroscopy as well as specific heat spectroscopy in some cases.

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Topology and dynamics in cyclic polymers: a PEG case study

Sebastian Goossen¹, Ana Rita Bras¹, **Wim PYCKHOUT-HINTZEN¹**, Andreas Wischnewski¹, Margarita Krutyeva¹, Rossana Pasquino², Dimitris Vlassopoulos², Dieter Richter¹

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Cyclic polymers are exquisite model systems for polymer investigations since the obvious lack of any chain ends, which themselves totally determine the relaxation behavior, allows to study critically details of the underlying mechanisms. The tube model of reptation by de Gennes and Doi and Edwards becomes invalid but also the local Rouse mode structure is expected to differ clearly from the linear analogon.

We will discuss first results, obtained on PEO rings, varying the molecular weight of the ring from M_e over M_c up to molecular weights where the linear analogons are well entangled.. The amount of linear contaminant was less than 0.1% .The structure and conformation of pure rings and their blends with the linear parents are obtained from SANS and the corresponding dynamics measured by NSE spectroscopy.

The combination of SANS, NSE, PFG-NMR and rheological measurements provides new insight into the microscopic details of this unexplored topology constraint. A link to similar systems in which the ring is dilute and enhances the elasticity is made as well.

[1] A. Bras et al, Soft Matter, 7, 11169(2011).

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October 8, 2012, 15:10h

Functional Materials

Structure and dynamics of mixtures of microemulsions Networks with end-capped star polymers of low functionality**Paula MALO DE MOLINA¹**, Christoph HERFURTH², André LASCHEWSKY^{2,3}, Michael GRADZIELSKI¹¹ Technische Universität Berlin, Stranski-Laboratorium, Berlin, Germany² Universität Potsdam, Institut für Chemie, Golm, Germany³ Fraunhofer-Institut für Angewandte Polymerforschung, Golm, Germany

Mixtures of telechelic polymers and microemulsions have found a big interest due their wide range of applications but also because they serve as model systems for networks where the concentration of nodes and the connectivity can be tuned separately and, therefore, the rheological properties of these materials can be controled.

Here we present a study where end-capped star polymers are the bridging elements of the network. We have investigated various multiply bridging polymers and their effect on the structure and dynamics of oil in water microemulsion droplets. For that purpose we employed such tailor made bridging amphiphilic polymers with multiple linkers by the RAFT procedure, allowing to control the number of arms (functionality), the length of the hydrophilic group (maximum length for connection) and of the hydrophobic chain (stickiness).

A detailed structural picture was obtained by SANS measurements, especially with respect to the effects on the droplet sizes and even more on the interactions in the microemulsion systems induced by the bridging star polymer. In addition, dynamic light scattering and rheology measurements going to high frequencies were carried out. The results of our experiments show an increase of the interaction between the droplets with increasing polymer functionality. Moreover, we observe the elasticity of the network is correlated with the polymer architecture and in DLS increasingly complex relaxation patterns are observed.

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Structure and gelation dynamics of tetra-PEG ion gels

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The structure of Tetra-PEG ion gel, having high ion conductivity and high mechanical properties, has recently established in our group [1]. The Tetra-PEG ion gel is tetra-arm poly(ethylene glycol) (Tetra-PEG) network in ionic liquid (IL). The network structure of Tetra-PEG ion gels was investigated by using small-angle neutron scattering (SANS) as functions of polymer concentration (ϕ) and molecular weight (M_w), and the results were compared with those of Tetra-PEG hydrogel [2]. The SANS functions, $I(q)$, for both the ion gels and hydrogels were represented by the so-called Ornstein-Zernike equation, suggesting absence of frozen inhomogeneities in this length scale. The same scaling relationship to the prepolymer solutions, $\xi \sim \phi^{-3/4}$, was also obtained for the ion gels. Furthermore, the SANS curves were successfully superimposed to a single master curve with $I(q)/\xi^{5/3}\phi$ vs ξq irrespective of M_w and ϕ , showing the universal nature of network structure free from significant inhomogeneities.

The dynamics of Tetra-PEG prepolymer in ionic liquid (IL) and its gelation kinetics were also investigated by means of dynamic light scattering (DLS). It was suggested that the Tetra-PEG prepolymers interpenetrated to each other or jammed in IL with increasing concentration. The intensity-correlation function (ICF) showed a double relaxation behavior and it remained until the end of gelation, while that of hydrogels showed a single relaxation behavior at the end of gelation reaction. It was conjectured that the gelation reaction did not complete in the case of ion gel and an imperfect gel was formed. Possible reasons for the imperfect network formation for the IL will be discussed from the viewpoints of the solvent viscosity, chain conformation in the prepolymer solutions, and difference in the solvated states.

[1] K. Fujii, H. Asai, T. Ueki, T. Sakai, T. Imaizumi, U. Chung, M. Watanabe, and M. Shibayama, *Soft Matter*, **8**, 1756 (2012).

[2] H. Asai, K. Fujii, T. Ueki, T. Sakai, U. Chung, M. Watanabe, Y.-S. Han, T.-H. Kim, and M. Shibayama, *Macromolecules*, **45**, 3902 (2012).

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October 8, 2012, 16:30h

Soft Matter Materials for Energy

Neutron scattering for energy and the environment – light harvesting and biofuels

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 Hugh O'NEILL¹, Marcus FOSTON², Dean A. MYLES¹, Paul LANGAN¹, Arthur
 RAGAUSKAS², Brian DAVISION¹, Barbara R. EVANS¹, Michelle LIBERTON³, Lawrence
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Renewable energy sources are more than ever in the focus of current fundamental research. In the Energy and the Environment Group of the Biology and Soft Matter Division at Oak Ridge National Laboratory, we utilize the unique capabilities of neutron scattering to investigate a diverse set of research topics that are use-inspired in their aim towards energy solutions, yet focus on very fundamental science aspects that hold promises for transformative results. Biofuels produced from lignocellulosic biomass hold promise as a renewable alternative energy and fuel source. To realize this potential in a cost and energy efficient way, a better understanding of the deconstruction of lignocellulose including processes such as thermochemical pretreatment designed to reduce biomass recalcitrance is needed. We have studied the structural changes over multiple length-scales (5 Å to 6000 Å) in switchgrass [1] and hybrid poplar biomass during dilute sulfuric acid pretreatment. Contrary to conventional knowledge our results show that cellulose crystallinity and lignin aggregates by themselves do not determine the efficiency of enzymatic digestion of cellulose. Instead, an intricate interplay between cellulose accessibility to enzymes, biopolymer spatial distribution and substrate surface interaction with enzymes may be more critical in governing the enzymatic hydrolysis efficiency. Cyanobacteria are prokaryotes that can use photosynthesis to convert sunlight into cellular fuel. Knowledge of the organization of the membrane systems in cyanobacteria is critical to understanding the metabolic processes in these organisms. We examined the wild type strain of *Synechocystis* sp. PCC 6803 and a series of mutants with altered light harvesting phycobilisome antenna systems for changes in thylakoid membrane architecture under different conditions. With SANS we observed that light induces an expansion in distances between the thylakoid membrane layers. These changes to the thylakoid system are reversible between light and dark, demonstrating a robust structural flexibility in the architecture of cyanobacterial cells.

[1] S.V. Pingali et al., *Biomacromolecules*, **11**, 2329-2335 (2010).

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In-situ observation of operating polymer electrolyte fuel cell (PEFC) by neutron small-angle scattering - Contrast variation by using deuterium gas -

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In order to visualize water distribution in an operating fuel cell, we combined two different methods using neutron as a probe, i.e., a combined method of small-angle & ultra-small-angle scattering (SANS) and radiography imaging. SANS observes water distribution in a membrane electrolyte assembly (MEA), whereas radiography observes bulk water appeared in a gas flow channel (so called “flooding”). The polymer electrolyte fuel cell (PEFC) was specially designed suitable for small-angle neutron scattering by replacing materials with aluminum in order to decrease background scattering. We employed hydrogen gas (H₂) and deuterated gas (D₂) as a fuel for operation. With exchange of H₂ and D₂, we aim to perform a contrast variation as for polyelectrolyte film (Nafion). When D₂ gas is used as a fuel, D₂O is produced at the cathode and diffuses back to the film. Then the film, originally swollen by H₂O, exhibits a change of coherent scattering contrast. By changing a fuel gas from H₂ to D₂, SANS quantitatively detected a decrease of scattering intensity at scattering maximum originating from the ion-channel in the electrolyte. After quantitative analyses on scattering intensity, which is related to water ratio (H₂O/D₂O) in the ion channel, we found that 30 wt% of the total water is replaced by D₂O by changing the gas from H₂ to D₂. In a stationary state of fuel cell operation using D₂, the scattering intensity rhythmically oscillates (respiration of fuel cell). The rhythmic oscillation found for the peak intensity is a non-equilibrium and non-linear phenomenon, in which “flooding” in a flow field is a feedback mechanism to slow down chemical reaction or water production by affecting mass transportation of air at the cathode. A valance between two diffusions, (i) back diffusion of D₂O from the cathode to the electrolyte and (ii) diffusion of H₂O supplied as humidity, determines a time interval of the respiration.

[1] H. Iwase et al. *Nucl. Instrum. Methods Phys. Res.*, **A 605**, 95-98 (2009).

[2] S. Koizumi et al. *Journal of Applied Crystallography*, vol. 40, supplement 1, pp. s474–s479, 2007.

[3] S. Koizumi, “Focusing USANS Instrument” *Neutrons in Soft Matter* (Chapter II.1.3.2), Edited by T. Imae, T. Kanaya, M. Furusaka, and N. Torikai, 2011 by John Wiley & Sons, Inc., Hoboken, New Jersey.

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Dynamics of microemulsions confined by a planar wall

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Aqueous surfactant systems have manifold applications for the enhanced oil recovery. The micelle formation of the surfactant leads to high viscosities, which is desired for many reasons. The cracking fluid needs to deposit the hydrostatic energy in the sand stone close to the bore hole, and, thus, cracks are generated. The proppant consists of sand particles, which are left inside the cracks and keep the porosity high for better production rates after the application. The fluid itself forms a microemulsion when in contact with oil. The microemulsion possesses a low viscosity, which is favorable for the easy production.

The static structure of a bicontinuous microemulsion as a model complex fluid has been studied statically by GISANS and reflectometry experiments and in parallel by computer simulations [1]. A lamellar structure was induced by the planar wall. The high order decayed with growing distance from the wall and finally the bulk structure is bicontinuous. The decay of the lamellar order was realized by a growing number of perforations as observed by the simulations. The typical lengths of the decay and the onset of the perforations were compared between the different methods.

Dynamically, the grazing incidence method was transferred to neutron spin echo spectroscopy [2]. We found three times faster relaxations close to the wall in comparison to the bulk structure. The hydrodynamic waves are reflected by the wall, which explains the faster undulations of the surface near lamellae. Faster dynamics explain also a lower viscosity, which in this case is known as the lubrication effect. This effect would theoretically explain a slip length indicating a facilitated sliding off of the oriented lamellae. This in turn is highly interesting for flow fields of complex fluids in porous materials or for an initial state in the capture process of immune cells at vessel walls.

[1] M. Kerscher, P. Busch, S. Mattauch, H. Frielinghaus, D. Richter, M. Belushkin, G. Gompper, Phys. Rev. E 83, 030401 (2011)

[2] H. Frielinghaus, M. Kerscher, O. Holderer, M. Monkenbusch, D. Richter, Phys. Rev. E 85, 041408 (2012)

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Small-angle neutron scattering studies of graft-copolymer electrolytes**Sandor BALOG^{1,2}**¹Adolphe Merkle Institute - University of Fribourg, Marly, Switzerland²Laboratory for Neutron Scattering, Paul Scherrer Institut, Villigen, Switzerland

The current focus regarding polymeric proton-exchange materials is (a) to improve the chemical stability of partially fluorinated or hydrocarbon polymers, (b) to obtain mechanical integrity at high ionic content, and (c) to moderate the loss in proton conductivity at low water content. Therefore, to comprehend the aspects of structure-property relationships is of paramount importance for identifying fundamental challenges for the development of novel cost-effective polymeric materials having improved functionality. Small-angle neutron scattering (SANS) is an excellent tool to investigate the structure of polymer electrolytes, and thus, provide insight into the correlations between fuel-cell-relevant properties, monomer composition, copolymer topology, and electrolyte structure. The objective is to review the findings of small-angle scattering studies dedicated to radiation-grafted block copolymers developed at Paul Scherrer Institut.

- [1] K. Mortensen, U. Gasser, S. Alkan-Gürsell, G. G. Scherer, *Journal of Polymer Science Part B: Polymer Physics* **46**, 1660 (2008).
- [2] S. Balog, U. Gasser, K. Mortensen, L. Gubler, H. Ben youcef, G. G. Scherer, *Macromolecular Chemistry and Physics* **211**, 635 (2010).
- [3] S. Balog, U. Gasser, K. Mortensen, L. Gubler, H. Ben youcef, G. G. Scherer, *Journal of Membrane Science* **383**, 50 (2011).
- [4] S. Balog, U. Gasser, K. Mortensen, L. Gubler, H. Ben youcef, G. G. Scherer, *Polymer* **53**, 175 (2012).

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Phase behavior of AB/BC diblock copolymer blends

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Binary blends of AB/BC diblock copolymers give rise to very complex and rich morphologies, which is of great interests for many applications, for example organic solar cells. These blends may undergo both macro- and microphase separations which are mainly controlled by the relative magnitudes of the Flory-Huggins interaction parameters χ_{AB} , χ_{BC} and χ_{AC} [1]. If $\chi_{AC} > \chi_{AB}, \chi_{BC}$, macrophase separation tends to occur [2, 3]. In contrast, if $\chi_{AC} < \chi_{AB}, \chi_{BC}$, microphase separation can occur. However, our study shows that the relative χ s alone do not necessarily lead to a micro-phase separation and a more complex phase behavior may happen. We investigate blends of polystyrene-b-poly(ethylene oxide) (PS-PEO) and polyisoprene-b-poly(ethylene oxide) (PI-PEO) with weight fractions of PI-PEO between 0 and 100% in steps of 10%. The PS-PEO is compositionally symmetric i.e. $f = 0.5$ meanwhile three PI-PEOs with PEO volume fractions $f_{PEO} = 0.65$ (PI-PEO1), 0.5 (PI-PEO2) and 0.45 (PI-PEO3) were used. These Blends series were studied in temperature ranges from RT to far above ODT. Nearly in all cases, the two components are well mixed and form a common lamellar phase with either component excess (also in lamellae) in crystallized state. However, above T_c the blends showed a very complex behavior. For example: during temperature increasing, the blend with 70% of PI-PEO3 changed the morphology of the PI-PEO excess from lamellae first to hexagonally packed cylinder next to gyroid then the originally mixed part started to separate to PS-PEO domains and PI-PEO domains which ordered themselves in lamellae and gyroid, respectively. After that these two component mix again and at last above ODT become one phase but disordered.

[1] K. Kimishima, H. Jinnai, and T. Hashimoto, *Macromolecules* **32**, 2585 (1999).

[2] H. Frielinghaus, N. Hermsdorf, K. Almdal, K. Mortensen, L. Messe, L. Corvazier, J. P. A. Fairclough, A. J. Ryan, P. D. Olmsted, and I. W. Hamley, *Europhys. Lett.* **53** 680 (2001).

[3] H. Frielinghaus, N. Hermsdorf, R. Sigel, K. Almdal, K. Mortensen, I. W. Hamley, L. Messe, L. Corvazier, A. J. Ryan, D. van Dusschoten, M. Wilhelm, G. Floudas, and G. Fytas, *Macromolecules* **34**, 4907 (2001).

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The dynamical landscape in ionic micelles

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Amphiphilic molecules in aqueous solution undergo self-association under specific conditions to form aggregates such as micelles. Local dynamics of such assemblies are important in understanding various properties such as the mechanism in releasing the solubilized drugs, micellar breaking time etc. Quasielastic neutron scattering (QENS) study on two surfactants used in everyday life products that form micelles, namely anionic sodium dodecyl sulfate (SDS) and cationic cetyltrimethylammonium bromide (C₁₆TAB) revealed the details of the fast local dynamics of surfactant molecules in these assemblies and their correlation with the microstructure. Detailed dynamical landscape is obtained by combining the data from different instruments providing wide dynamical energy range. High-resolution QENS data show the presence of two distinct motions; global motion of the whole micelles and segmental motion of the monomers. The global motion follows Fick's law; and it is found to be slower for C₁₆TAB than SDS micelles, which may be attributed to the difference in their sizes. The segmental dynamics within a micelle has been described with a model, which accounts for the dynamics of head group and the hydrophobic alkyl chain separately. Flexibility of the alkyl chain manifests in a form where the hydrogen atoms move within a spherical volume; size and associated diffusivities go up linearly from head towards tail. In addition, a faster conformational dynamics ascribed to the torsional isomerisation of some of the CH₂ groups in the hydrocarbon chain, is also found to exist. A comprehensive description of the complex dynamics present in the micelles has been provided. Molecular dynamics simulation study also supports the QENS results. Effect of varying chain length on the dynamical behaviour of alkyl trimethylammonium bromide (C_nTAB) micelles (n=10,12,14 and 16) is also investigated. It is found that increase in chain length hinders both internal and global dynamics of the micelles.

- [1] V. K. Sharma, S. Mitra, V. Garcia Sakai and R. Mukhopadhyay, J. Phys. Chem. B (2012) (submitted).
- [2] V. K. Sharma, S. Mitra, V. Garcia Sakai, P. A. Hassan, J. Peter Embs and R. Mukhopadhyay, Soft Matter, **8**, 3151 (2012).
- [3] S. Mitra, V. K. Sharma, V. Garcia Sakai, J. Peter Embs and R. Mukhopadhyay, J. Phys. Chem. B, **115**, 9732 (2011).
- [4] V.K. Sharma, S. Mitra, G. Verma, P. A. Hassan, V. Garcia Sakai and R. Mukhopadhyay, J. Phys. Chem. B **114**, 17049 (2010)
- [5] V. K. Sharma, et al., Z. Phys. Chem., **224**, 253 (2010).

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Stimuli sensitive polymer coatings with different film architectures

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For fabrication of stimuli responsive coatings one of the challenges is to generate stable films which are still mobile and sensitive to outer parameters. The talk will focus on different types of thin polymer films at solid interfaces: polyelectrolyte multilayers which are built up by alternating deposition of polyanions and polycations from aqueous solutions [1, 2] films formed by deposition of hydrogel microparticles [3] and multicompartments films. The water content was studied by neutron reflectometry. The temperature effects of polyelectrolyte multilayers are minor due to strong interdigitation between adjacent polyelectrolyte layers [4]. Therefore another strategy is to separate thermosensitive compartments from stabilizing ones.

During the last decades microgels made of N-isopropylacrylamide (NIPAM) have attracted much interest and were studied by several techniques like microscopy and light scattering. These polymer particles show thermoresponsive behaviour and can therefore be classified as “smart” materials. By copolymerisation with organic acids such as acrylic acid (AAc) the temperature of the volume phase transition as well as the swelling ratio can be influenced. Moreover charged copolymers are sensitive to changes in pH and ionic strength. Our work focuses on the fabrication of stimuli responsive films and on the effect of geometrical confinement on the phase volume transition of these microgel particles [3,5]. The effect of cross-linker and co-monomers on the swelling behaviour and on the elasticity is presented [6,7].

The third example is a multicompartment system which consists of PNIPAM brushes and polyelectrolyte multilayers. The question is addressed, how the different compartments affect each other with respect to their sensitivity to outer stimuli.

References:

- [1] G. Decher, *Science*, 1997, **277**,1232.
- [2] R. v. Klitzing, *PCCP*, 2006, **8**, 5012.
- [3] S. Schmidt, H. Motschmann, T. Hellweg, R. v. Klitzing, *Polymer*, 2008, **49**, 749.
- [4] R. Steitz, V. Leiner, K. Tauer, V. Khrenov, R. v. Klitzing, *Applied Physics A* 2002, **74**, 519.
- [5] A. Burmistrova, R. v. Klitzing *J. Mat. Chem*, 2010, **20**, 3502.
- [6] A. Burmistrova, M. Richter, C. Üzü, R. v. Klitzing, *Coll. Polym. Sci.* 2011, **289**, 613.
- [7] A. Burmistrova, M. Richter, M. Eisele, C. Uzum, R. v. Klitzing *Polymers* 2011, **3** 1575.

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Structure of soft lyotropic crystals and quasicrystalsA. EXNER¹, P. LINDNER², J. PERLICH³, and **Stephan FÖRSTER**¹¹University of Bayreuth, Bayreuth, Germany²Institute Laue Langevin, Grenoble, France³HASYLAB/DESY, Hamburg, Germany

Micelles are the most abundant example of self-assembly. In aqueous solutions micelles can form highly ordered lyotropic liquid crystalline phases. Using shear orientation it is possible to obtain highly ordered single crystalline samples showing more than 100 Bragg reflections. With scanning small-angle neutron diffraction it is possible to map the complete reciprocal space and analyse the structure of such soft crystals in great detail. With this method we could not only characterize structures exhibiting classical crystallographic order, but also newly discovered lyotropic quasicrystals with 12- and 18-fold rotational symmetry.

[1] S. Fischer, A. Exner, K. Zielske, J. Perlich, P. Lindner, S. Deloudi, W. Steurer, S. Förster, *Proc. Nat. Acad. Sci.* **108**, 1810 (2011).

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Polyelectrolyte multilayers under mechanical stress: Studying changes in structure, elasticity, and swelling behavior with neutron and x-ray reflectometry

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For investigation of thin films on molecular level, X-ray (XR) and neutron reflectometry (NR) are favorable techniques: Both obey a high experimental precision combined with the ability to detect buried structures. NR, in addition, allows investigating deuterium-labeled structures, easily to prepare in Polyelectrolyte Multilayers (PEM) - our thin film model [1, 2].

However, stressed thin films tend to wrinkle and, thus, prove to be problematic for use of reflectometry techniques. A home-made gripping device, allowed for studying stressed films by bending the substrates of the films. XR and NR technique were adapted accordingly [5].

Up to now, mainly macroscopic properties (e.g. the Young's modulus) of PEM films were investigated [3]. After having studied the effect of large strain on the structure of PEM [4], now, we focus on small elongations. Upon stretching, an increase of the overall thickness of the PEM was observed. This contra-intuitive behavior is very likely a result of stress-induced disturbances in the structure of the PEM and represents a change of the chemical potential of the film. Flory-Huggins theory can describe the observed swelling as change of the solvent affinity of PEM. Besides the swelling, also a variation of the inner layer structure of the PEM takes place. NR measurements on (deuterium)-labeled PEM show an irreversible degradation of the Bragg peak when mechanically loaded, indicating a destruction of the layered superstructure. At an elongation of $\epsilon \geq 0.2\%$, a transition from elastic to plastic stretching behavior occurs. Our method allows for investigation of thin films under mechanical stress, and new insight into the molecular mechanism of stress response. In extra, physico-chemical properties of the films can be followed: It is possible to relate the change of swelling behavior and water uptake of the film with the applied external stress.

[1] Decher et al., Thin Solid Films **210/211** (1992). Decher et al., Science **277** (1997).

[2] Schmitt et al., Macromolecules **26** (1993). Lösche et al., Macromolecules **31** (1998).

[3] Mueller et al., Macromolecules **38** (2005). Nolte et al., Macromolecules **38** (2005).

[4] Früh et al., Langmuir **26** (2010).

[5] Früh et al. (in prep.).

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Equilibrium between miscible pseudo-phases for theta-shaped surfactants

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Theta-shaped rigid surfactant molecules such as COSAN show complex multi-scale patterns in aqueous solutions as seen by small angle neutron and X-ray scattering. At wide angles a correlation between COSAN (bis(1,2-dicarbollide) cobaltate, $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$) is seen, while oligomeric aggregates that correspond to charged micelles scatter in the intermediate q-regime ($\sim 0.1\text{nm}^{-1}$). The low-q part finally exhibit a scattering intensity that is modelled by vesicles made of one or several monolayers of adjacent COSAN.

Vesicles form at lower concentration than micelles [1]. However, there is a coexistence range of these two aggregates. Therefore, the scattering spectra can be modelled as the sum of two intensities. Exploitation of absolute scale with and without salt allows determining the area per molecule in the two pseudo-phases, as well as equilibrium shape of the aggregates.

Thermodynamic reasons of coexistence of vesicles and micelles are consistent with cryo-TEM and surface tension measurement. Entropic terms like required of Onsager transition favour the enclosure of vesicles, as predicted by Ninham and Marcelja twenty years ago.

Some points of lateral equation of states involved can be derived from the quantitative exploitation of SANS patterns; SAXS is less quantitative since contrast with water is very low. Last but not least, a new and direct method for determining the free energy of transfer between micelles and vesicles seen as miscible pseudo-phases is proposed.

[1] Bauduin, P., Prevost, S., Farràs, P., Teixidor, F., Diat, O. and Zemb, T., *Angewandte Chemie*, **123** (23), 5410-5412 (2011).

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Nanostructured Systems

Structure and vibrational dynamics of poly(ethylene oxide) confined in graphite oxide by inelastic neutron spectroscopy

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We explore the effects of both chain size and host nature on the structure and vibrational dynamics of poly(ethylene oxide) (PEO) intercalated in a series of graphite oxides (GOs). To this end, a PEO series of increasing chain length, from a single monomeric unit [i.e., ethylene glycol (EG)] to several thousand repetitive ethylene-oxide units, have been studied by means of high-resolution inelastic neutron spectroscopy (INS) on the TOSCA spectrometer in ISIS, UK. We find that EG is accommodated in a layer of thickness ~ 3 Å within the GO substrate and adopts a preferential, yet largely disordered, *gauche* conformation. Longer PEO chains give rise to a layer thickness in the range 3.0–3.4 Å characterized by planar zigzag (*trans-trans-trans*) conformations. Moreover, we observe a strong reduction of vibrational motions for the confined EG and polymer phases, as clearly evidenced by the disappearance, shift, and/or broadening of mode-specific INS spectral features, as well as by the complete suppression of crystallization and glass transition. All of these effects are surprisingly insensitive to the length of the PEO chains. Careful control over the degree of GO oxidation and exfoliation reveals two distinct cases of spatial confinement: (i) subnanometer 2D-confinement, and (ii) surface immobilization. Case (i) results in drastic changes to PEO conformational and collective vibrational as detailed above. In case (ii), the INS data unequivocally show that PEO chains adsorb firmly onto graphene sheets, with a substantial increase in the population of *gauche* conformers. Well-defined glass and melting transitions associated with the confined polymer phase are recovered in case (ii), albeit at significantly lower temperatures than those of the bulk.

- [1] F. Barroso-Bujans, F. Fernandez-Alonso, S. Cervený, S. Arrese-Igor, A. Alegría, J. Colmenero. *Macromolecules* **45**, 3137 (2012).
- [2] F. Barroso-Bujans, F. Fernandez-Alonso, J. A. Pomposo, S. Cervený, A. Alegría, J. Colmenero. *ACS Macro Letters* **1**, 550 (2012).
- [3] F. Barroso-Bujans, F. Fernandez-Alonso, S. Cervený, S. Parker, A. Alegría, J. Colmenero. *Soft Matter* **7**, 7173 (2011).

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Small-angle neutron scattering – Recent results on colloids and future trends**Matthias BALLAUFF**

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Small-angle neutron scattering (SANS) is certainly among the most important methods in soft matter research. The specific labeling by deuterons is still unsurpassed by any other method and contrast variation in mixtures of H₂O and D₂O allows us to analyze virtually any system in aqueous phase. At the same time, the systems we wish to analyze have become more complicated and we need to look into time-resolved measurements. In my lecture I shall discuss some trends which we are following up at the HZB:

1. Use of time-of-flight instruments for the study of polymer colloids in suspension. Here I'll report on our recent work on the commissioning of the new SANS-instrument VSANS at the HZB.
2. Combining SANS with cryogenic electron microscopy (cryoTEM). Here I'll discuss our recent efforts to combine small-angle scattering studies with cryoTEM which gives precise information about the shape and the polydispersity of the particles. SANS and SAXS can subsequently be evaluated to obtain the fine structure but with a fit procedure that starts directly from the cryoTEM results.
3. Combination of small-angle scattering with simulations. Recent progress in MD-simulations now leads to the prediction of equilibrium structures which in turn can directly be compared to SANS or SAXS. We used this method to evaluate the spatial structure of dendrimers and more recently the structure of micelles by anomalous small-angle neutron scattering. The combination of simulations and SANS/SAXS allows us to assess the influence of correlated fluctuations on the measured scattering function. In case of micelles this influence is shown to be very important at higher scattering angles.

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Modeling polymer nanocomposite structure and dynamics**Sanat K. KUMAR**

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Large-scale computer modeling is a well-developed third tool in the arsenal of the polymer scientist, one which can readily complement theory and experiments. The two cases we shall focus on in this talk are: (i) The dispersion and self-assembly of nanoparticles tethered with polymer chains in a polymer matrix to create nanocomposites with desired properties. We ask why spherical particles spontaneously assemble into non-spherical superstructures ? (ii) The flow behavior of polymer melts filled with spherical nanoparticles. Recent experimental results suggest that the viscosity of filled melts can be larger than or smaller than that of the pure polymer. In some cases both dependences can be seen in the same system as a function of nanoparticle loading! We attempt to understand these unusual results through the device of large scale Molecular Dynamics simulations, and then use these results to organize all available experimental data into what appears to be “universal” behavior.

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SANS studies on the effect of organic matter on calcium-phosphate mineralization in order to elucidate the scaling of RO-membranes in desalination of wastewater

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Reclaimed municipal wastewater is considered today as an important source for maintaining adequate fresh water supply for growing populations, especially in arid and semi-arid areas. Major limitations of using membrane-based desalination techniques are biofouling and calcium phosphate scaling. The formation of biofilm and scaling is the topic of our research. In particular we are exploring the effect of components representing the biofilm on calcium phosphate mineralization at a molecular level, i.e. the mineralization of hydroxyapatite on biopolymers which are dissolved in the bulk as monomers or on biopolymers that are attached on particles such as modified gold nanoparticles in a model solution simulating secondary waste water effluents (SSE). In a previous study we have used Langmuir Blodgett pressure area isotherms to study these effects [1]; in this study we present SANS, which is a promising tool as demonstrated in the similar field of biomineralization [2,3]. We studied the mineralization in diluted solutions of several proteins such as BSA, lysozyme, and fibrinogen as well as the polysaccharide alginic acid in SSE as well as the behavior of the biopolymers in salt free water using SANS and USANS techniques delivering information on particles of sizes between the order of 10 and 10⁴ Å and their evolution with time. We also widely applied contrast variation of aqueous H₂O/D₂O mixtures in order to identify the particles.

This work is part of a joined German-Israeli Cooperation in Water Technology Research and is funded by the Ministry of Science, Culture and Sport (MOST) and the Bundesministerium für Bildung und Forschung (BMBF).

- [1] Z. Steiner, H. Rapaport, Y. Oren, and R. Kasher, *Environmental Science & Technology* **44**, 7937 (2010).
- [2] V. Pipich, M. Balz, S.E. Wolf, W. Tremel, and D. Schwahn, *J. Am. Chem. Soc. (JACS)* **130**, 6879 (2008).
- [3] A. Heiss, V. Pipich, W. Jahnen-Dechent, and D. Schwahn, *Biophysical Journal* **99**, 3986 (2010).

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Structural changes in epoxy-based gels induced by external stimuli investigated by small-angle neutron scattering

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Polymer gels are crosslinked polymers (polymer networks) swollen in a solvent. It is well-known that small-angle X-ray and neutron scattering (SAXS/SANS) from polymer networks swollen in good solvents (gels) is governed by frozen and dynamic heterogeneities, respectively, originating from spatial distribution of network junctions and thermal movement of polymer segments [1]. On the other hand, if solvent is good only for some of network building blocks these contributions might be superimposed by heterogeneities due to nanophase separation of the system into solvent-rich and solvent-poor domains [2].

We have prepared series of epoxy networks by end-linking reaction of α,ω -diamino terminated poly(oxypropylene)-*block*-poly(oxyethylene)-*block*-poly(oxypropylene) (POP-POE-POP) and diglycidyl ether of Bisphenol A propoxylate (PDGEBA). The networks were swollen to equilibrium in deuterated methanol (CD_3OD) and heavy water (D_2O), respectively. Whereas methanol is good solvent for all the blocks built into the network (POE, POP and PDGEBA), water is good solvent for POE only. Consequently, SANS patterns of the networks swollen in CD_3OD and D_2O differ significantly. In methanol the scattering patterns expected for polymer network swollen in good solvent were found. By contrast, in water nanophase separated structure consisting of water-rich and water-poor domains was revealed [2].

Polymer gel formation is a result of delicate interplay between elasticity of crosslinked polymer chains and thermodynamic compatibility of polymer network blocks with solvent. Therefore, polymer gel responds very sensitively to changes of external parameters (temperature, pressure, chemical composition of surrounding medium, presence of species specifically interacting with chemical moieties attached to gel network structure, etc.) by adaptation of its structure. In this communication SANS study of structural changes in epoxy-based gels induced by external stimuli (change of temperature, pressure, pH, electrolyte and surfactant concentration) will be discussed.

[1] M. Shibayama, Bull. Chem. Soc. Jpn., **79**, 1799 (2006).

[2] I. Krakovský, N.K. Székely, Eur. Polym. J., **47**, 2177 (2011).

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Polymer-particle nanocomposites: influence of nanoparticles dispersion, of polymer chains conformation and of filler orientation on the macroscopic properties of materials

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We work on nanocomposites formed by inclusion of nanoparticles in a polymer matrix using different strategies to adjust the dispersion for correlating the local structure (dispersion, orientation) of the particles and the chains conformation with the macroscopic reinforcement. The first processing way (mixing silica with polystyrene (PS)) permits to control the filler connectivity inside the polymer matrix: using a combination of scattering (SAXS) and microscopy (TEM), we show that the particles organizes as non connected finite size fractal aggregates at low silica concentration, which percolates as a connected 3D filler network when the silica concentration increases [1]. The conformation of the chains, determined with neutron scattering (SANS) using the Zero Average Contrast method, is not modified by the filler [2-3] illustrating that chains deformation does not contributes significantly to reinforcement. For high deformations, reinforcement is dominated by filler connectivity and non affine reorganization of filler network while at low deformation it could be attributed to long range modification of the chains diffusion/reputation modes [4-5]. The second tuning way (polymer-grafted silica mixed with matrix chains [6-7]) permits to control the local dispersion of the particles inside the matrix with the mass ratio between grafted and free PS chains: when the grafted chains are smaller than the free ones, the particles organizes as dense aggregates and when both chains are similar, the particles are individually dispersed in the matrix [8]. Using a specific neutron contrast variation (SANS) method, we show that these dispersions can be related to a collapsed or stretched conformation of the grafted corona [9] while the elastic modulus seems to depend mainly on the local particle-particle interactions. Finally, using magnetic nanoparticles of maghemite, we succeeded in orientate the filler (grafted [10] or not) in a 1D network inside the PS matrix with an external magnetic field [11-13]. By following the evolution of the filler structure with SAXS and of the polymer chain deformation with SANS under stretching, we confirm that reinforcement at large deformation is mainly dominated by dynamical particle reorganization while polymer chain contribution appears to be rather limited.

[1] Jouault et al. *Macromolecules*, **42**, 2031 (2009). [2] Jouault et al. *Physical Review E*, **82**, 031801 (2010). [3] Jouault et al. *Macromolecules*, **43**, 9881 (2010). [4] Jouault et al. *Polymer*, **53**, 761 (2012). [5] Chevigny et al. *Journal of Polymer Sciences Part B: Polymer Physics*, **49**, 781 (2011). [6] Chevigny et al. *Soft Matter*, **5**, 3741 (2009). [7] Chevigny et al. *Polymer Chemistry*, **2**, 567 (2011). [8] Chevigny et al. *Macromolecules*, **44**, 122 (2011). [9] Chevigny et al. *Macromolecules*, **43**, 4833 (2010). [10] Robbes et al. *Soft Matter*, **8**, 3407 (2012). [11] Jestin et al. *Advanced Materials*, **20**, 2533 (2008). [12] Robbes et al. *Macromolecules*, **43**, 5785 (2010). [13] Robbes et al. *Macromolecules*, **44**, 8858 (2011).

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October 9, 2012, 14:00h

Physics of Life

Elastic and quasielastic neutron scattering investigation of biomolecules in glassy environments**Alessandro PACIARONI**

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Biomolecules exhibit intriguing properties when they are in the presence of non-aqueous media. In the past the features of proteins have been principally investigated when they are solved with water, which is the classic physiological milieu, while it is now becoming more and more clear that some crucial properties, such as thermal and chemical stability, can be greatly improved by properly choosing their molecular environment. In this respect, one can roughly distinguish two different classes of media, i.e. plasticizers and stabilizers. The former class is made of compounds that enhance the protein flexibility. Water is the archetype of plasticizers, as it is crucial to activate the dynamics of biomolecules on wide temporal and spatial ranges. On the other hand, stabilizers prevent protein to jump between the conformational substates, thus inhibiting the relative dynamical processes. Here we show how elastic and quasielastic neutron scattering technique has been successfully used to link dynamical features of proteins to their thermal stability properties, and what is the role of the molecular environment around the biomolecule's surface. Key concepts such as protein "dynamical transition temperature" and "glass transition temperature" are also discussed and revised thanks to the comparison with the case of common glassformers.

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Proteins in solution: Determination of domain structure and dynamics**Ralf BIEHL¹**

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The biological function of enzymes is often related to large-scale domain motions, which are sometimes induced by the binding of a substrate. These configurational changes are observed by methods like x-ray crystallography giving a static image of the protein structure and suppressing large-scale domain motions. Configurational changes can be related to the substrate binding or the crystal packing, which favors specific configurations. The structure of a protein in solution can deviate from the crystal structure, but also allows fluctuations between different configurations. Are these fluctuations important for protein function?

We present here examples of large-scale structure determination by SANS and SAX combined with Neutron Spin Echo Spectroscopy to determine the dynamics of the proteins on nanometer length scale and a timescale up to several hundred nanoseconds.

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Protein self-diffusion in crowded solutions

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Quasi-elastic neutron backscattering is an ideal tool to study the self-diffusion of nanometer-scale soft matter such as proteins in solution. By probing and analyzing the self-diffusion in aqueous solutions of the model globular protein bovine serum albumin (BSA) using backscattering, we establish and validate a framework [1] separating internal dynamics from motions of the entire protein. Using this framework, the full dynamics of soft nanoscale biological objects on nanosecond time scales can be accessed in the native environment of aqueous solutions.

First, we present a systematic study of the self-diffusion of BSA in aqueous solution as a function of the protein volume fraction ϕ , investigating the effect of macromolecular crowding [1]. The measured diffusion coefficient $D(\phi)$ strongly decreases with increasing ϕ . We briefly outline the complex methodological issues arising, such as the separation of the rotational $D_r(\phi)$ and translational $D_t(\phi)$ contributions to $D(\phi)$. The resulting $D_t(\phi)$ of the proteins is found consistent with colloid short-time self-diffusion models of hard spheres within experimental accuracy. Second, we report further experiments systematically exploring the influence of temperature and showing that protein denaturation can be monitored and analyzed consistently combining quasi-elastic and elastic data [2]. Third, we give an outlook on recent results on protein dynamics with a controlled variation of the inhomogeneous surface charge of the protein. Finally, we also draw future perspectives with new-generation backscattering spectrometers.

[1] F. Roosen-Runge, M. Hennig, F. Zhang, R. M.J. Jacobs, M. Sztucki, H. Schober, T. Seydel, F. Schreiber; *Proc.Natl.Acad.Sci. (USA)* **108**, 11815 (2011).

[2] M. Hennig, F. Roosen-Runge, F. Zhang, S. Zorn, M. W. A. Skoda, R. M. J. Jacobs, T. Seydel, F. Schreiber; *Soft Matter* **8**, 1628 (2012).

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Proteins need it wet. Do they ?François-Xavier GALLAT^{1,2}, **Martin WEIK**¹¹Institut de Biologie Structurale CEA-CNRS-UJF, Grenoble, France²Institut Laue-Langevin, Grenoble, France

As molecular workhorses, proteins fulfill a multitude of tasks that keep the complex machinery in biological cells alive. Soluble proteins bath in water and the layer of hydration covering their surfaces is esteemed crucial for biological activity [1]. Do proteins really need it wet? In order to answer this question, we investigated nano-hybrids of polymer-coated myoglobin that contain neither water nor any other solvent. Yet, these nano-hybrids surprisingly display biological activity. By examining deuterium labeled hybrids with neutron scattering, we revealed that the polymer coating exhibits similar flexibility than does hydration water, thus allowing the proteins they wrap to undergo motions necessary for biological activity [2]. These results highlight the potential for polymer-protein hybrids in that they show that the polymer coating can functionally and dynamically substitute for water or any other solvent and generate a new species that may be able to function in anhydrous environments, such as those frequently encountered in industry.

These pieces of research are the fruit of collaborations with colleagues whose names appear in references 1 and 2. We are deeply indebted to them.

- [1] Gallat, F.-X., Laganowski, A., Wood, K., Gabel, F., van Eijck, L., Wuttke, J., Moulin, M., Härtlein, M., Eisenberg, D., Colletier, J.-P., Zaccai, G., Weik, M. *Biophys. J.* **103**, 129 (2012).
- [2] Gallat, F.-X., Brogan, A.P.S., Fichou, Y., McGrath, N., Moulin, M., Härtlein, M., Combet, J., Wuttke, J., Mann, S., Zaccai G., Jackson, C.J., Perriman, A.W. and Weik, M. A polymer surfactant corona dynamically replaces water in solvent-free protein liquids and ensures macromolecular flexibility and activity. *Submitted*.

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October 9, 2012, 16:10h

Physics of Life

Frontiers in membrane biophysics

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One of the major challenges of modern physics is to contribute to biology and life-sciences. Modern neutron sources are premier research tools to tackle this important challenge. Neutron beams allow us to study molecular structure, dynamics and interactions in membranes in-situ under physiological conditions. I will talk about current topics in membrane biophysics and the associated experimental challenges. These challenges include the available neutron flux, however, more importantly the accessible length and time scales and fundamental interactions between the neutron probe and disordered and fluctuating materials.

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Collective dynamics in DNA hydration water and intracellular water in living cells

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One of the challenges of major interest in modern biophysics is the understanding of the strong interplay between biomolecules and hydration water structure and dynamics. Indeed it is well known that proteins and nucleic acids need a minimum quantity of water to achieve their conformational stability and biological functionality. A vast literature on incoherent dynamics of hydration [1] and intracellular [2] water pointed out peculiar features compared to pure water. On the contrary little is known about the coherent counterpart.

The existence of coherent collective density fluctuations at THz frequencies in biological materials was proved by a pioneering experiment on hydrated C-Phycocyanin [3]. Only more recently, thanks to state-of-the-art neutron instrumentation, a study on hydration water of Ribonuclease A [4] revealed that high-frequency collective modes do propagate also in the protein hydration shell. Compared to bulk water, the relevant dispersion curves are almost unaffected by the interaction with the protein, whereas the modes damping factors appear markedly increased. The latter experimental observation is discussed as a dynamic signature of the disordering effect induced by the protein on the local structure of water, is in strong agreement with density of vibrational states measurements [5], and establishes a remarkable analogy with the dynamics of glassy systems.

In such a framework, we present here an extended study of coherent collective dynamics in more complex systems, namely DNA hydration water [6] and intracellular water in fully-deuterated living *Escherichia Coli* cells at physiological conditions [7], by means of ultrasonic and neutron scattering measurements. Such an analysis allows to compare these systems to bulk and protein hydration water, to discuss the biological relevance of collective modes and to extract information about the elasticity of biological living matter in the MHz and THz frequency range.

[1] P. Ball, Chem. Rev., **108**, 74-108 (2008) and references therein.

[2] M. Jasnin et al., EMBO Reports, **9**, 543-547 (2008) and references therein.

[3] M-C. Bellissent-Funel et al., Biophys. J., **56**, 713-716 (1989).

[4] A. Orecchini et al., J. Am. Chem. Soc., **131**, 4664 (2009).

[5] A. Paciaroni et al., Phys. Rev. Lett., **101**, 148104 (2008).

[6] E. Cornicchi et al., J. Chem. Phys., **135**, 025101 (2011).

[7] A. Orecchini et al., J. Phys. Conf. Series, **340**, 012091 (2012).

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Domain motions in the mercuric ion reductase - MerA

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Bacterial resistance to inorganic and organic mercury compounds is mediated by the *mer* operon, a suite of genes typically located on transposons or plasmids. The *mer* operon consists of several structural genes encoding proteins involved in Hg(II) transport, Hg(II) reduction and Hg-C bond cleavage of organomercurials [1,2]. We have chosen to focus on the structure and dynamics of the mercuric ion reductase, MerA, an enzyme responsible for catalyzing the NADPH-dependent reduction of Hg(II) to uncharged, and much less harmful, Hg(0). This enzyme consists of a large homodimeric catalytic core unit (core-MerA) which is connected to two small metallochaperone-like N-terminal domains (NmerA) by flexible linkers [2]. Studies of intact full-length MerA have been hampered by proteolysis in the flexible linkers, however studies of the separately expressed core-MerA and NmerA domains have shown that NmerA can bind Hg(II) with its pair of cysteines and deliver it to core-MerA for reduction [3]. For this reason it is important to understand the internal dynamics of the intact full length protein, in particular the motions of the NmerA domains relative to the core of the enzyme. We have recently expressed pure, full-length MerA [4] and here address this question using neutron spin-echo spectroscopy, a technique that has previously been used to gain valuable insight into the internal dynamics in proteins [5].

[1] A.O. Summers, *J. Bac.*, **174**, 3097 (1992).

[2] T. Barkay *et al*, *FEMS Microbio. Rev.*, **27**, 355 (2003).

[3] R. Ledwidge *et al*, *Biochemistry*, **44**, 11402 (2005).

[4] A. Johs *et al*, *J. Mol. Biol.*, **413**, 639 (2011).

[5] R. Biehl *et al*, *Biophys. J.*, **99**, 2309 (2010).

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October 10, 2012, 8:30h Advanced Instrumentation for Soft Matter Research

Views from a soft matter neutron instrument scientist

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The ability of neutron instrumentation to enable access to the structure and dynamics in soft condensed matter systems has proved to play an important role. Advances in technology and experimental methods, theory and simulation, and the search for new ‘smart’ materials and systems to address social and global challenges, continue to expand the research in this field. In some cases neutrons can provide more detailed and/or different information, but they are still not necessarily all that is needed to fully characterize and understand such systems. Trends in our fields are constantly changing, so are user types and neutron usage, demands on sample environment, etc., all of which need re-consideration for existing sources but probably more with the advent of new source construction.

Albeit structural characterization being the initial step to understanding soft materials, ultimately many of their macroscopic properties such as viscosity, conductivity or enzymatic activity are related to their molecular motions. Focusing primarily on the aspect of soft matter dynamics, I will give my personal perspective on where things are going based on what I have seen during the last ten years, and what things we need to consider for the future. From a broad perspective, how can we further exploit neutron scattering effectively to answer new important questions in our field?

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October 10, 2012, 9:00h Advanced Instrumentation for Soft Matter Research

New developments in neutron backscattering with applications in soft matter and perspectives for studies of slow dynamics

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Several new neutron backscattering spectrometers came on line during recent years and others are projected. After a brief progress review on instrumentation - with emphasis on the new IN16B backscattering spectrometer at ILL - we present some of our recent and ongoing scientific applications of neutron backscattering in the field of soft matter and slow dynamics. The examples chosen cover dynamics in confinement, local dynamics of polymers and some studies related to energy materials. We try to conclude on the technical needs in the field of slow dynamics concerning high resolution spectroscopy and to vision possible instrumental progress.

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October 10, 2012, 9:30h Advanced Instrumentation for Soft Matter Research

Development of multi-spectral direct geometry chopper spectrometers for the future European Spallation Source

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Within the ESS Design Update Phase Programme funded by the German Federal ministry of education and research, we investigate the performance of a set of spectrometer concepts at the future long pulse source of the ESS, which promises the applicability to a wide manifold of scientific activities of research: strongly correlated electron materials, disordered systems, functional materials, magnetism, soft-matter and biophysics.

Here we present the current state-of-the-art in the study of the instrument conceptual design.

The chopper system is a crucial aspect in order to achieve useful resolution for a manifold of scientific purposes, make an efficient use of the flux provided by the source, by means of the Repetition Rate Multiplication and reduce contaminations due to very fast and very slow neutrons. We present the chopper layout under investigation and the method for the RRM implementation, based on the commensurate choppers technique.

The useful beam at the sample position is an important figure of merit in the evaluation of the instrument performance and can be a limit to possible scientific applications in several circumstances, when high flux is requested. The problem of the beam transport to the sample is under consideration, in order to transport as much as possible of the phase space density provided by the source, maintaining as low as possible the back-ground contamination coming from the direct view of the pulsed source.

The technical implications of the polarization analysis option are discussed.

The necessary requirements for the detector development in terms of spatial and time resolution are already evaluated and the implications deriving from technical limitations on this task are discussed.

Preliminary results of virtual experiments performed by means of beam neutron ray-tracing simulation packages are presented, especially focusing on the resolution function evaluation.

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October 10, 2012, 9:50h Advanced Instrumentation for Soft Matter Research

KWS-2 – the high-intensity / wide Q-range small-angle neutron diffractometer with tunable resolution at the FRM II optimized for soft-matter and biology

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KWS-2 is a classical pinhole SANS diffractometer where the exploration of wide momentum transfers Q , from 6×10^{-4} to $0.5 \text{ \AA}^{-1}$, is possible by the variation of the sample-to-detector distance between 1m and 20m and of the wavelength between $4.5 \text{ \AA}$ and $20 \text{ \AA}$. The instrument was recently upgraded and optimized towards high-intensity/extended Q -range investigations with tunable resolution of mesoscopic structures and structural changes due to rapid kinetics in soft-matter and biology. The high-intensity mode is sustained by (i) the high flux supplied by the cold neutron source of FRM II, (ii) the high efficiency ($>95\%$ for $\lambda > 4.5 \text{ \AA}$) ^6Li -scintillation detector, (iii) the fast detection electronics enabling high counting rates up to 0.6 MHz , (iv) the high-intensity dedicated velocity selector ($\Delta\lambda/\lambda=20\%$), (v) the upgraded collimation system allowing for a routine use of large beam-size and (vi) the focusing elements – MgF_2 aspherical lenses – allowing for intensity gain compared to the conventional pinhole mode for the same resolution, due to increasing of the sample size (up to 5 cm in diameter). With these opportunities the study of rapid kinetic processes within the sub-second range became a routine option. A double-disc chopper enables the tuning of the resolution and an improved characterization of the scattering features within different Q ranges using the time-of-flight method. The available Q -range was extended towards low Q (up to $1.0 \times 10^{-4} \text{ \AA}^{-1}$) by means of MgF_2 lenses, which used in combination with the chopper (minimizing the chromatic aberrations and gravity effects) and a high resolution (0.5 mm) position-sensitive detector, enable exploration of sizes up to 1 micron in a direct easy-to-handle fashion. With all these upgrades allowing for the boosting of its performance KWS-2 will be routinely operational in complete multi-functional configuration – standard pinhole, extended Q -range, high-intensity and tunable-resolution modes – by the end of 2012. Near future upgrades will concern the improvement of the instrument performance for the exploration of short length scales typical for biological and semicrystalline systems. The extension of the Q -range towards $1 \text{ \AA}$ is foreseen by aiming to shorter wavelength (down to $\lambda=3 \text{ \AA}$) achievable by tilting the velocity-selector. Additionally, the unambiguous acquisition of weak coherent signals from small and/or highly diluted structures fully corrected of incoherent scattering background that typically prevails at high Q will be possible after the installation of a transmission polarizer which will be used in combination with a wide-angle ^3He spin analyzing cell. The instrument options and performance will be reported.

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October 10, 2012, 10:10h Advanced Instrumentation for Soft Matter Research

NREX - Neutron / X-ray contrast reflectometer

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NREX is a classical angle dispersive, fixed wavelength reflectometer at the cold neutron source of the FRM II in Garching/Munich. It is operated by the Max Planck Society. The instrument provides grazing incidence small angle scattering (GISANS), specular and off specular reflectometry all in polarized and non-polarized modes. These techniques are well suited to determine structural properties such as chemical aggregation, polymer and surfactant adsorption, interdigitation etc. in low dimensions (surfaces, interfaces and thin film systems) at solid/liquid and solid/air interfaces. With a conventional x-ray add on (Cu K α), the instrument offers the unique possibility to combine x-ray- and neutron-reflectometry in situ. The recent developments, exemplary measurements and future perspectives of NREX will be presented.

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October 10, 2012, 10:30h Advanced Instrumentation for Soft Matter Research

Measurement of transient domains in biological membranes using coherence length dependent neutron diffraction

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Clusters, rafts, nanodomains, and patches are a central issue in cell membrane studies; however, the experimental observation of rafts has proven to be challenging, as they are short-lived. In order for experimental techniques to unambiguously observe such structures, they must be capable of simultaneously accessing small (nanometer) length scales and fast (nano to microsecond) time regimes. We have developed a neutron scattering technique to study nanometer sized heterogeneities in membranes [1]. By tuning the coherence length of the neutron beam to match domain sizes, nanometer sized structures can be directly observed under physiological conditions. The measurements were conducted using a triple-axis neutron spectrometer at the CNBC at Chalk River and the coherence length of the neutron beam was controlled by varying the incident energy of the neutrons and the energy resolution of the spectrometer. To demonstrate the technique, we present the first direct experimental evidence for the co-existence of gel and fluid lipid domains in a single-component phospholipid membrane as it undergoes its main phase transition. The measured Bragg peaks correspond to the co-existence of nanometer sized structures, observed in both the out-of-plane and in-plane scans. This co-existence of gel and fluid domains is indicative of a first order phase transition, rather than the commonly accepted continuous transition defined by pseudocritical behaviour. This novel technique offers new opportunities for the study of rafts in membranes containing cholesterol, lipid mixtures, and, eventually, biological membranes.

[1] C.L. Armstrong, M. Barrett, L. Toppozini, N. Kučerka, Z. Yamani, J. Katsaras, G. Fragneto, M.C. Rheinstädter, “Co-existence of Gel and Fluid Lipid Domains in Single-component Phospholipid Membranes”, *Soft Matter*, **8**, 4687-4694 (2012).

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Chain dynamics in un-entangled polymer blends with dynamic asymmetry. A generalized Rouse incoherent scattering function based on the GLE formalism

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Recent molecular dynamics (MD) simulations in both bead-spring models [1] and atomistic blends [2] as well as different experimental investigations have put forward evidence that the chain dynamics of linear un-entangled polymers are drastically modified when they form part of dynamically asymmetric polymer blends. These are miscible polymer systems where the two components display very different mobility (or glass transitions temperatures). MD simulations show that this dynamic asymmetry between the two components induces strong non-exponentiality of the Rouse mode correlators corresponding to the fast component of the blend. This non-exponentiality is a signature of the breaking of one of the main assumptions of the Rouse model: *the time un-correlation of the external forces acting on the tagged chain*. Moreover, a scaling $\tau_p \sim (N/p)^X$ was reported [1], where τ_p is the relaxation time corresponding to the p-Rouse correlator and N the number of “beads” of the chain. The parameter X, strongly depends on the temperature, T, varying from $X \approx 2$ (Rouse prediction) at high T – where the dynamic contrast between the two blend components is very small – to $X \approx 3.5$ at rather low T, where the slowing down of the slow component gives rise to high dynamic contrast. These simulation results, obtained for a generic bead-spring model, suggest that the molecular weight dependence of the Rouse time τ_R (τ_p ; $p=1$) should also depend on temperature and be given by $\tau_R \sim N^X$. This behavior has been recently confirmed by dielectric spectroscopy in asymmetric blends of polyisoprene with different molecular weights and poly(tert-butylstyrene) [3].

The abovementioned results can be understood in a theoretical framework based on the generalized Langevin equation (GLE) formalism. In this framework, a direct and nontrivial correlation between the $X(T)$ parameter giving the molecular weight dependence of the Rouse time τ_R and the non-exponential parameter of the Rouse mode correlator ($p=1$) has been deduced [3]. This correlation is nicely corroborated by the MD simulation results. Here we show that a generalized Rouse incoherent scattering function can also be deduced with some approximations within the GLE formalism. The obtained expression reduces to the well know Rouse incoherent scattering function in the limit of pure Rouse behavior. The validity of the expression found is checked by neutron scattering data and fully atomistic MD simulations on poly(ethylene oxide)-poly(methyl methacrylate) blends, which were previously published [2].

[1] A. Moreno and J. Colmenero, Phys. Rev. Lett., **100**, 126001 (2008).

[2] M. Brodeck et al., Macromolecules, **43**, 3036 (2010).

[3] S. Arrese-Igor, A. Alegría, A. J. Moreno and J. Colmenero, Soft Matter, **8**, 3739 (2012).

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Scattering Intensity of Bicontinuous Microemulsions from Simulations at the Mesoscale**Matti PELTOMÄKI¹**, Daniel M. KROLL², Gerhard GOMPPER¹,¹Theoretical Soft Matter and Biophysics, Institute of Complex Systems, Forschungszentrum Jülich, 52425 Jülich, Germany²Department of Physics, NDSU Department 2755, North Dakota State University, Fargo, North Dakota 58108-6050, USA

Neutron scattering is an important tool to unravel the structure of complex fluids. A paradigmatic example are bicontinuous micremulsions in oil-water-surfactant mixtures, in which two intertwined networks of oil- and water-channels are separated by a surfactant monolayer [1].

We investigate the neutron scattering intensities of such bicontinuous microemulsions by Monte Carlo simulations of dynamically triangulated surfaces of variable topology [2,3]. We show that the scattering intensity in bulk contrast follows the Teubner-Strey expression [4], and extract the domain size and the correlation length from the bulk scattering peaks as a function of the bending rigidity and saddle-splay modulus of the surfactant monolayer, and of the surfactant density [3].

The results are compared to earlier theories based on Gaussian random field models [5]. In particular, we show [3] that the ratio of the correlation length and the domain size is well described by a linear combination of logarithmically renormalized bending rigidity and saddle-splay modulus. The prefactors in the linear combination appear universal.

The dependence of the correlation length on the saddle-splay modulus is in contrast to earlier theories predicting scattering intensities to be independent of it. Such predictions are often used to estimate the elastic coefficients of the lipid layer using scattering intensities. The consequences of the present finding for such interpretations are discussed.

[1] G. Gompper and M. Schick, *Self-Assembling Amphiphilic Systems*, in Phase Transitions and Critical Phenomena, Vol. 16, edited by C. Domb and J. Lebowitz (Academic Press, London, 1994).

[2] G. Gompper and D.M. Kroll, Phys. Rev. Lett. **81**, 2284 (1998).

[3] M. Peltomäki, G. Gompper, and D.M. Kroll, J. Chem. Phys. **136**, 134708 (2012).

[4] M. Teubner and R. Strey, J. Chem. Phys. **87**, 3195 (1987).

[5] P. Pieruschka and S. A. Safran, Europhys. Lett. **31**, 207 (1995).

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Mesoscale Simulations of Multi-Domain Protein Dynamics**Simon POBLETE¹**, Roland G. WINKLER¹, Gerhard GOMPPER¹

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The movement of the subdomains of a protein can play a fundamental role in functions like catalysis, regulation of activity or formation of protein assemblies, to name a few. Neutron spin-echo spectroscopy has been shown to be a powerful analysis tool to study such motions, since it is able to resolve time and length scales on which this dynamics develops. Such technique has been applied in the study of proteins like alcohol dehydrogenase (ADH) and phosphoglycerate kinase (PGK) [1,2].

Computer simulations can provide a deeper insight of the protein dynamics and complement the experimental analysis with, for example, details about the different contributions to the interdomain motion. In this context, our goal is to contribute to the understanding of the function of the MerA protein, a fundamental element in the mercury reduction process of certain bacteria. We employ a highly coarse-grained model at a mesoscopic scale, composed of three subdomains which resemble the basic geometry of the protein: two end groups attached to the protein core by short polymer chains. The simulation is performed using Multiparticle Collision Dynamics [3], a particle-based simulation approach able to capture the hydrodynamic interactions between the protein domains.

We analyze dynamic features of the protein domains, like the diffusion coefficient, velocity and angular autocorrelation functions and hydrodynamic radii. In addition, we study the effect of the terminal motion, by contrasting two models with rigid and flexible linkers respectively. The effective diffusion coefficient, obtained from the intermediate scattering function, can be directly compared to experimental data.

[1] R. Inoue et al., *Biophys.* **99**, 2309 (2010).

[2] R. Biehl, M. Monkenbusch and D. Richter, *Soft Matter* **7**, 1299 (2011).

[3] G. Gompper et al., *Adv. Polym. Sci.* **221**, 1 (2009).

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Recent applications of time resolved SANS combined with a stopped-flow equipment**Isabelle GRILLO¹**¹Institut Laue Langevin, DS-LSS, Grenoble, France

Stopped-flow apparatus coupled with a large variety of detection techniques is one of the most frequently used instruments to study rapid kinetics. With the recent technical advances of small angle scattering beam-lines, the 10 last years have seen the development of combined stopped-flow and small angle neutron experiments. Time resolutions of the order of 50 ms allow one to follow the very early stages of the sample formation. Such studies may reveal pathways and intermediate states during phase transitions, which are of fundamental importance to understand and control the properties at equilibrium [1].

In recent years, the spontaneous formation and growth of vesicles has been extensively studied. Vesicles have been considered as model for biological membranes, and have been used in applications such as microreactor and for drug encapsulation and drug delivery. One major challenge such in formulations is to generate thermodynamically stable aggregates with a well-defined size. It has been shown that mixing single and double chain surfactants favor the spontaneous formation of vesicles. Herein, we are interested in the ternary system DDAB/C12E4/D2O. The dilute part of the phase diagram at equilibrium determined by combined DLS, SANS, surface tension and optical observations has revealed a rich phase behavior, where mixed micelles, very small vesicles (less than 10 nm) and multi layer large vesicles are formed as the amount of DDAB is increased [2].

Time-resolved SANS experiments with a time resolution of 100ms was performed to follow the formation of the different types of aggregates. Moreover, deuterated surfactants were used to isolate the signal from DDAB or C12E4 and establish the diffusion rates of the two surfactants onto the objects. The experiments have demonstrated that the two molecules were evolving in parallel at the same rate, passing through various intermediate states before to reach the equilibrium. The formation time depends strongly of the nature of aggregates.

With this challenging experiment, working at low volume fractions (<0.1%) in contrast match conditions, it is hoped to demonstrate the potential of the new generation of SANS spectrometers related to biological and soft matter systems.

[1] I. Grillo, COCIS, **14**, 402 (2009).

[2] I. Grillo et al, Langmuir, **25**, 3932 (2009),

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**Flow-induced polymer crystallization
- effects of molecular weight on shish-kebab formation -**

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It is well known when polymers are crystallized under flows they show a very different morphology from that in quiescent crystallization: the so-called shish-kebab structure which consists of extended chain crystal (shish) and folded chain lamella crystals (kebabs) periodically attached along the shish. This structure is believed to be a structural origin of ultra-high modulus and ultra-high strength fibers. Therefore, extensive studies have been made on the shish-kebab structure, however, its formation mechanism is not still clear.

In this work we have studied the role of high and low molecular weight components for the shish-kebab formation. In a previous paper [1], we have studied role of high molecular weight component in the shish-kebab formation using SANS and SAXS. We prepared a blend of low molecular weight deuterated polyethylene (DPE, $M_w=200000$) and high molecular weight protonated PE (HPE, $M_w=2000000$, $C=3$ wt%) and drew the blend at a temperature just below the melting temperature. Small- and wide-angle neutron scattering as well as small- and wide-angle X-ray scattering measurements were performed on this sample in a very wide Q range from 2×10^{-4} to $3 \text{ \AA}^{-1}$. The data were analyzed in terms of the multicore-shell cylinder model and found that the high molecular weight component was included in shish (extended chain crystal) in nm scale and large shish-like structure (large fibril structure) in μm scale. However, it was reported [2] that low molecular weight components were included in shish more than high molecular one, which seemed to be completely opposite to our results. In order to disclose the contradiction we have studied again effects of high and low molecular weight components for shish-kebab formation by SANS and SAXS. In the study we prepared blends of DPE ($M_w=600,000$) and HPE ($C=3$ wt%) for various molecular weights of HPE, and drew at 125°C at very slow drawing rate. It was found that the low molecular weight component was merged into shish in the late stage of drawing process more easily than the high molecular weight component, resulting that low molecular weight component are included more than the high molecular component. In the meeting we will discuss the formation mechanism of shish-kebab during the drawing process of PE at a temperature just below the melting temperature.

[1] Kanaya, T.; Matsuba, G.; Ogino, Y.; Nishida, K.; Shimizu, H. M.; Shinohara, T.; Oku, T.; Suzuki, J.; Otomo, T. *Macromolecules* **2007**, 40, 3650-3654.

[2] Kimata, S.; Sakurai, T.; Nozue, Y.; Kasahara, T.; Yamaguchi, N.; Karino, T.; Shibayama, M.; Kornfield, J. A. *Science* **2007**, 316, 1014-1017.

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**Kinetics of collapse and aggregation in micellar solutions
of thermoresponsive triblock copolymers – a time-resolved SANS investigation**

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Thermoresponsive, polymeric hydrogels respond in a controlled and reversible way with a volume change to a small change of temperature across the cloud point. These switchable and nanostructured materials are of great interest, e.g. for controlled molecular ultrafiltration. A widely used thermoresponsive polymer is poly(N-isopropylacrylamide) (PNIPAM) which exhibits a cloud point at 32 °C. We investigate self-assembled, physically crosslinked thermoresponsive hydrogels formed by amphiphilic, symmetric triblock copolymers having short, fully deuterated polystyrene (P(S-*d*₈)) end blocks and a large (PNIPAM) middle block [1].

Small-angle neutron scattering (SANS) with contrast matching allowed us to reveal the core-shell structure of the micelles as well as the network structure. We found that, at the cloud point, the shell collapses and the distance between the P(S-*d*₈) cores shrinks abruptly. Since the building blocks of the micellar network – the micelles – are very small (radius < 20 nm), we expect very short switching times. Using in-situ, real-time SANS during a temperature jump across the cloud point, we characterized the collapse and the subsequent aggregation behavior [2]. The collapse of the micellar shell is very fast (< 1 s). The aggregation process of the collapsed micelles is complex and involves several steps, such as the formation of small and loosely packed aggregates, their densification and eventually their coagulation. The pathway of the process as well as the final structure depends on the polymer concentration as well as on the target temperature. Scattering techniques can thus give detailed information on the structure and dynamics as well as on the kinetics of switching.

[1] J. Adelsberger, A. Laschewsky, P. Müller-Buschbaum, C.M. Papadakis et al., *Macromolecules*, **43**, 2490 (2010).

[2] J. Adelsberger, A. Laschewsky, P. Müller-Buschbaum, C.M. Papadakis et al., *Macromolecular Rapid Communications*, **33**, 254 (2012).

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Kinetics of the collapse transition of poly(2-oxazoline)s in aqueous solution

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At their cloud point, thermo-responsive polymers react strongly to a temperature stimulus, e.g. with a discontinuous change in conformation and solubility. Poly(2-oxazoline)s (POx) are very versatile and attractive polymers of this class, as their cloud point can be tuned in a wide range by including hydrophobic moieties. Along with their excellent biocompatibility, this makes them attractive in medical applications, e.g. as drug delivery agents. To characterize the nature of the phase transition for various amounts of hydrophobic moieties, we have investigated aqueous solutions of poly(2-iso-propyl-2-oxazoline)₅₀ (PiPrOx₅₀), and gradient copolymers P[iPrOx₄₈NOx₂]_{grad} and P[iPrOx₄₆NOx₄]_{grad} which contain hydrophobic (2-*n*-nonyl-2-oxazoline) monomers (NOx). Using small-angle neutron scattering (SANS), we have identified an intermediate regime just above the cloud point for the gradient copolymers [1]. In this intermediate regime, small precursor aggregates, formed already below the cloud point coexist with few large aggregates. The latter dominate only at higher temperatures. To investigate the stability of these small precursor aggregates, we performed temperature jumps from a temperature below the cloud point into the intermediate regime and followed the structural changes using time-resolved SANS. We found that for both P[iPrOxNOx]_{grad} samples, the precursor aggregates form within ~1 min and are stable; moreover, no large aggregates form during the time of observation (~45 min). The surface of the large aggregates is initially a surface fractal, then smoothens before a surface concentration gradient develops. Quenches to temperatures far above the cloud point revealed that both the kinetics of formation of the large aggregates and the final conformation of the small precursor aggregates strongly depend on the target temperature of the jump and the amount of hydrophobic moieties incorporated into the chain: Whereas a higher amount of hydrophobic moieties leads to larger aggregates, high quenching depths lead to a stronger collapse and smaller aggregates. Time-resolved, in-situ SANS thus reveals detailed information about the collapse and aggregation behavior in dependence of the chain architecture.

[1] S. Salzinger, S. Huber, S. Jaksch, P. Busch, R. Jordan, C. M. Papadakis, *Colloid Polym Sci*, **290**, 385 (2012).

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Kinetic Processes

Formation of a multiscale aggregate astructure through spontaneous blebbing of an interface

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Various kinds of biological systems are spatially and temporally ordered under non-equilibrium conditions, which is one of essential features of lives. Softmatters mimicking biological properties, such as spontaneous motion and self-organizations, are a field of science for understanding in nature of lives, since essentially the same physics are involved in these systems.

So far, we have showed a non-biological system to mimic amoeba-like blebbing motion, which is the spontaneous motion of an interface under a far-from-equilibrium condition. [1] When an organic phase (tetradecane including parmitic acid, PA) is deposited to float on an aqueous phase (water including stearyl-trimethyl-ammonium chloride, STAC), the interface between them deforms locally and repeatedly. We interpreted the origin of the interfacial motion as follows; STAC molecules pass through the interface, and elastic aggregates are formed continuously with tetradecane and PA. The aggregate is pushed out by the newly formed aggregates, which is stretched by increasing internal pressure and bleb grows. Subsequently, it starts to collapse when the stress within it exceeds a certain critical value, and leads to the failure of homogeneous squeezing of the droplet.

In this study, a nano-scale structure of the gel-like aggregates formed at the interface is observed by micro-beam SAXS, which indicates a highly-ordered lamellar structure. The mean repeat distance of the lamellar structure is about 30 nm, which is unexpectedly larger than that in an equilibrium phase in typical water, oil, surfactant and co-surfactant systems. Thus we concluded that the lamellar structure was conformed only under non-equilibrium conditions. This process, the construction of the ordered structure and the evacuation from the moving interface, is analogous to the construction and destruction of actomyosin gel to drive the extension of pseudopods in the amoeboid movement.

[1] Y. Sumino, et al., Phys. Rev. E **76**, 055202(R) (2007); J. Phys. Chem. B, **113**, 15709 (2009); Soft Matter, **7**, 3204 (2011); Langmuir **28**, 3378 (2012).

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Dynamics of polymer/ polymer nano-composites**Debsindhu BHOWMIK¹**, Arantxa ARBE², Juan COLMENERO^{1,2,3}, Josetxo POMPOSO³¹Donostia International Physics Center, 20018, San Sebastián, Spain²Centro de Física de Materiales, CISC-UPV/EHU, 20018, San Sebastián, Spain³Departamento de Física de Materiales, UPV/EHU, 20018, San Sebastián, Spain

The combination of polymers with nano-particles (NPs) has opened up new possibilities to engineer different compounds, useful in diverse emerging domains– from nano-optics, nano-electronics to nano-medicine etc [1]. One among their several unexpected effects, is the improvement of mechanical properties and processability of structural materials based on polymers. Both directly related to the dynamics- catch attention because of their high potential industrial impact. These functional NPs are fundamental units of beneficial blends. Interesting results have been reported for nano-composites based on polystyrene (PS) NPs such as addition of only ~1wt% PS-NPs to natural rubber causes a decrease of >50% in the viscosity [2] [3].

In this work, we consider a nano-composite system consisting of soft polymethyl methacrylate (PMMA) NPs (~7nm) dispersed in polyethylene oxide (PEO) of similar dimensions. Previously we have characterized the dynamics of bulk PMMA [3], bulk PEO [4] and PEO under different confinement: hard confinement in Alumina pores [5] and blended with PMMA [6]. Here we have a system rich in linear chains– as usually nano-composites are- (75%PEO/ 25%PMMA-NPs) and another rich in NPs (75%PMMA-NPs/ 25%PEO). Using a sample where PEO is protonated and PMMA-NPs are deuterated, we follow the local dynamics of PEO. With inverse labeling, the dynamics of the hydrogens of PMMA-NPs is accessed. PMMA-NPs-rich samples are particularly interesting because of their analogy to the earlier investigated blend of linear chains of PMMA and PEO where confinement effects on PEO were observed [7]. The structure of these systems are also studied by SANS where the mixture of PEO(d) and PEO(h) had matched the protonated PMMA component and vice-versa. Our results show extremely stretched functions are observed for both components in both compositions. The dynamics of PEO in PEO-rich nano-composite is slower than bulk PEO but always much faster than the PEO in the NPs-rich nano-composite. There is a large dynamic contrast between the components (the dynamics of the PMMA-NPs are always much slower than those of PEO). The NP-structure of PMMA has a visible impact on the PEO dynamics (PEO dynamics in the nano-composite with 75%PMMA-NPs content is markedly slower than that of PEO in the blend with linear PMMA chains). The large impact of the NPs on PEO is indicated by 2 fold increase of R_g (radius of gyration) with respect to bulk.

[1] A. C. Balazs *et al*, Science, 314, 1107 (2006). [2] Ruiz de Luzuriaga *et al*, Macromol. Rapid Commun., 29, 1156 (2008). [3] J. A. Pomposo *et al*, Advanced Materials, 22, 3038 (2010). [4] A. -C. Genix *et al*, Macromolecules 39, 6260 (2006). [5] M. Brodeck *et al*, Journal of Chemical Physics 130, 094908 (2009). [6] M. Krutyeva *et al*, Journal of Chemical Physics 131, 174901 (2009). [7] A. -C. Genix *et al*, Physical Review E 72, 031808 (2005)

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Posters

**The Jülich Neutron Spin Echo Spectrometer (J-NSE):
dynamics with depth resolution**

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Neutron spin-echo (NSE) spectroscopy is neutron scattering technique with the highest energy resolution down to the sub- μeV range, which enable investigation of very slow dynamic processes in soft matter systems. Accessible time and length scales are relevant for observation of thermal fluctuations in mesoscopic systems.

High energy resolution, low background and good instrumental stability of J-NSE spectrometer at FRM II research reactor in Garching makes the instrument suitable for grazing incidence technique (GINSES). Along with conventional NSE spectroscopy GINSES developed to be used as push-button to resolve the depth dependent near surface dynamics.

Scientific applications of J-NSE instrument include dynamics of classical and critical microemulsions, microgels, polymer blends, polymers in solution and different confinement, membranes and much more. Some examples of recent experiments will be presented.

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Solvent distribution in block copolymer thin films

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Well-ordered structures formed by self-assembling of diblock copolymer have attracted increasing interest due to the potential applications, especially as templates for structuring inorganic materials [1]. However, the usual preparation methods often result in defects which hamper the application. Solvent vapor treatment is frequently used to anneal such defects [2]. The aim of the project is to elucidate the solvent distribution and the structure evolution in the lamellar poly(styrene-*b*-butadiene) (P(S-*b*-B)) thin film as a function of solvent content in the thin films. Time-of-flight neutron reflectometry (TOF-NR) at the instrument REFSANS together with the use of deuterated solvents may enable us to determine the asymmetry of the lamellae upon swelling and thus the distribution of the solvent [3].

We investigated fully protonated, lamellar P(S-*b*-B) diblock copolymer (28 kg/mol) and fully deuterated cyclohexane (CHX-*d*₁₂) as a solvent. At REFSANS at FRM II, NR curves in a q_z -range of 0-0.1 Å⁻¹ were measured at four incident angles between 0.15° and 1.2°. A custom-made vapor cell connected to a solvent bubbler was used to swell the film with CHX-*d*₁₂ vapor. The film thickness and the overall degree of swelling were determined in-situ using a VIS interferometer. The TOF-NR curve of the as-prepared film shows a first-order Bragg reflection at $q_z = 0.045$ Å⁻¹, thus evidence of parallel lamellar structures with a layer spacing of 140 Å. No second-order Bragg reflection is observed, in accordance with the system having symmetric lamellae where the PS and the PB parts have the same thickness. The TOF-NR curves of the swollen film show the shifts of the first-order Bragg reflections as a function of solvent content, reflecting the increase of lamellar thickness. A shape change of the Bragg reflection indicates a change of lamellar structure. Compared to the as-prepared film, the lamellar thickness of the subsequently dried film is increased.

[1] Hamley, I.W. *Progr. Polym. Sci.* **34**, 1161 (2009).

[2] Papadakis, C.M.; Di, Z.; Posselt, D.; Smilgies, D.-M. *Langmuir* **24**, 13815 (2008).

[3] Sepe, A.; Hoppe, E.T.; Posselt, D.; Moulin, J.-F.; Smilgies, D.-M.; Papadakis, C.M. *FRM II scientific highlight*, **93** (2011).

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In-situ light scattering during small angle neutron scattering experiments: First results and lessons learned

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Samples in soft matter research or biological samples sometimes show degradation on the time scale of hours. This is the reason why these samples have to be prepared freshly either on site or shortly prior to a neutron scattering experiment. For this reason, a control of the sample quality even during the neutron scattering experiment is desirable. In case the sample shows degradation features the neutron scattering experiment can be restarted with a fresh sample or the data can at least be carefully looked at.

So called in-situ techniques - meaning sample control during the neutron scattering experiments - are very suitable to serve this purpose but require the adaption of standard sample control techniques to the needs of the neutron scattering experiment. Among those techniques light scattering [1,2] techniques provide results on the sample quality with short acquisition times as compared to the typical small angle neutron scattering experiment. Optical fibers can deliver the required laser light to the sample cell in the neutron beam. Fiber connected collimators can be used to collect the scattered light and deliver it to detectors. This minimizes the mechanical manipulation necessary at the neutron scattering instruments.

In this presentation we focus on dynamic light scattering at multiple angles as a method and show that it can be nicely combined with the small angle scattering instrument KWS2 of the Jülich Centre for Neutron Science at the FRM II. First results on calibration samples will be presented to show its performance. First improvement of the set ups used so far will be discussed.

[1] S. Romer, C. Urban, V. Lobaskin, F. Scheffold, A. Stradner, J. Kohlbrecher, and P. Schurtenberger, *Journal of Applied Crystallography* **36**, 1 (2003).

[2] J. Kohlbrecher, A. Bollhader, R. Vavrin, and G. Meier, *Review of Scientific Instruments*, **78**, 125101 (2007).

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Focusing mirror VSANS diffractometer KWS-3: merging nano- and micrometer worlds.

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KWS-3 is a very-small-angle-neutron-scattering (VSANS) diffractometer using focusing mirror to achieve a high Q-resolution $4 \cdot 10^{-5} \text{Å}^{-1}$ built as a complimentary instrument aimed to fill the gap between the Bonse-Hart and pinhole cameras. A number of improvements that have been carried out during the last years and a high brilliance of the FRM-II reactor in Garching allowed for the increase in neutron flux by more than twenty times in comparison to the FRJ-2 reactor in Jülich; a further significant flux gain is expected after refurbishment the neutron guide. The Q-range of KWS-3 covers almost three decades - from $4 \cdot 10^{-5}$ to $3 \cdot 10^{-2} \text{Å}^{-1}$. VSANS applications can be found in different branches of soft matter, like colloid science (mixtures of particles, strongly correlated colloid crystals, particles of micron size, silicon macropore arrays), materials science (filled polymers, cements, microporous media) and polymer science (constrained systems, emulsion polymerization).

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The high resolution neutron backscattering spectrometer SPHERES**Michaela ZAMPONI¹, Gerald J. SCHNEIDER¹, Joachim WUTTKE¹**

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The SPectrometer for High Energy RESolution (SPHERES) is a third generation neutron backscattering spectrometer with focusing optics and a phase space transform chopper. It provides high energy resolution ($\sim 0.65\mu\text{eV}$) with a very good signal-to-noise ratio [1]. By filling the instrument housing with argon in order to avoid air scattering in the secondary spectrometer the signal-to-noise ratio has been increased by about 50%. A further gain in flux will be achieved by a more efficient phase space transform chopper which is currently under development. SPHERES is a versatile spectrometer for investigating atomic and molecular dynamics on a GHz scale. Typical applications include molecular reorientations and rotational tunneling, diffusion processes in various systems, relaxation in viscous liquids, dynamics in polymers and proteins. The high count rates also allow inelastic temperature scans and real-time kinetic experiments.

[1] J. Wuttke et al., Rev. Sci. Instr., in press, (2012).

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Design of a spin-echo-spectrometer for ESS**Stefano PASINI¹ and Michael MONKENBUSCH¹**¹Jülich Centre for Neutron Science, Forschungszentrum Jülich, Jülich, Germany

Within the German ESS design update project [1] we are investigating optimized designs for a high-resolution and a wide-angle spin-echo spectrometer (NSE). The design started from the high resolution type. The optimization was separated into two main parts: the beam transport from a (cold) moderator to the sample and the magnetic layout of the secondary spectrometer to enable the best resolution. The design of the beam transport and of the beam polarization is the same for both the high-resolution and the wide-angle NSE's. A straight, 8 cm x 8 cm neutron guide and a comparatively short (~2m) polarizing bender, with 4 channels and a m=4 FeSi multilayer coating provide the best performance. The moderator-detector distance may be chosen between 35 and 55 m. A system of 4 disc choppers to select the used wavelength frame and to suppress frame overlap is placed along the neutron guide section.

The optimization of the proper (secondary) spectrometer is limited by the achievable precision of the correction elements and by the current density they can withstand. On the same wavelength of the strategy used by Farago to device new IN15 coils that shall be implemented in the 2014 break of ILL operation, we have designed a magnetic layout for the high-resolution spin echo with minimal intrinsic field integral inhomogeneity. Moreover we have further enforced the condition on the stray field by compensating each precession coil with a concentric coil. Starting from the expertise on SNS-NSE a full operative, superconducting coil configuration is presented that is optimized for the simultaneous minimum of field-integral inhomogeneity, depolarization and stray-field. The resulting configuration has a 3 times reduced intrinsic inhomogeneities of field integrals and low stray fields allowing for a working NSE-configuration up to 2 Tm field integral. The superconducting configuration to be realized is more challenging than the SNS-NSE configuration, however, not so complicated or bulky to be prohibitive.

[1] BMBF-Projekt 05E10CJ1 "Verbundprojekt: Mitwirkung der Zentren der Helmholtz-Gemeinschaft und der Technischen Universität München an der Design-Update-Phase der ESS, Teilprojekt FZJ."

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Internal structure and dynamics of microgel films at solid interfaces

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Stimuli-responsive polymers alter their physico-chemical properties in response to changes in their environment (e.g. temperature, ionic strength) which leads to great interest in basic research and a lively discussion of potential technical applications. A prominent example are microgel systems prepared by Poly-(N-Isopropylacrylamide), PNIPAM, which undergoes a temperature induced phase transition at approx. 32 °C corresponding to a discontinuous shrinking with increasing sample temperature. Microgel particles can be organized as ultra-thin films at solid surfaces, e.g. silicon single crystal surfaces. This allows the formation of thermo-responsive surface coatings, where a simple temperature control can tune physical properties of the coating. The presence of the solid surface leads to changes in the shrinking behaviour and the LCST. For example, the LCST is reduced between 1°C and several °C with respect to the bulk phase. These findings raise the question how the interactions with the solid surface affect the internal structure and dynamics of the microgel particles. In a series of surface sensitive scattering experiments we addressed this question mainly focussing on the correlation length in the polymer network. Here, we present GISANS measurements done at the D16 instrument at the ILL investigating a microgel containing the monomer NIPAM, cross-linked with BIS (2 mol-% with respect to the mass of NIPAM). The low BIS content was chosen to obtain a less cross-linked polymer network to allow for the study of the shrinking behaviour. Additionally, first measurements addressing the internal dynamics in this system using neutron spin-echo spectroscopy under grazing incidence (GINSE) are discussed.

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Neutron scattering of self-healing model polymers

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Supramolecular polymers are an increasingly important class of polymers, where designed intermolecular interactions allow a specific tailoring of polymer properties. One of the most recent additions to this field are self-healing polymers, which base on the hydrogen-bonding interaction of groups on parts of the molecules. Neutron scattering measurements were performed on recently synthesized model systems, using DNA-inspired end-groups like Thymine-1-acetic acid, Diaminotriazine and 2-aminoethyl-imidazolidone with properties closer to natural materials. The backbone was polypropylene(glycol) and polyethylene(glycol) based polymer, respectively. The chemical modification of the end groups allowed to go from one to three reactive sites of hydrogen bonding, which shifted the association equilibrium to stronger bonding.

Both Small Angle Neutron Scattering (SANS) and Neutron Spin-Echo Spectroscopy (NSE) allowed to demonstrate that with decreasing temperature these polymers show an increasingly strong aggregation. Particularly, the NSE data in the nanosecond time domain revealed that the dynamics slowed down with decreasing temperature, significantly stronger than expected from the known temperature dependence of the solvent viscosity.

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Cononsolvency in aqueous solutions of P(S-*b*-NIPAM) diblock copolymers

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Thermoresponsive hydrogels are of great importance due to the wide range of applications that they find in various technological fields (e.g. as micro-switches). Poly(N-isopropyl acrylamide) (PNIPAM) has a very prominent place among these materials, exhibiting a lower critical solution temperature (LCST) of 32 °C. Recently, a strong interest has arisen regarding the phenomenon of cononsolvency in aqueous solutions of PNIPAM, which appears upon the addition of a second polar solvent (e.g. methanol) [1], resulting in a miscibility gap for specific mixing ratios. Different theoretical models [1,2] have been proposed to explain the mechanism behind this behavior, but still the picture is far from complete. Amphiphilic diblock copolymers of PNIPAM with a second hydrophobic part (e.g. polystyrene (PS)) exhibit the tendency to form core-shell (flower-like) micelles in aqueous solution with a thermoresponsive shell.

We report here on an investigation of the shell collapse and the subsequent aggregation. The experiment was realized in a stopped-flow set up with time-resolved small angle neutron scattering (SANS), where *d*-MeOH was added in various mixing ratios to micellar solutions of P(S-*b*-NIPAM) diblock copolymers in D₂O. For all chosen solvent ratios, the collapse of the shell has been found to be faster than 0.1 sec, while the growth of the clusters follows a logarithmic law. Moreover, as time evolves, the initially slightly elongated aggregates become more symmetrical (spherical). The amount of added *d*-MeOH had an influence on the time scales of the kinetic behavior of the cluster growth. Time-resolved, in-situ SANS thus allows the elucidation of the mechanisms of the phase transition.

[1] F. Tanaka et al., *Macromolecules* **44**, 2978 (2011)

[2] G. Zhang et al., *JACS* **123**, 1376 (2001)

[3] K. Troll, C.M. Papadakis et al., *Colloid Polym. Sci.* **286**, 1079 (2008)

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Exchange kinetics in aqueous dispersions of n-alkyl-PEO polymers by TR-SANS

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We present the equilibrium chain exchange kinetics of star-like n-alkyl-PEO5 (C_nH_{2n+1} -O-PEO5 with $n = 18/21/24/27/30$) polymeric micelles in water obtained by time-resolved SANS experiments [1]. To access the kinetics we applied a specific h/d labeling technique as already used in earlier studies. The n-alkyl-PEO polymers were taken as model system to study the effect of chain length and polydispersity on the exchange behavior. Structurally the n-alkyl-PEO polymers are hybrids between low-molecular weight surfactants and block copolymers as they carry a relatively short but strictly mono-disperse core-block ($M_w/M_n=1$). It was found that the kinetics extremely depends on alkyl chain length n . For instance, molecular exchange for C_{18} -PEO5 is too fast, whereas for C_{30} -PEO5 is too slow to be measured by TR-SANS at room-temperature. As expected from theory we observed a first-order kinetic process for C_{24} -PEO5 which is characterized by a single-exponential relaxation function. Both findings directly confirm that polydispersity of the core-forming block leads to a pseudo-logarithmic time dependence as previously found for block copolymers with finite polydispersity [2,3]. Furthermore, the relaxation is independent of concentration in the dilute limit supporting that single-unimer exchange is the dominant kinetic mechanism. Ideal conditions for TR-SANS measurements are obtained for the C_{27} -PEO5 polymer (goldilocks polymer). Real-time measurements have shown that chain exchange is moderate at room-temperature, but can be effectively accelerated by slightly increasing the temperature such that the full relaxation process conveniently can be followed within a time window of 30min. It was further observed that an increase in PEO molecular weight leads to a slow down of micellar exchange.

[1] T. Zinn *et al.*, *Soft Matter*, **8**, 623 (2012).

[2] S.-H. Choi *et al.*, *Phys. Rev. Lett.*, **104**, 1 (2010).

[3] R. Lund *et al.*, *Phys. Rev. Lett.*, **104**, 049902, Erratum: *Phys. Rev. Lett.*, **96**, 1-4 (2006).

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The influence of solid surface on the dynamics of polymer melt

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Understanding the structure and dynamics of polymer melt close to the confining solid surface (interface) and in the intermediate phase between the interface and a bulk phase (interphase) is important for applications in nanotechnology such as coatings for electrical devices, lubricants, and polymer nanocomposite materials. The aim of this work is to study the influence of the solid surfaces and their interaction with polymers on the dynamics of polymer melt by neutron scattering methods. The confining systems are presented by well-ordered cylindrical nanopores (2D confinement) of anodic aluminum oxide (AAO) [1].

First, we are focusing on the segmental dynamics on the local time scale. The experiments with poly(ethylene oxide) (PEO) demonstrate that the only surface layer with a thickness of approx. 1 nm is affected by the presence of the confinement [2]. This effect was attributed to the attractive interactions between AAO pore walls and polymer segments.

The investigation of dynamics of PEO confined in AAO at larger time scale (> 1 ns) demonstrates that the certain dynamical modes of the polymer chain are affected by polymer-wall interactions and/or modified confinement in the interphase [3]. In a first approximation the adsorption effect was modelled by a Rouse chain with pinned segments, such that on average all segments “touching” the surface are (transiently) pinned. To elucidate the influence of the surface/polymer interactions on the Rouse dynamics we study the polydimethylsiloxane (PDMS). The dynamics of the confined PDMS was found to slow down as compared to the bulk dynamics. The slowing down of PDMS dynamics in confinement is induced by the surface adsorption effect as we observed for PEO. We found that the dynamics of 70% of PDMS chains in AAO nanopores are influenced by the confinement and can be described by the Rouse model suppressing CM diffusion and 4 low-frequency Rouse modes. 30% of the chains show bulk-like Rouse behaviour.

[1] H. Masuda, K. Fukuda, *Science* **268**, 1466 (1995).

[2] M.Krutyeva et al. *J.Chem.Phys.* **131** (19), 174901 (2009).

[3] J.Martín, M.Krutyeva et al., *Phys.Rev.Lett.* **104**, 197801 (2010).

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Role of H-bonding on the structure and the dynamics of coconcentrated polymeric solutions**Guido GORACCI¹**, Arantxa ARBE¹, Juan COLMENERO^{1,2}, A.ALEGRIA¹¹Centro de Fisica de Materiales (CSIC-UPV/EHU) and Materials Physics Center (MPC),
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Water plays a fundamental role in biological processes. The deep understanding of such processes requires clarifying the structure and dynamics of water in a biological environment and how it interacts with the surrounding medium. Aqueous polymer solutions can be considered as suitable simple model systems to approach these questions since polymers are much less complex than biological systems. In recent works we have investigated the component dynamics in concentrated aqueous solutions of polymeric macromolecules (poly(vinyl methyl ether) (PVME), poly(dimethyl amino ethyl methacrylate) (PDMAEMA) and polyamide (PA)) [1]. We have found a similar peculiar phenomenology of the dynamics, including extreme stretching and deviations from Gaussian behavior that can be attributed to the existence of diverse environments in the samples. In the case of the polymer we also find that the formation of H-bonds with water plays a crucial role. An important arising question is whether the underlying structural heterogeneities, invoked to explain the results, are a consequence of the H-bond formation. We performed FOCUS measurements ($\lambda = 6 \text{ \AA}$) on concentrated solutions of PDMAEMA with tetrahydrofuran (THF), which do not form H-bonds. The percentage in weight was $w_{\text{THF}} = 30\%$. By using deuterated solvent we studied the polymer dynamics. The solvent dynamics has been extracted from the oppositely labeled sample. After reducing the data, we have calculated their Fourier Transform delivering the incoherent intermediate scattering function. In a preliminary first approach, the data above 2 ps (where the fast processes are not active anymore) have been described by KWW functions $F(Q,t) = A\exp(-t/\tau)\beta$. For both components we obtain extremely low values of the β -parameter ($\beta \sim 0.2$), indicating pronounced stretching of the scattering functions. This observation would be again compatible with the presence of structural heterogeneities, even in absence of H-bonding.

[1] S. Capponi et al, J. Chem. Phys 134, 204906 (2011).

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Detailed SANS contrast variation on toluene-based Co ferrofluid

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Contrast variation is a powerful technique [1], which is widely applied for studies of complex systems in small-angle neutron scattering experiments. The advantage of H/D substitution in the solvent without change in its chemical properties makes it possible to study such many-component systems in detail. In case of polydisperse systems one has to consider averaging of the scattering intensity over the particle size distribution. Thus, the direct modeling of the scattering intensities requires a certain number of free parameters, which can give the researcher a wrong result. The developed approach of contrast variation for polydisperse systems [2] allows researcher to obtain parameters, which can be later fixed in the model. A successful application of the approach in contrast variation on iron oxide magnetic fluids can be found in [3, 4].

In the present work we report about the contrast variation study of cobalt ferrofluid based on toluene with oleoyl sarcosine coating. The initial magnetic fluid (1.2 vol. % of Co) was diluted with toluene in the ratio 1:5. Several contrasts were prepared so that the amount of deuterated toluene in the solvent varied in the range 0-85%. The corresponding buffer solutions were prepared and used for background subtraction. Structural parameters of the nanoparticles were precisely obtained and used for further modeling of the scattering curves.

[1] H.B. Stuhrmann, Small-Angle X-ray Scattering, edited by O. Glatter and O. Kratky, pp.197-213, London: Academic Press (1982).

[2] M.V. Avdeev, J.Appl.Cryst. **40**, 56 (2007).

[3] A.V. Feoktystov, M.V. Avdeev, V.L. Aksenov, et al., Solid State Phenomena **152-153**, 186 (2009).

[4] M.V. Avdeev, E. Dubois, G. Meriguet, et al., J.Appl.Cryst. **42**, 1009 (2009).

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Polymerdynamics in silicabased nanocomposites with attractive interaction

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The interaction mechanism between polymer and nanoparticle influences the properties of nanocomposites.

In case of attractive surface interactions a layer of adsorbed chains is formed on the particle surface. Thus, the nanocomposite dynamics are modified, leading to a change in e.g. viscoelastic and dielectric properties.

We use a model system comprising polybutyleneoxide (PBO) blended with silica nanoparticles to investigate these changes and getting a better understanding of the underlying interaction mechanisms between polymer chains and nanoparticles within the nanocomposite.

Therefore samples have been prepared by solution-blending PBO with unmodified silica nanoparticles. They differ by nanoparticle size and concentration.

Rheological and dielectrical measurements show a strong influence by addition of nanoparticles on the relaxation process of the composite system in the frequency range of the chain relaxation, especially for filling levels higher than 3 vol%, while there is no impact of the segmental dynamics.

Also effects like an effective chain elongation occur which are not observed for composite systems with a repulsive interaction.

This poster shows these results of linear rheology and broadband dielectric spectroscopy measurements

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Shear induced brush deformation of soft colloidal mixtures

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The shear-induced ‘brush deformation’ of soft colloids, i.e. regular star polymers with functionality $f = 6, 16$ and 32 , in the presence of linear polymers with varying molecular weight has been investigated by rheology and Rheo-SANS experiments. Previously, we observed two decay modes (fast and slow modes) in the flow curves of pure star polymers solutions (two step shear thinning behavior). However, these modes have not yet been predicted by theory and simulations. Whereas the slow mode is due to the expected overall relaxation of stars as confirmed by Rheo-SANS experiments, the fast mode can be attributed to the relaxation of its outermost blob occurring only at very high shear rates. In soft colloidal mixtures, the presence of linear polymer affects strongly the characteristics frequencies of both modes. An increase in molecular weight of the linear polymer results in an earlier start of the shear thinning regimes than for pure star polymer solutions. We interpret this observation as shrinkage of the star polymers due to the increased osmotic pressure induced by the linear chains.

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Microscopic study of branched polymer systems

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This molecular rheology study focuses on the hierarchical relaxation processes in a 2nd generation cayley-tree polymer, dispersed in linear polyisoprene (PI) using a Rheo-SANS combination. Within a random phase approximation treatment, taking into account the different degrees of freedom, the observed loss of anisotropy after a fast step strain can be correlated with the fast relaxation of the outer arms and a slow one for the inner section: a hierarchical relaxation from the tips inwards to the branching point leads to isotropization of the chain ends with loss of orientation in a diluted tube. Furthermore, the combination of the branching points mobility and the matrix chain relaxation play a fundamental role for understanding the full relaxation process of the branched polymer blend.

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On the small angle scattering curves arising from oppositely charged polyelectrolyte surfactant mixtures: the case of chitosan – alkyl ether carboxylates.

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Mixtures of oppositely charged polyelectrolytes and surfactant are used in a variety of fields, such as cosmetics, detergency, pharmaceutical formulations, etc.. In order to tailor such mixtures to the different needs a detailed knowledge of the structure formed by the complexes in solution is often necessary. For this purpose, small angle scattering is a key technique. Furthermore, small angle neutron scattering (SANS) experiments, due to unique contrast conditions, can be used to determine the structural features of the single components.

Several scattering curves arising from complexes between polyelectrolytes and surfactants are reported in literature, many of them showing a q^{-1} scattering law at intermediate scattering vectors, which was justified by the presence of elongated micelles [1]. While this can be the case for ionic surfactants with a relatively small headgroup, it is unlikely for surfactants with a bulky head group or globular proteins [2]. The q^{-1} scattering law indicates a cylindrical symmetry within the complexes, which can also originate from a linear ordering of surfactant aggregates in a polyelectrolyte matrix.

We present here results for complexes of industrial compounds, namely biopolycation chitosan and bioderived alkyl ether carboxylates. The analysis of SANS data required the development of a new scattering form factor for linear clusters of ellipsoids, which provides a physically realistic description of our system where the large surfactant headgroup is not compatible with the presence of cylindrical micelles.

[1] I. Hoffmann et al., *Langmuir*, **27**, 4386-4396 (2011).

[2] I. Morgfin et al., *Biomacromolecules*, **12**, 859-870 (2011).

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