

Dynamics of Soft Matter Workshop

December 4-6, 2008

A Satellite of the Fall MRS 2008 Annual Meeting

Boston, MA

Complex Fluids Session

Thursday, December 4, 2008

Hynes Convention Center, 2nd Floor, room 200

Christiane Alba-Simionesco, Chair

1:30 pm

Workshop Introduction

Robert McGreevy, ISIS, Rutherford Appleton Laboratory, CCLRC, England.

1:45

On supramolecular polymers and networks and their unusual properties and dynamics

Ludwik Leibler, Matière Molle et Chimie, UMR7167 ESPCI-CNRS, ESPCI, 10 rue Vauquelin, 75005 PARIS, France

2:30

Colloidal dispersions at interfaces and in thin films

Regine v. Klitzing, Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, TU Berlin, Strasse des 17. Juni 124, D-10623 Berlin, Germany

3:00

Self-assembly in surfactant solutions: kinetics and pathways.

Stefan Egelhaaf, Institut für Physik der kondensierten Materie, Heinrich-Heine-Universität Düsseldorf, Germany

3:30 Break

4:00

Are colloidal and molecular glass formation related?

Johan Mattsson, H.M. Wyss, A. Fernandez-Nieves, K. Miyazaki, Z. Hu, D.R. Reichman & D.A. Weitz. Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden.

4:30

Neutron scattering studies on the structure and dynamics of microemulsions - from droplet shape fluctuations to local dynamics in soft confinement.

Bernhard Frick and Tinka Spehr, Institut Laue Langevin, Grenoble, France.

5:00

Experimental studies of selected soft self-organized nanostructures

Jon Otto Fossum, Bao-Xiang Wang, Zbigniew Rozynek, Henrik Hemmen, Davi de Miranda Fonseca, Nils Ivar Ringdal, Elisabeth Lindbo Hanssen, Matteus Hager from Department of Physics, Norwegian University of Science and Technology-NTNU, Trondheim, Norway; *Kenneth D. Knudsen, Physics Department, Institute for Energy Technology-IFE, Kjeller, Norway; Kanak P.S. Parmar, Dept. of Chem. Eng., Pohang University of Science and Technology, Postech, Pohang, South-Korea; Do Yoing Noh, Gwangju Institute of Technology, South Korea and PLS synchrotron lab at Postech, Pohang, South Korea; Yves Meheust, Université de Rennes, Geosciences Rennes, France; Eduardo de Azevedo and Mario Englesberg, Universidade Federal de Pernambuco-UFPE, Depart.de Fisica, Recife-PE, Brazil; Paul Dommersnes, Université Paris, Laboratoire Matière et Systèmes Complexes, Paris, France.

5:15

Dynamics and confinement in clays: combining experiment and simulation.

N. Malikova¹, E. Dubois², V. Marry² and P. Turq².
¹Laboratoire Leon Brillouin (CEA-CNRS), CEA Saclay, France. ²Laboratoire Liquides Ioniques et Interfaces Chargées, Université Pierre et Marie Curie, Paris, France.

5:30 Session Ends

Polymers Session

Friday, December 5, 2008

Sheraton Hotel – 3rd floor – Fairfax A/B

Victoria Garcia Sakai, Chair

8:30 am

Polymer dynamics from synthetic to biological macromolecules

Dieter Richter, Institut für Festkörperforschung; Forschungszentrum Jülich, D-52425 Jülich, Germany

9:15

Chain dynamics: The smallest Rouse bead and the friction mechanism

Alexei Sokolov, Univ. Akron, Akron, OH.

9:45

Anisotropic self-assembly of spherical polymer-grafted nanoparticles

Sanat K. Kumar, Department of Chemical Engineering, Columbia University, New York, NY.

10:15 Break

10:45

Thoughts on the interplay of neutron scattering, structure, and polymer dynamics on ion transport in solid polymer electrolytes.

Janna Maranas, Pennsylvania State University.

11:15

Nanoconfinement through self-assembly in homopolymers with long alkyl side-groups: observation of anomalous relaxation

Arantxa Arbe¹, Juan Colmenero^{1,2}, A.-Caroline Genix³, Dieter Richter⁴, Peter Fouquet⁵. ¹Centro de Fisica de Materiales CSIC-UPV/EHU, San Sebastián, SPAIN; ²Donostia International Physics Center, San Sebastián, SPAIN; ³Université de Montpellier II, Montpellier, FRANCE; ⁴Institut für Festkörperforschung, Forschungszentrum Jülich, Jülich, Germany; ⁵ILL, Grenoble, France.

11:45

Branch point motion in star polymer melts

M.Zamponi¹, W.Pyckhout-Hintzen¹, M.Monkenbusch¹, A.Wischnewski¹, L.Willner¹, D.Richter¹, G.Kali²
¹Research Centre Jülich, 52425 Jülich, Germany
²Institut Laue-Langevin, 6 rue Jules Horowitz, 38000 Grenoble, France

Noon

DPD simulations of polymer melts:

From Rouse dynamics to reptation using soft potentials

F. Lahmar and B. Rousseau, Laboratoire de Chimie Physique, Université Paris-Sud, France

12:15 pm Session ends

Biology Session

Friday, December 5, 2008

Sheraton Hotel – 3rd floor – Fairfax A/B

Sow-Hsin Chen, Chair

1:30 pm

Neutron Scattering and Computer Simulation in Biology

Jeremy C. Smith, Center for Molecular Biophysics, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

2:15

Collective molecular dynamics in proteins and membranes

Maikel C. Rheinstadter, University of Missouri-Columbia, Columbia, MO, USA.

2:45

Collective dynamics in systems of biological interest investigated by Neutron Spin Echo spectroscopy

Antonio Faraone, NIST Center for Neutron Research and Department of Material Science and Engineering, University of Maryland

3:15 Break

3:45

Dynamical coupling between hydration water and proteins: a comparison of membrane and soluble proteins

Kathleen Wood[‡], D. Tobias[□], G. Zaccai^{*}, M. Weik[#]
[‡]Biophysical Chemistry, Groningen, the Netherlands; [□]University of California, Irvine, USA. ^{*}Institut Laue Langevin, Grenoble, France; [#]Institut de Biologie Structurale, Grenoble, France.

4:15

Nanoscale coupled protein domain motion revealed by neutron spin echo spectroscopy

David Callaway, New York University School of Medicine, New York, NY.

4:45

Dynamics and function of the archetypal Ca²⁺/Mg²⁺-binding EF-hand parvalbumins, a combined study by NMR and neutron scattering

Joseph Parello¹, Jean-Marc Zanotti² and Marie-Claire Bellissent-Funel², ¹Vanderbilt Univ. School of Medicine, Department of Pharmacology, Nashville, TN. ²Laboratoire Léon Brillouin (CEA-CNRS), CEA-Saclay, Gif-sur-Yvette, France.

5:00

Internal Dynamics in Proteins studied by Neutrons and X-rays

Jyotsana Lal¹, Peter Fouquet², Marco Maccarini², Diane J. Rodi³ and Lee Makowski³. ¹IPNS, Argonne National Laboratory, IL. ²Institut Laue-Langevin, Grenoble, France. ³Biosciences Division, Argonne National Laboratory, IL.

5:15 Session ends

Poster Session

Friday, December 5, 2008

Sheraton Hotel, 2nd Floor, Independence Ballroom

Al Hurd, Chair

5:30 Poster Session begins

Dynamics in Shear Flow Studied by Neutron Spin Echo and X-ray Photon Correlation Spectroscopy

Péter Falus¹, Marco Walz² and Andrei Flueraș³. ¹Institut Laue Langevin, Grenoble, France. ²University of Erlangen, Erlangen, Germany. ³European Synchrotron Radiation Facility, Grenoble, France.

Dynamics of breathable poly(N- isopropylacrylamide) network with controllable hydration which supports model lipid membrane

Michael Jablin[†], Hillary Smith[†], Ryan Toomey[‡], Jessica Saiz[†], Jaroslaw Majewski[†]. [†]Manuel Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory. [‡]Department of Chemical Engineering, University of South Florida.

Dynamics of constitutional terphenyl isomers adsorbed onto graphite

Edward J. Kintzel, Jr.¹, Kenneth W. Herwig², and Inma Peral³. ¹Department of Physics and Astronomy, Western Kentucky University. ²Spallation Neutron Source, Oak Ridge National Laboratory. ³NIST Center for Neutron Research, National Institute for Standards and Technology.

Dynamics of RNA and protein at different levels of hydration

^{1,3}J. H. Roh, ¹R. M. Briber, ³A. Damjanovic, ²D. Thirumalai, ³S. A. Woodson, and ⁴A. P. Sokolov. ¹Department of Materials Science and Engineering, University of Maryland, College Park, MD. ²Biophysics Program, Institute For Physical Science and Technology, University of Maryland, College Park, MD. ³T. C. Jenkins Department of Biophysics, Johns Hopkins University, Baltimore, MD. ⁴Department of Polymer Science, University of Akron, Akron, OH

Effect of polymer mobility on conductivity of single-ion conductors

Kokonad Sinha, and Janna Maranas, Department of Chemical Engineering and Department of Material Science and Engineering, The Pennsylvania State University, University Park, PA 16802

The fragile to strong dynamic crossover transition in confined water: molecular dynamics results

Paola Gallo¹, M. Rovere¹, and S. H. Chen²
¹ Dipartimento di Fisica, Università Roma Tre, Via della Vasca Navale 84, I-00146 Roma, Italy. ² Department of Nuclear Science and Engineering, M.I.T., Cambridge, Massachusetts, USA.

High and low temperature dynamic crossover phenomena in protein hydration water

Yang Zhang¹, Sow-Hsin Chen¹, Antonio Faraone², John Copley², Dazhi Liu³, Eugene Mamontov³, Mark Hagen³, Marco Lagi^{1,4}, Emiliano Fratini⁴, Piero Baglioni⁴, Francesco Mallamace⁵. ¹MIT, ² NIST

Center for Neutron Research, ³SNS, ⁴University of Florence, ⁵University of Messina

High resolution NSE spectrometer for the SNS

M. Ohl¹, N. Arend¹, M. Monkenbusch¹ and D. Richter¹
¹ Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany.

Ligand induced changes in protein dynamics: comparison of simulations with NMR experiments

M. Krishnan and Jeremy C. Smith, Oak Ridge National Laboratory, Oak Ridge, TN.

Nanotube representation for a photon

^{*}M. Saglam and ^{**}G. Sahin. ^{*}Ankara University, Department of Physics 06100 Tandogan, Ankara, Turkey. ^{**} Miami University, Department Electrical and Computer Engineering, Oxford, Ohio 45056.

Neutron scattering investigations of molecular motion at interfaces

J.Z. Larese^{1,2}, T. Arnold³, P. Fouquet⁴, R. J. Hinde², A. J. Ramirez-Cuesta⁵, T. Seydel⁷, B. Sumpter², M. Telling⁵
¹Chemistry Dept., University of Tennessee, Knoxville, TN 37996. ²Oak Ridge National Laboratory, Oak Ridge, TN 37831. ³Diamond Light Source, Chilton, Didcot, OX11 0DE, UK. ⁴Institut Laue-Langevin, Grenoble Cedex 9, France. ⁵ISIS Neutron Source, Chilton, Didcot, OX11 0DE, UK.

Si backscattering spectrometer at the pulsed neutron source of J-PARC

Nobuaki Takahashi¹, Kaoru Shibata¹, Yukinobu Kawakita^{1,2}, Taku J. Sato^{1,3}, Itaru Tsukushi^{4,5}, Hiroshi Nakagawa⁵, Satoru Fujiwara⁵, Kenji Nakajima¹, Masatoshi Arai¹. ¹J-PARC Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan. ²Department of Physics, Kyushu University, 810-8560, Japan. ³Institute for Solid State Physics, University of Tokyo, Tokai, Ibaraki 319-1106, Japan. ⁴Department of Physics, Chiba Institute of Technology, 275-0023, Japan. ⁵Quantum Beam Science Directorate, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan.

Structure and dynamics of weak polyelectrolyte layer-by-layer films

Eugenia Kharlampieva^{**}, John F. Ankner[§], Michael Rubinstein[&] and Svetlana A. Sukhishvili[#]
[#]Department of Chemistry, Chemical Biology and Biomedical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030. [&]Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599. [§]Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37831. ^{*} current address: Department of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332.

Swell or not swell? An improved Dreiding III molecular dynamics study on PAMAM dendrimer in aqueous solution

Yi Liu, V. Bryantsev, M. Diallo, and W. A. Goddard III
Materials and Process Simulation Center, California
Institute of Technology, Pasadena, California

Understanding ion transport in ionomers using dielectric spectroscopy

U Hyeok Choi¹, Sharlene R. Williams², Timothy E. Long²
and Ralph H. Colby¹. ¹Materials Science and
Engineering, Penn State University, University Park, PA
16803. ²Chemistry Department, Virginia Tech,
Blacksburg, VA 24061.

Weakening ion interactions in ionomers using ionic liquid counterions

Gregory J. Tudryn and Ralph H. Colby, Materials Science
and Engineering, Penn State University, University Park,
PA 16803.

7:00 Poster Session ends

Surfaces Session

Saturday, December 6, 2008
Sheraton Hotel – 3rd floor – Fairfax A/B
Ian Anderson, Chair

8:00 am

Role of interfaces on the long-time dynamics of polymers

Peter F. Green, University of Michigan

8:45

Polymer dynamics under quasi-uniaxial confinement: the case of PEO in porous alumina

K. Lagrené¹, M. Daoud², J.-M. Zanotti¹
¹Laboratoire Léon Brillouin (CEA-CNRS), CEA Saclay,
91191 Gif-sur-Yvette, France. ²CEA/Service de Physique
de l'Etat Condensé, CEA Saclay, 91191 Gif-sur-Yvette,
France.

9:15

Dynamics of soft matter and complex fluids in confined geometry.

D. Morineau¹, R. Lefort¹, R. Busselez¹, Q. Ji¹, R. Guégan²,
G. Chahine^{1,3}, M. Guendouz⁴, J.-M. Zanotti³ and B.
Frick⁵. ¹Institut de Physique de Rennes, CNRS-Université
de Rennes 1, Rennes France; ²Institut des Sciences de la
Terre, Orléans, France; ³Laboratoire Léon Brillouin, CEA-
Saclay, Gif-sur-Yvette, France; ⁴Laboratoire d'Optronique,
Université de Rennes 1, Lannion France; ⁵Institut Laue-
Langevin, Grenoble, France.

9:45 Break

10:15

The dynamics of simple organic molecules in aqueous solution and confined in swelling clays

Neal Skipper, Univ. College, London

10:45

Neutron and x-ray scattering experiments on stable molecular glasses

Mark D. Ediger, University of Wisconsin, Madison,
Wisconsin.

11:15

Near-surface structure and dynamics explored by grazing incidence neutron scattering

Marco Walz¹, Max Wolff², Peter Falus³, Nicole Voss¹,
Hartmut Zabel², and Andreas Magerl¹. ¹Chair for
Crystallography and Structural Physics, University of
Erlangen-Nürnberg, Erlangen, Germany. ²Ruhr-
University Bochum, Bochum, Germany. ³Institut Laue-
Langevin, Grenoble, France

11:30

Shear induced relaxation of polymer micelles at the solid-liquid interface

Max Wolff^{*},¹ Roland Steitz², Philipp Gutfreund¹, Nicole
Voss³, Stefan Gerth³, Marco Walz³, Andreas Magerl³,
Hartmut Zabel¹. ¹Institute for Experimental Physics/Solid-
State Physics/EP IV, Ruhr-University Bochum, Bochum,
Germany. ²Helmholtz Centre Berlin for Materials and
Energy, Berlin, Germany. ³Crystallography and Structural
Physics, University of Erlangen-Nürnberg, Erlangen,
Germany. ^{*}present address: Institute Laue-Langevin,
Grenoble, France.

11:45 Break

Summary Session

Rob McGreevy, Chair

Noon

Lunch and Instrumentation Current Capabilities and Future Needs

Ken Herwig, Oak Ridge National Laboratory

1:00

Panel Discussion to Summarize Workshop

Christiane Alba-Simionesco
Sow-Hsin Chen
Victoria Garcia Sakai

2:30 Session and Workshop End

Abstracts: Complex Fluids Session
Thursday, December 4, 2008
Hynes Convention Center, 2nd Floor, Room 200
Christiane Alba-Simionesco, Chair

1:30 pm

Workshop Introduction

Robert McGreevy, ISIS, Rutherford Appleton Laboratory, CCLRC, England.

1:45

On supramolecular polymers and networks and their unusual properties and dynamics. Ludwik Leibler, Matière Molle et Chimie, UMR7167 ESPCI-CNRS, ESPCI, 10 rue Vauquelin, 75005 PARIS, France. Supramolecular chemistry provides a powerful and attractive tool to design and synthesize small-molecule systems exhibiting polymer-like properties. Ditopic molecules – molecules able to directionally associate with two other molecules thanks to the presence of self-complementary or key-lock functional groups - can form long-lived structures and exhibit polymer-like behaviour both in solutions and bulk. In the conceptually simplest case, of supramolecular polymers, they associate to form linear chains and show visco-elastic behaviour and governed by both association-dissociation kinetics of functional groups and energy of associations. Very often, supramolecular chains, organize into fascinating mesophases and form fibres, tubules, or lamellas in solutions and show-gel like behaviour. Similarly in bulk, they can organize into mesophases or partially crystallize and behave like semi-crystalline polymers, supramolecular plastics. By mixing ditopic and multi- topic molecules—which are able to associate with more than two other molecules—supramolecular networks could be formed. By using carefully designed mixtures of molecules bearing a variety of strongly associating groups, crystallization and phase separation can be suppressed and supramolecular rubbers with remarkable self-healing properties can be synthesized. It is the very dynamics of associations, diffusion and stress relaxation that conspire to make these materials able to self-heal when fractured or cut into pieces while not being self-adhesive and resist creep under load. In all these abovementioned situations the kinetics of structures formation and dynamics at different spatial and time scales which are coupled in a subtle way, arouse many fascinating and challenging questions both for experiments and theory.

2:30

Colloidal dispersions at interfaces and in thin films. Regine v. Klitzing, Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, TU Berlin, Strasse des 17. Juni 124, D-10623 Berlin, Germany. The presentation focuses on the effect of geometrical confinement on the structuring and dynamics of polymer chains and colloidal suspensions in thin films. Two types of films will be presented: Coatings by adsorption of polymers and aqueous films containing polymers or particles. The coatings (thickness: 1 – 500 nm) are either produced by alternating adsorption of polyanions and polycations or by deposition of polymeric microgel particles. The correlation between structure profile, ion distribution and dynamics within polymer films and their sensitivity to external stimuli like pH, temperature, humidity or ionic strength is of interest. This is of high impact for many applications like sensors or drug delivery systems. But film stability and sensitivity (mobility) are often counteractive. Hence, one challenge is to study and to control the “interphase” between film bulk (continuum) and solid substrate. For the characterisation e.g. x-ray and neutron reflectometry, x-ray fluorescence, AFM, ellipsometry and FRAP are used. The second type of films (thickness: 5 – 200 nm) is produced by confining aqueous polymer solutions or particle suspensions between two solid interfaces, between a solid and a fluid interface (wetting film) or between two fluid interfaces (foam film). The structuring of colloidal dispersions in confined geometry in general is of interest for e.g. nano- and microfluidics, cosmetics and cleaning processes. Force measurements with Colloidal Probe AFM and TFPB give an insight into the structure within the film, which is compared with the structure in solution on basis of results of SANS and SAXS measurements.

3:00

Self-assembly in surfactant solutions: kinetics and pathways. Stefan Egelhaaf, Institut für Physik der kondensierten Materie, Heinrich-Heine-Universität Düsseldorf, Germany. Surfactants can self-assemble into various structures, such as micelles, vesicles or liquid crystalline phases. Most early studies on surfactant systems have addressed their equilibrium structure, phase behaviour and dynamics at equilibrium. These remain a prerequisite for further progress, but attention has started to turn to non-equilibrium phenomena. These include question like: How does a sample relax back to equilibrium after, for example, a temperature- or concentration jump? How are new phases formed during (de)mixing? How do phases merge when placed in contact? I will illustrate these processes with a few examples and show how time-resolved elastic and inelastic scattering experiments can be used to follow these processes and thus contribute to our understanding of the kinetics and pathways of structural transitions in surfactant systems.

3:30 Break

4:00

Are colloidal and molecular glass formation related? Johan Mattsson, H.M. Wyss, A. Fernandez-Nieves, K. Miyazaki, Z. Hu, D.R. Reichman & D.A. Weitz. Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden. Understanding why and how a glass is formed on a microscopic level remains an outstanding problem in condensed matter physics. A molecular glass is normally formed by cooling of a liquid. Upon entering the supercooled state, the structural dynamics slows down dramatically and eventually the liquid enters the non-equilibrium glassy state. On route towards the glass, the behaviour shows a range of highly general, near universal characteristics, such as stretched exponential behaviour of dynamic correlation functions and cooperative dynamics. Such generalities exist even though molecular glasses can be formed from liquids encompassing a wide range of molecular structures and interactions. Glass formation also occurs in altogether very different systems. One of the most interesting, both from a fundamental and an applications point of view, is that of colloidal suspensions. The high degree of control that can be achieved regarding colloidal particle size, shape and interactions makes this a fantastic model system for learning about glass-formation. We know that a range of properties observed during dynamic arrest in molecular systems for decreasing temperature are indeed mirrored in the arrest of a colloidal suspension upon increase of particle volume fraction. However, the richness in phenomenology observed for liquids has generally not been observed for colloids. We will discuss to what extent colloidal glass formation can be viewed as equivalent to molecular glass formation and present recent experimental work on the dynamic arrest in aqueous suspensions of soft polymeric microgel particles that suggests a remarkably direct connection. The observed link between dynamic arrest in colloids and liquids means that studies on colloids could inspire and direct studies on supercooled liquids and vice versa. One of the foremost experimental tools for studying supercooled liquids is neutron scattering. We will briefly discuss some possible implications our results could have for future neutron scattering studies.

4:30

Neutron scattering studies on the structure and dynamics of microemulsions - from droplet shape fluctuations to local dynamics in soft confinement. Bernhard Frick and Tinka Spehr, Institut Laue Langevin, Grenoble, France. Reverse micelle droplets, e.g. water in oil mediated by surfactants, are of large interest for the study of supercooling, glass formation or freezing in soft confining environment and they offer the advantage to tune parameters like droplet size, concentration or elasticity. On the other hand, the complexity of these systems calls for a detailed characterization of the stability range and of the self-dynamics of the confining systems. We present temperature dependent static investigations, mainly from SANS, on the droplet phase of water-in-oil microemulsions with AOT as surfactant to define the structural stability regime. We find that the droplets shrink at low temperatures to a size which still contains unfrozen water and that the stability range widens towards lower temperatures with decreasing droplet size. Inelastic neutron scattering studies (time-of-flight, backscattering and NSE) aim for an understanding of the complex dynamics which extends from the local dynamics of the constituents to droplet shape fluctuations and droplet diffusion. All these studies take advantage of the possibility to vary the neutron scattering contrast via H/D exchange for some of the constituents, water, surfactant and oil. We discuss the results concerning the undercooling, freezing and the local dynamics of water confined in different droplet sizes. Similar to the structural droplet instability we find that the freezing of the supercooled water depends as well on the confinement size. The confined water shows in these soft systems a strong slowing down of the dynamics with respect to bulk water. With NSE we follow for the first time the droplet shape fluctuations in the supercooled water regime and below the droplet stability temperature. Finally we extend the view to recent inelastic neutron scattering experiments on other glass forming liquids in soft confinement.

5:00

Experimental studies of selected soft self-organized nanostructures. Jon Otto Fossum, Bao-Xiang Wang, Zbigniew Rozynek, Henrik Hemmen, Davi de Miranda Fonseca, Nils Ivar Ringdal, Elisabeth Lindbo Hanssen, Matteus Hager from Department of Physics, Norwegian University of Science and Technology-NTNU, Trondheim, Norway; *Kenneth D. Knudsen, Physics Department, Institute for Energy Technology-IFE, Kjeller, Norway; Kanak P.S. Parmar, Dept. of Chem. Eng., Pohang University of Science and Technology, Postech, Pohang, South-Korea; Do Yoing Noh, Gwangju Institute of Technology, South Korea and PLS synchrotron lab at Postech, Pohang, South Korea; Yves Meheust, Universite de Rennes, Geosciences Rennes, France; Eduardo de Azevedo and Mario Englesberg, Universidade Federal de Pernambuco-UFPE, Depart.de Fisica, Recife-PE, Brazil; Paul Dommersnes, Universite Paris, Laboratoire Matiere et Systemes Complexes, Paris, France. In the general context of self-organization of particles, and transitions in such structures, we study complex physical phenomena such as: (i) spontaneous gravitationally induced phase separation and nematic self-organization in systems of anisotropic nanoparticles in aqueous suspension, including studies of isotropic to nematic transitions [1,2]. (ii) transitions from biaxial to uniaxial nematics by application of external magnetic field to self-organized systems of the same anisotropic

(diamagnetic) nanoparticle systems [3,4]. **(iii)** guided self-organization into chainlike structures of the same (surface modified) anisotropic nanoparticles in oil suspension, when subjected to external electrical fields (electrorheological structures of polarized nanoparticles), and the stability of, and transitions of, such structures, when subjected to external mechanical stress [5,6]. The model particles we are studying are clay platelet nanoparticles, and the experimental techniques we have used include synchrotron X-ray scattering, neutron scattering, rheometry, microscopy and magnetic resonance. We have demonstrated that clays may be used as good model systems for studies of universal physical phenomena and transitions in self-organized nanostructured soft and complex matter. Self-organization and related transitions in clay systems in particular, may have practical relevance for nano-patterning, properties of nanocomposites, and macroscopically anisotropic gels, among many other applications [7]. The synchrotron experiments have been performed at LNLS-Brazil, PLS- Korea, BNL-USA and ESRF-France, and the neutron experiments at IFE, Kjeller, Norway. *Acknowledgments:* Collaborators, postdocs and students at NTNU-Norway, UiO-Norway, IFE-Norway, BNL-USA, LNLS-Brazil, UFPE-Brazil, UnB-Brazil, Univ. Amsterdam-Netherlands, Univ.Paris 7-France and other places. The research is supported by the Research Council of Norway (RCN), through the NANOMAT, SUP and FRINAT Programs. [1]. J.O. Fossum, E. Gudding, D.d.M. Fonseca, Y. Meheust, E. DiMasi, T. Gog, C. Venkataraman, *Observations of orientational ordering in aqueous suspensions of a nano-layered silicate*, ENERGY The International Journal 30, 873 (2005). [2]. D. M. Fonseca, Y. Méheust, J. O. Fossum, K. D. Knudsen, K. J. Måløy and K. P. S. Parmar, *Phase behavior of platelet-shaped nanosilicate colloids in saline solutions: A small-angle X-ray scattering study* J. Appl. Cryst. 40 292 (2007). [3]. E. N. de Azevedo, M. Engelsberg, J. O. Fossum, R. E. de Souza, *Anisotropic water diffusion in nematic self-assemblies of clay nano-platelets suspended in water*, Langmuir 23, 5100 (2007). [4]. Nils Ivar Ringdal, Master thesis, Department of Physics, NTNU (2008); Elisabeth Lindbo Hansen, Mater Thesis, Department of Physics, NTNU (2008); Henrik Hemmen, Master Thesis, Department of Physics, NTNU (2008); Davi de Miranda Fonseca, PhD Thesis, Department of Physics, NTNU (2008). [5]. J.O. Fossum, Y. Meheust, K.P.S. Parmar, K.D. Knudsen, K.J. Maloy, D.d.M. Fonseca, *Intercalation-enhanced electric polarization and chain formation of nano-layered particles*, Europhys. Lett., 74, 438 (2006), and in the Scientific Highlights 2006 of the European Synchrotron Radiation Facility - ESRF (2007). [6]. K.P.S. Parmar, Y. Meheust, B. Schelderupsen and J.O. Fossum, *Electrorheological suspensions of laponite in oil: rheometry studies*, Langmuir 24,1814 (2008). [7]. F. Bergaya, B. K. G. Theng, and G. Lagaly, editors. *Handbook of Clay Science*. Elsevier (2006).

5:15

Dynamics and confinement in clays: combining experiment and simulation. N. Malikova¹, E. Dubois², V. Marry² and P. Turq². ¹Laboratoire Leon Brillouin (CEA-CNRS), CEA Saclay, France. ²Laboratoire Liquides Ioniques et Interfaces Chargées, Université Pierre et Marie Curie, Paris, France. Clays are layered aluminosilicates with water retention and ion exchange properties, which are responsible for many natural phenomena such as retention of molecules by soil and exploited in the many technological applications of clays, e.g. in catalysis and radioactive waste disposal. We investigate here the motion of water and ions in low hydrated clays, where these molecules are found in a quasi two-dimensional confinement and very high ionic concentrations (order of 10 water molecules per ion). Using the examples of a natural montmorillonite clay and a synthetic hectorite clay we present a comparison of experimental (quasi-elastic neutron scattering) and simulated (classical Molecular Dynamics) dynamic data. These agree in the diffusion coefficient of water confined in clay, predicting its decrease by a factor of 10 and 3 with respect to bulk water, when a single and a double water layer is confined between clay layers respectively [1,2]. Further, the effect of confinement on water and ionic motion in clays is presented. In case of simulated data, the decoupling of motion in directions parallel and perpendicular to the clay layers points clearly towards a two-dimensional nature of both water and ion diffusion [1]. In case of neutron scattering data regarding water in clays, the use of powder clay samples does not permit the same treatment. A novel method is demonstrated to highlight the signature of reduced dimensionality in molecular motion, for data from powder samples. It is based on analysing the most pertinent part of the experimentally measured scattering function, the intensity at zero energy transfers, and using simultaneously information from a wide range of experimental resolutions. This analysis of neutron scattering data shows unambiguously the two-dimensional nature of water motion in clays [3].

[1] N. Malikova, A. Cad`ene, V. Marry, E. Dubois and P. Turq, J. Phys. Chem B 110, 2006, pp. 3206-3214.

[2] N. Malikova, A. Cad`ene, E. Dubois, V. Marry, S. Durand-Vidal, P. Turq, J. Breu, S. Longeville and J-M. Zanotti, J. Phys. Chem C 111, 2007, pp. 17603-17611.

[3] N. Malikova, S. Longeville, J.-M. Zanotti, E. Dubois, V. Marry, P. Turq and J. Ollivier, submitted.

5:30 Session Ends

Polymers Session
Friday, December 5, 2008
Sheraton Hotel – 3rd floor – Fairfax A/B
Victoria Garcia Sakai, Chair

8:30 am

Polymer dynamics from synthetic to biological macromolecules. Dieter Richter, Institut für Festkörperforschung; Forschungszentrum Jülich, D-52425 Jülich, Germany. In soft materials entropic and enthalpic contributions are of similar magnitude and balance each other. Therefore, the macroscopic mechanical and rheological properties and the phase changes are determined to a high degree by thermal motion of the atoms and molecules. Most of the relevant dynamics takes place on mesoscopic length and time scales in between the picosecond atomic scale and the macroscopic frame. Allowing for the proper space time observation window, neutron spin echo (NSE) spectroscopy uniquely allows to address these motions. Here I will briefly present some key experimental results on the mesoscopic dynamics of polymer systems. In the second part I touch on some new developments relating to large scale internal dynamics of proteins by neutron spin echo. There it has become possible to directly access the interdomain motions in proteins that are essential to enable or promote biochemical function. I report on NSE results on the domain dynamics within alcohol dehydrogenase. The collective motions of the domains as revealed by their coherent form factor relates to the cleft opening dynamics between the binding and the catalytic domains enabling the binding and the release of the functional important cofactor.

9:15

Chain dynamics: The smallest Rouse bead and the friction mechanism. Alexei Sokolov, Univ. Akron, Akron, OH. Bead-and-spring model is the basis of the polymer physics. It assumes that a polymer chain can be represented as a number of beads connected by entropic springs and moving in some viscous environment. In order to relate the bead-and-spring model to a real polymer chain, knowledge of the bead size and the friction mechanism is required. Usually the bead size (the size of the smallest Rouse-like sub-chain) is related to the Kuhn segment. Neutron scattering spectroscopy provides direct measure of the dynamic bead size. We overview neutron scattering studies of polymer melts and solutions and demonstrate strong disagreement between the traditionally defined Kuhn segment length and the smallest sub-chain size. We propose more general definition of the dynamic and static bead size that can resolve this controversy. The second parameter, chain friction coefficient, is usually assumed to be the same as the segmental friction coefficient. This is the basis for the time-temperature superposition (TTS) principle – the cornerstone of the Polymer Rheology. It is known, however, that TTS breaks down as temperature approaches glass transition. We overview different experimental data and demonstrate the decoupling of chain and segmental dynamics. The presented results suggest strong difference in segmental and chain friction mechanism. We propose a model that explains the difference and can predict the temperature dependence of the chain dynamics.

At the end, we emphasize the importance of the understanding the bead size and the chain friction coefficient not only for our fundamental knowledge of polymer dynamics, but also for application of polymers in various nano-technologies and energy related topics. We also discuss the future neutron scattering experiments that can help to unravel the microscopic details of the chain dynamics.

9:45

Anisotropic self-assembly of spherical polymer-grafted nanoparticles. Sanat K. Kumar, Department of Chemical Engineering, Columbia University, New York, NY. It is easy to understand the self-assembly of particles having anisotropic shapes or interactions, such as Co nanoparticles or proteins, into highly extended structures. However, there is no experimentally established strategy for creating anisotropic structures from common spherical nanoparticles. We demonstrate that spherical nanoparticles, uniformly grafted with macromolecules, robustly self-assemble into a range of anisotropic superstructures when they are dispersed in the corresponding homopolymer matrix. Theory and simulations both suggest that this self-assembly process reflects a balance between the energy gain when particle cores approach and the entropy of distorting the grafted polymers. The effectively directional nature of the particle interactions is thus a many-body emergent property. Our experiments demonstrate that this approach to particle self-assembly allows for considerable control for the creation of polymer nanocomposites with enhanced mechanical properties. In particular, we combine TEM, SANS and USAXS, which allow us to characterize structure, with QENS and XPCS to delineate the local dynamics of the particles and how they relate to macroscopic rheology. Grafted nanoparticles are thus versatile building blocks for creating tunable and functional particle superstructures with significant practical applications.

10:15 Break

10:45

Thoughts on the interplay of neutron scattering, structure, and polymer dynamics on ion transport in solid polymer electrolytes. Janna Maranas, Pennsylvania State University. This presentation discusses the role of neutron scattering, in combination with other techniques, to understand the features controlling lithium transport in solid polymer electrolytes. Both liquids and ceramics conduct lithium to an extent that is practical for lithium ion batteries, but neither has the mechanical properties to enable applications where flexibility and light weight are required. These properties are realized by solid polymer electrolytes, but conductivity at room temperature remains insufficient despite many years of investigation. We use small angle and quasi-elastic neutron scattering to study two features important in these systems: the semi-crystalline nature of these electrolytes, unavoidable at room temperature in PEO-based systems, and the use of nano-particle fillers.

11:15

Nanoconfinement through self-assembly in homopolymers with long alkyl side-groups: observation of anomalous relaxation. Arantxa Arbe¹, Juan Colmenero^{1,2}, A.-Caroline Genix³, Dieter Richter⁴, Peter Fouquet⁵. ¹Centro de Física de Materiales CSIC-UPV/EHU, San Sebastián, SPAIN; ²Donostia International Physics Center, San Sebastián, SPAIN; ³Université de Montpellier II, Montpellier, FRANCE; ⁴Institut für Festkörperforschung, Forschungszentrum Jülich, Jülich, Germany; ⁵ILL, Grenoble, France. We have exploited the selectivity of neutron scattering combined with isotopic substitution to study the structure and dynamics of poly(n-alkyl methacrylates). Our diffraction data strongly support the suggested nanosegregation of main-chains and side-groups. Moreover, we have been able to separately follow the dynamics of both subsystems at a molecular scale. While the structural relaxation observed at the main-chain level is standard, for high-order members the correlations involving side groups within the alkyl nanodomains relax through an exotic logarithmic decay. In these polymers, a strong dynamic asymmetry also develops. We can find similarities with other soft materials where nanoconfinement is a key ingredient, like dynamically asymmetric miscible polymer blends. These analogies suggest a general scenario for the anomalous relaxation situation observed which could be explained in terms of a high-order Mode Coupling transition.

11:45

Branch point motion in star polymer melts. M.Zamponi¹, W.Pyckhout-Hintzen¹, M.Monkenbusch¹, A.Wischnewski¹, L.Willner¹, D.Richter¹, G.Kali². ¹ Research Centre Jülich, 52425 Jülich, Germany. ² Institut Laue-Langevin, 6 rue Jules Horowitz, 38000 Grenoble, France. Using Neutron Spin Echo (NSE) spectroscopy and a labeling scheme unique to neutron scattering it is possible to observe different relaxation processes in polymer melts separately directly on the length scale of the chain. In comparison to linear polymer melts stars are more confined due to the branch point. Following the concept of hierarchical relaxation the star arms have to fully retract to the star center before the whole star can move. Using the contrast between protons and deuterons the branch point of a 3 arm polyethylene star has been labelled. Within the accessible time range of NSE the dynamic structure factor shows a clear transition to a plateau, signifying the stronger confinement of the star center in comparison to a corresponding center labelled linear chain ('2 arm star'). Shortening of one star arm to about only one entanglement length leads to the same topological confinement as for the symmetric star. This reflects a stronger slowing down of the branch point motion than expected for such a small star arm, and also as found in recent MD simulations by Zhou et al. (Macromolecules 2007). The NSE results are in accordance with rheological measurements on the same system, which shows that only at longer times (outside the accessible NSE time range) the difference in the branch length comes into play and the asymmetric star displays a flow behavior similar to the linear chain.

Noon

DPD simulations of polymer melts: From Rouse dynamics to reptation using soft potentials. F. Lahmar and B. Rousseau, Laboratoire de Chimie Physique, Université Paris-Sud, France. We used a coarse-grained model of polyethylene and dissipative particle dynamics (DPD) to study the onset of entanglements in polymer chains with different length. We employed a bottom-up approach to derive the conservative potentials describing beads interactions. Because of the large coarse-graining level retained in our approach, where one bead corresponds to 20 carbon atoms, beads can easily overlap. In order to avoid bond crossing, we have introduced and parameterized a segmental repulsive potential (SRP) adapted to our model. We demonstrate that the segmental repulsive potential can reproduce the dynamical transition from an unentangled to an entangled polymer melt. For short chain unentangled systems, we observe a deviation from the pure Rouse behaviour attributed to the presence of chain stiffness, non-bonded interactions and bond uncrossability which are not considered in the Rouse model. For the longest chains, global dynamics is typical of reptation dynamics with chain length dependence of viscosity and self-diffusion described by a power law with exponent equal to 3.2 and -2.3, respectively. However, topological constraints alter polymer dynamics at length scales much shorter than the length scales implied in the reptation model. This is evidenced both by the static, topological analysis, and the analysis of global and local dynamics. The approach proposed here can be applied

to the study of many different systems in soft matter, from linear, branched and star polymers, to membranes and colloids, and serves as a tool to interpret neutron scattering experiments and get an enhanced understanding of matter.

12:15 pm Session ends

Biology Session
Friday, December 5, 2008
Sheraton Hotel – 3rd floor – Fairfax A/B
Sow-Hsin Chen, Chair

1:30 pm

Neutron scattering and computer simulation in biology. Jeremy C. Smith, Center for Molecular Biophysics, Oak Ridge National Laboratory, Oak Ridge, Tennessee. A review will be presented of how the integration of neutron scattering and computer simulation techniques provides insight into biomolecular structure, dynamics and interactions. References: I. DAIDONE, M. ULMSCHNEIDER, A. DI NOLA, A. AMADEI and J.C. SMITH. *Proc Natl Acad Sci (U.S.A.)* 104 39 15230-15235 (2007). L. MEINHOLD, F. MERZEL and J.C. SMITH. *Phys Rev Letts* 99 (13):138101 (2007). L. MEINHOLD, J.C. SMITH., A. KITAO and A.H. ZEWAIL. *Proc Natl Acad Sci (U.S.A.)* 104 44 17261-17265 (2007). L. MEINHOLD, D. CLEMENT, M. TEHEI, R. DANIEL, J.L. FINNEY & J.C. SMITH. *Biophys J* 94(12):4812-8 (2008). V. KURKAL-SIEBERT, R. AGARWAL & J.C. SMITH. *Phys Rev Letts.* 100 (13) 138102 (2008). M. KRISHNAN, V. KURKAL-SIEBERT & J.C. SMITH. *J Phys Chem B.* 112(17):5522-33 (2008). T. NEUSIUS, I. DAIDONE, I.M. SOKOLOV & J.C. SMITH. *Phys Rev Letts.* 100 (18) 188103 (2008). S. E. MCLAIN, A. K. SOPER, I. DAIDONE, J. C. SMITH and A. WATTS, *Angewandte Chemie Intl. Ed.* In press.

2:15

Collective molecular dynamics in proteins and membranes. Maikel C. Rheinstädter, University of Missouri-Columbia, Columbia, MO, USA. The understanding of dynamics and functioning of biological membranes and in particular of membrane embedded proteins is one of the most fundamental problems and challenges in modern biology and biophysics. The impact of membrane composition and properties and of structure and dynamics of the surrounding hydration water on protein function can be addressed by modern experimental and computational techniques. Very recently, inter protein motions in a protein crystal were reported from a molecular dynamics simulation [*Phys. Rev. Lett.* 100, 138102 (2008)] and phonon like excitations were found in protein molecules by inelastic x-ray scattering [*Phys. Rev. Lett.* 101, 135501 (2008)]. We present experimental evidence for a cooperative long range protein-protein interaction in purple membrane (PM). The dynamics was quantified by measuring the spectrum of the acoustic phonons in the 2d Bacteriorhodopsin (BR) protein lattice using inelastic neutron scattering. The data were compared to an analytical model and the effective spring constant for the interaction between protein trimers was determined. [1] Maikel C. Rheinstädter, Karin Schmalzl, Kathleen Wood, Dieter Strauch, <http://arxiv.org/abs/0803.0959>.

2:45

Collective dynamics in systems of biological interest investigated by Neutron Spin Echo spectroscopy. Antonio Faraone, NIST Center for Neutron Research and Department of Material Science and Engineering, University of Maryland. Neutron Spin Echo (NSE) spectroscopy allows the study of the relaxational dynamics in the time range from few picoseconds to hundreds of nanoseconds at length scales from the fraction of an Angstrom to hundreds of Angstroms. For these characteristics, it is well suited for investigating collective relaxational process in systems of biological interest. Phospholipids unilamellar vesicles can be used as model systems for biological membranes. Measuring the bending modulus of rigidity by NSE it has been possible to gain new insight into the mechanism of interaction of the membranes with melittin, a helical peptide which is the main active component of bee venom. In a similar way the cryoprotective properties of trehalose have been investigated. As a third example of NSE applications to biological studies, the conformational and dynamical properties of a protein partially unfolded by a photoresponsive surfactant will be discussed. In its partially unfolded state the protein shows a seven times increase of its activity which is accompanied by the appearance of collective domain motion dynamics, as revealed by NSE. By exposing the system to UV light, because of the characteristics of the surfactant, the protein returns to its native state. These results allow us a better understanding of the form-dynamics-function triad in the system.

3:15 Break

3:45

Dynamical coupling between hydration water and proteins: a comparison of membrane and soluble proteins. Kathleen Wood[‡], D. Tobias[○], G. Zaccai^{*}, M. Weik[#] [‡]Biophysical Chemistry, Groningen, the Netherlands; [○]University of California, Irvine, USA. ^{*}Institut Laue Langevin, Grenoble, France; [#]Institut de Biologie Structurale, Grenoble, France. The relationship between the dynamics of a protein and its environment is important for the understanding of protein function in a cellular context. The dynamics of specific components of a complex system can be explored by combining neutron spectroscopy with isotope labelling. Here we studied deuterated systems, hydrated in H₂O and the corresponding hydrogenated systems in D₂O, to study separately hydration water and macromolecular dynamics, respectively. We present data on the maltose binding protein, a soluble protein, where we find a dynamical transition in the hydration water at 210 K triggers a transition in the protein at the same temperature, implying a tight coupling between the two entities (1). A similar study performed on the purple membrane revealed a different scenario for the dynamical relationship between a membrane protein, bacteriorhodopsin, and its hydration water (2): a transition occurs at 200 K in the water, and in the protein at 250 K. For both the soluble and membrane protein studies presented, molecular dynamics simulations at temperatures spanning the observed transitions reproduced well the experimental data (1,2). The simulations then allow an investigation at the microscopic level of the observed transitions: the hydration water transitions observed are due to the onset of translational diffusion. The results suggest an important role of lipids in the dynamical control of membrane proteins. ¹Wood, K., Frölich, A., Paciaroni, A., Moulin, M., Hartlein, M., Zaccai, G., Tobias, D. J. & Weik, M. (2008) *J Am Chem Soc*, 130, 4586-4587. ²Wood, K., Plazanet, M., Gabel, F., Kessler, B., Oesterhelt, D., Tobias, D. J., Zaccai, G. & Weik, M. (2007) *Proc Natl Acad Sci U S A* 104, 18049-18054.

4:15

Nanoscale coupled protein domain motion revealed by neutron spin echo spectroscopy. David Callaway, New York University School of Medicine, New York, NY. Long-range conformational changes in proteins are essential for the transmission and amplification of biological signals, as well as for transition state dynamics during enzymatic catalysis. Such changes can be initiated by nanoscale protein domain motion. Understanding how such conformational changes are triggered requires the characterization of protein motion on nanosecond timescales and on distance scales comparable to protein domain sizes. Using neutron spin-echo spectroscopy, normal mode analysis, and a statistical-mechanical framework, we reveal overdamped, coupled domain motion within DNA polymerase I from *Thermus aquaticus* (Taq polymerase). This protein uses coupled domain dynamics to coordinate nucleotide synthesis during DNA synthesis and repair. Neutron spin-echo spectroscopy thus provides dynamical information about a protein that is functionally important and inaccessible by other methods.

4:45

Dynamics and function of the archetypal Ca²⁺/Mg²⁺-binding EF-hand parvalbumins, a combined study by NMR and neutron scattering. Joseph Parello¹, Jean-Marc Zanotti² and Marie-Claire Bellissent-Funel², ¹Vanderbilt Univ. School of Medicine, Department of Pharmacology, Nashville, TN. ²Laboratoire Léon Brillouin (CEA-CNRS), CEA-Saclay, Gif-sur-Yvette, France. The dynamics and function of biomacromolecules are intimately related. Thus, an understanding of physiological phenomena requires a comprehensive knowledge of internal molecular dynamics as they occur under the crowded macromolecular conditions that characterize the intracellular environment. Such an environment gives rise to a high degree of dispersion of the intracellular water molecules at the surface of the different macromolecular components. We have observed that hydration has a major influence on the dynamics of a small-sized (~11 kDa) globular protein, namely the Ca²⁺/Mg²⁺-binding EF-hand protein, parvalbumin, which plays a critical role in regulating the Ca²⁺-signal in excitable cells (neurons and muscle cells). We have detected internal molecular motions using two experimental approaches, incoherent quasielastic neutron scattering and solid-state ¹³C-NMR, with correlation times in the 10-20 ps range (diffusive motions) and in the 10 ns range, respectively. Both experimental approaches indicate an increase in protein dynamics upon progressive hydration of the dry protein. Regulation of the Ca²⁺-signal by parvalbumin (and related EF-hand proteins) is achieved in the presence of a high concentration (mM range) of intracellular Mg²⁺ under physiological conditions. Parvalbumin displays an affinity for Ca²⁺ larger by 3-4 orders of magnitude than that for Mg²⁺. The variations in intracellular Ca²⁺ concentration that occur during the excitation-relaxation cycle (ca 10⁻⁵M and ca 10⁻⁷M, respectively) are accompanied by the switch of parvalbumin from its Ca²⁺-loaded form to its Mg²⁺-loaded form and vice versa. Both forms differ by their internal dynamics. Inelastic neutron scattering was used to investigate the dynamics of these forms to better understand the parvalbumin-mediated Ca²⁺/Mg²⁺-exchange processes that underlie the functioning of specific excitable cells.

5:00

Internal Dynamics in Proteins studied by Neutrons and X-rays. Jyotsana Lal¹, Peter Fouquet², Marco Maccarini², Diane J. Rodi³ and Lee Makowski³. ¹IPNS, Argonne National Laboratory, IL. ²Institut Laue-Langevin, Grenoble, France. ³Biosciences Division, Argonne National Laboratory, IL. Biomolecular systems are intrinsically dynamic, and a complete

understanding of the function of a system requires the characterization of its dynamics. In particular, a complete description of protein motion is critical to an understanding of the function of a protein. Here we will discuss collective internal motions of proteins in solution, an environment that closely resembles the inside of a cell. No single technique is capable of measuring the range of motions needed to develop a complete understanding of such complex systems. To study the dynamics of fluctuations from nanosecond to picosecond time scales we have developed a methodology at Argonne National Laboratory that involves coordinated use of Neutron Spin Echo (NSE) scattering and Wide Angle X-ray solution scattering (WAXS). The X-ray data provides important information about the ensemble of structures present in the scattering volume - and thereby a measure of the spatial extent of internal motions of the protein in solution. NSE is used to characterize the dynamics of the fluctuations observed with the X-ray measurements and determine the rate of relaxation of fluctuations on particular length scales. Results from correlated studies of hemoglobin and myoglobin demonstrate the power of this approach. The unprecedented intensities available at new, high-powered Spallation Neutron Sources (SNS) and X-ray sources like the Advanced Photon Sources (APS) will enable exciting new science in this area.

5:15 Session ends

Poster Session
Friday, December 5, 2008
Sheraton Hotel, 2nd Floor, Independence Ballroom
Al Hurd, Chair

5:30 Poster Session begins

Dynamics in Shear Flow Studied by Neutron Spin Echo and X-ray Photon Correlation Spectroscopy. Péter Falus¹, Marco Walz² and Andrei Fluerașu³. ¹Institut Laue Langevin, Grenoble, France. ²University of Erlangen, Erlangen, Germany ³European Synchrotron Radiation Facility, Grenoble, France. It is well known that shear flow strongly influences spectroscopy studies [1, 2]. The Doppler effect, which enables Doppler velocimetry is a strong artifact which may prohibit spectroscopy measurements. While these distortions are well explored for Dynamic Light Scattering (DLS), many interesting problems in shear flow manifest at nanometer length scales, which are accessible only by X-ray and neutron scattering techniques. In this presentation I will explore characteristic parameters of shear flow experiments, and show how Neutron Spin Echo (NSE) and X-ray Photon Correlation Spectroscopy (XPCS) differ from visible light measurements due to the changed time and length scales. I will shortly present proof of the principle XPCS measurements [3], which will leave me to conclude that Neutron Spin Echo is better suited to study polymeric liquids under shear flow. Finally Neutron Spin Echo experiments will be presented on the boundary layer dynamics of polymer melts. It has been shown that the glass transition temperature decreases for thin polystyrene films [4], additionally the viscosity is reduced next to the interface, thus under shear the conventional non slip boundary condition becomes invalid (apparent slip). It will be described in detail how Neutron Spin Echo measurements are possible in liquids under shear, and the first NSE spectroscopy measurements will be presented on the shear dependence of dynamics of polymer melts. 1. Ackerson, B. J. & Clark, N. A. *J. Physique*, **42**, 929–936 (1981). 2. Fuller, G. G., Rallison, J. M., Schmidt, R.L. & Leal, L.G. *J. Fluid Mech.* **100**, 555–575 (1980). 3. Fluerașu, A. et al. *Journal of Synchrotron Radiation* Accepted for publication OT-5581 (2008). 4. Pastorino, C, Binder K, Kreer T, and Mueller M, *J. Chem. Phys.* **124**, 064902 (2006).

Dynamics of breathable poly(N- isopropylacrylamide) network with controllable hydration which supports model lipid membrane. Michael Jablin[†], Hillary Smith[†], Ryan Toomey[‡], Jessica Saiz[†], Jaroslaw Majewski[†]. [†] Manuel Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory. [‡]Department of Chemical Engineering, University of South Florida. The interaction of a model lipid bilayer composed of dipalmitoyl-phosphatidylcholine (DPPC) with a surface-tethered poly(N-isopropylacrylamide) (poly(NIPAAm)) network was explored with neutron reflectometry. The Langmuir-Blodgett / Langmuir-Schaeffer method was used to deposit a lipid bilayer of DPPC onto a poly(NIPAAm) coated quartz substrate. Previous experiments demonstrated that the structure and hydration of the poly(NIPAAm) network is sensitively dependent on temperature. Low temperatures (15-28 °C) cause the thickness of the network to swell while high temperatures (32-44 °C) result in the collapse of the network. Neutron reflection measurements were used to determine the combined structure of the lipid bilayer and the poly(NIPAAm) as a function of temperature. Our measurements suggest that a poly(NIPAAm) thin film is capable of supporting a lipid bilayer and through its thermoresponsive characteristics, controlling the volume and hydration of the space between the solid support and the model membrane. The lipid bilayer rides the polymer cushion from its thinnest, collapsed-state thickness of 150 angstroms at 37 °C to its extremely hydrated, swollen thickness of over 800 angstroms at 25 °C, and finally returns back to its collapsed state with the bilayer in-tact at a temperature of 37 °C. As the temperature of the

system is decreased, the membrane is far from being flat and develops out-of-plane undulations with average amplitude much greater than the thickness of the lipid bilayer. This is accompanied by the appearance of off-specular neutron scattering. Analysis of the off-specular can shed light on the in-plane dynamical properties of the membrane undulations. The separation of the lipid bilayer from the solid support of a substrate constitutes a significant step towards a more realistic model of biological membranes. Contact: Michael Jablin, Manuel Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory, mjablin@lanl.gov, tel: (505)-665-3953.

Dynamics of constitutional terphenyl isomers adsorbed onto graphite. Edward J. Kintzel, Jr.¹, Kenneth W. Herwig², and Inma Peral³. ¹Department of Physics and Astronomy, Western Kentucky University. ²Spallation Neutron Source, Oak Ridge National Laboratory. ³NIST Center for Neutron Research, National Institute for Standards and Technology. The dynamics of constitutional terphenyl isomers within ultrathin films adsorbed onto the surface of graphite has been investigated using quasielastic neutron scattering. Initial dynamic results indicate a phase change within these films at approximately 250 K. At temperatures below this value, the scattering is consistent with reorientation of the phenyl rings around the long molecular axis. At temperatures above 250 K, the scattering is much stronger and appears at lower momentum transfers, indicating some form of translational motion in combination with reorientation of the phenyl rings.

Dynamics of RNA and protein at different levels of hydration. ^{1,3}J. H. Roh, ¹R. M. Briber, ³A. Damjanovic, ²D. Thirumalai, ³S. A. Woodson, and ⁴A. P. Sokolov. ¹Department of Materials Science and Engineering, University of Maryland, College Park, MD. ²Biophysics Program, Institute For Physical Science and Technology, University of Maryland, College Park, MD. ³T. C. Jenkins Department of Biophysics, Johns Hopkins University, Baltimore, MD. ⁴Department of Polymer Science, University of Akron, Akron, OH. Fast dynamics on the nanosecond timescale are investigated using neutron scattering spectroscopy and molecular dynamics (MD) simulations for tRNA and the protein lysozyme as a function of the level of hydration. Our results show that the fast conformational motions of tRNA exhibit a stronger hydration-dependence than those of lysozyme. The characteristic temperature of the so-called “dynamical transition” (TD) and time scale of the fast conformational motions shifts significantly a function of hydration level for tRNA, while they remain largely unchanged for lysozyme. The characteristic length scale of the motions in fully hydrated tRNA is twice as large as in fully hydrated lysozyme. We attribute these hydration-induced dynamical differences between tRNA and lysozyme to their differing chemical structure, which includes a larger fraction and different nature to the hydrophilic sites as well as a more open and flexible structure for tRNA.

Effect of polymer mobility on conductivity of single-ion conductors. Kokonad Sinha, and Janna Maranas, Department of Chemical Engineering and Department of Material Science and Engineering, The Pennsylvania State University, University Park, PA 16802. Scientists are turning to the use of polymers as substitutes for liquid electrolytes in lithium ion batteries, because of their mechanical flexibility and non-toxic properties. Physical mixtures of lithium salt and poly(ethylene oxide) (PEO + LiClO₄) are commonly chosen because they have potential for high ionic conductivities. However, high mobility of ions in these mixtures results in electrode polarization, which affects battery performance. To isolate the effect of the cation and to reduce the obstacle of concentration polarization, the anion is chemically incorporated into the backbone of the polymer, thereby rendering it immobile. These single-ion conductors are called ionomers. It is a widely accepted theory that in polymer electrolytes, ion conduction is aided by the segmental mobility of the polymer. The cation electrostatically coordinates with 5-7 ether oxygen atoms and these cations “hop” from one polymer segment to another by making and breaking temporary “cross-links”. This study determines how the mobility of the ionomer affects the ion conductivity and how the ion content affects segmental mobility in return. Neutron scattering experiments have been conducted on ionomers with varying degrees of ionization. We observed that there is an optimum ion content that has the maximum ionomer mobility and the highest conductivity. This can be explained by the fact that when ion content increases, there are more ions present to contribute to conductivity, but electrostatic coordination of cations with ether oxygen atoms reduces the polymer mobility. Neutron scattering experiments further show that polymers with ions have a second process, which is absent in polymers with no ion concentration at all. This second process is slower than the segmental motion of the polymer and it constitutes of making and breaking of electrostatic cross-links. This feature becomes more prominent with increasing ion content. On comparison of the timescales for segmental mobility and the second process we noted that for PEO+LiClO₄ mixtures, this second process is significant in improving conductivity. However, for ionomers, this process does not play a major role in the mechanism of conduction. This comparison in terms of mobility as a function of ion concentration gives a better insight for understanding the fundamental mechanism of ion conduction in ionomers. This will enable us to choose an ion loading that gives optimum performance. We measured ionomer mobility using the High-Flux Backscattering Spectrometer [HFBS] and the Disk Chopper Time-of-Flight Spectrometer [DCS] at the NIST Center for Neutron Research in Gaithersburg, Maryland. DCS primarily detects segmental motion of the polymer, which lies in a timescale between 0.1 ps and 40 ps. HFBS detects motion on a

timescale between 240 ps and 2 ns, and this primarily constitutes of the second process. Mobility is measured for ionomers with from 0%, 5%, 10%, 25%, 50% and 100% ionization, at temperatures of 298K, 325K and 350K.

The fragile to strong dynamic crossover transition in confined water: molecular dynamics results. Paola Gallo¹, M. Rovere¹, and S. H. Chen². ¹ Dipartimento di Fisica, Universita' Roma Tre, Via della Vasca Navale 84, I-00146 Roma, Italy. ² Department of Nuclear Science and Engineering, M.I.T., Cambridge, Massachusetts, USA. Studies on water confined in different substrates, like protein surfaces, have shown a very rich scenario where approaching the glass transition and observation of different polymorphs are easier. This is one of the reasons, besides its biological and technological importance, for which most recently, great attention has been devoted to the study of water confined in nanoporous systems. A number of recent experimental results on water confined in MCM-41 obtained by using neutron scattering [1,2] and NMR [3] have been interpreted in terms of a fragile to strong transition in the dynamical behaviour of water. These experiments support also the presence of a liquid-liquid critical point in water. In order to make contact with experiments Molecular Dynamics simulations of supercooled water confined in a silica nanopore of MCM-41 type have been performed down to T=200 K. The nanopore has been realized by quenching a fused silica cell to a glassy state and by carving inside it a cavity which mimics the main features of the real system. Water inserted in the pore has been studied upon supercooling. The mean square displacement in the long time limit has a subdiffusive behavior already at T=300 K. Correspondingly, the self intermediate scattering function shows a two step relaxation scenario with a plateau at intermediate times and an alpha relaxation decay at long time. The stretching exponent results lower with respect to the typical values found in alpha relaxation of supercooled bulk water. The relaxation times extracted from the analysis show a peculiar behavior with a change of slope as function of temperature. We find in fact a crossover from a non-Arrhenius (Vogel-Fulcher-Tammann, VFT) to an Arrhenius law at T=220 K. This represents the evidence of a fragile to strong transition at a temperature close to the experimental finding [1]. [1] Li Liu, A.-H. Chen, A. Faraone, C.-W. Yen and C.-Y. Mou, Phys. Rev. Lett. 95, 117802 (2005). [2] S.-H. Chen, F. Mallamace, C.-Y. Mou, M. Broccio, C. Corsaro, A. Faraone and L. Liu, Proc. Natl. Acad. Sci. USA 103, 12974 (2006). [3] F. Mallamace, M. Broccio, C. Corsaro, A. Faraone, U. Wanderlingh, L. Liu, C.-Y. Mou and S. H. Chen, J. Chem. Phys. 124, 161102 (2006).

High and low temperature dynamic crossover phenomena in protein hydration water. Yang Zhang¹, Sow-Hsin Chen¹, Antonio Faraone², John Copley², Dazhi Liu³, Eugene Mamontov³, Mark Hagen³, Marco Lagi^{1,4}, Emiliano Fratini⁴, Piero Baglioni⁴, Francesco Mallamace⁵. ¹MIT, ² NIST Center for Neutron Research, ³SNS, ⁴University of Florence, ⁵University of Messina. Incoherent Quasi-Elastic Neutron Scattering (QENS) is used to investigate the high temperature (290K – 380K) diffusional behavior of lysozyme hydration water. The state-of-the-art backscattering spectrometer BASIS at SNS was used in the study. A high temperature dynamic crossover phenomenon of lysozyme hydration water at TD = 345 ± 5 K was observed. We present evidence, both from the neutron scattering experiment and the MD simulation, that this dynamic crossover temperature in the hydration water coincides with that of the reversible denaturation of lysozyme determined by specific heat measurements. Above TD the hydrogen bonded network of water molecules is not able to constrain the shape of the protein, which initiates the first stage of the unfolding process, the reversible denaturation of the protein (the high-T limit of the biological function of the protein). Incoherent Inelastic Neutron Scattering (INS) is used to investigate the low temperature (180K – 260K) dynamics of both lysozyme and its hydration water. The DCS spectrometer at NIST was used in the study. An enhanced boson peak was observed at and below the dynamic crossover temperature TL = 220 ± 5 K in the incoherent dynamic structure factor of both the protein and its hydration water. This result implies that slow-down of the mobility of hydration water across the low-T dynamic crossover temperature triggers the dynamic transition (previously called glass transition) of protein (the low-T limit of the biological function of the protein).

High resolution NSE spectrometer for the SNS. M. Ohl¹, N. Arend¹, M. Monkenbusch¹ and D. Richter¹. ¹ Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany. Neutron spin-echo (NSE) spectrometers are the neutron scattering instruments with the highest available effective energy resolution. Here we report on the science case and status of the new NSE spectrometer for the SNS. Huge dynamic ranges and ultra - high resolution in combination with flexibility and reliability are the primary design goals for this instrument. The dynamic range of the planned instrument will cover more than 6 decades in time $1\text{ps} < \tau < 1\text{s}$ with the maximal resolution $\tau \sim 1\text{ps}$. Huge Q range coverage combined with low sensitivity caused by a magnetic shielding are the remarkable characteristics of this new NSE spectrometer, too. The major scientific role of the instrument will be to supply a unique facility to analyze the dynamics contained in the SANS intensity from various systems. E.g. unravel molecular motions and mobilities at the nano- and mesoscopic level in “soft matter” which relate to research fields as molecular rheology of polymer melts, relaxation phenomena in networks and rubbers, interface fluctuations in complex fluids, polyelectrolytes, transport in polymeric electrolytes and gel systems. Also glasses and the evolution of structural and molecular relaxation dynamics on the path towards the glass transition is a very active research field. Further topics range from the stability of nanoparticle suspensions to transport phenomena in porous media

Ligand induced changes in protein dynamics: comparison of simulations with NMR experiments. M. Krishnan and Jeremy C. Smith, Oak Ridge National Laboratory, Oak Ridge, TN. Molecular recognition and association/binding are essential processes associated with almost all biomolecular reactions. Upon binding to a ligand, the potential energy surface, and consequently the structure, dynamics (both vibrational and conformational fluctuations) and thermodynamics of proteins change. Molecular recognition and protein-ligand binding substantially change the conformational entropy of proteins. By examining the dynamical response of a protein to target recognition and binding, such entropy changes can be estimated. Nuclear magnetic resonance (NMR) spectroscopy has been used to characterize the backbone dynamics while ^{13}C and ^2H relaxation of methyl-bearing residues are used to understand side-chain dynamics. We have characterized the site-specific dynamics and thermodynamics of methyl groups in CaM/peptide complex using molecular dynamics simulations and the umbrella sampling method. The results obtained from MD simulations provide microscopic insight into changes in the thermodynamic and conformational flexibility of the protein induced by ligand binding.

Nanotube representation for a photon. *M. Saglam and **G. Sahin. *Ankara University, Department of Physics 06100 Tandoğan, Ankara, Turkey. **Miami University, Department Electrical and Computer Engineering, Oxford, Ohio 45056. We argue that photon itself is a nanotube carrying a magnetic flux quantum of $\pm \Phi_0 = \pm hc/e$ with itself along the propagation direction. Here the plus sign stands for the right hand helicity and the minus sign does for the left hand helicity. We show that the circumference of this nanotube is exactly equal to the wavelength λ of the corresponding electromagnetic wave which varies from 10^{-3} nm to 10^3 . The present result supports the recent result about electron which states that electron (which is a spin $\frac{1}{2}$ particle carries an intrinsic flux quantum of $\pm \Phi_0/2$ depending on the spin orientation. We also argue that neutron also should carry a quantum flux of $\pm \Phi_0/2$ depending on its spin orientation. The present result is believed to help to understand the interaction of light with matter. [1] Saglam M. and Boyacioglu B., (2002), Int. J. of Mod. Phys. B, **16**, 607. [2] Wan K. K. and Saglam M., (2006) International Journal of Theoretical Physics, **45** (6) 1171. [3] Yilmaz O., Saglam M and Aydin Z.Z., (2007), The Journal of the Old and New Concepts in Physics, **4** (1) 141. [4] Saglam M., Saglam Z., Boyacioglu B and Wan K. K. (2007), Journal of Laser Optic, **28**, (3), 267. [5] Saglam M., Saglam Z. and Boyacioglu B (2007), Journal of Laser Optic, **28**(4), 377.

Neutron scattering investigations of molecular motion at interfaces. J.Z. Larese^{1,2}, T. Arnold³, P. Fouquet⁴, R. J. Hinde², A. J. Ramirez-Cuesta⁵, T. Seydel⁷, B. Sumpter², M. Telling⁵. ¹Chemistry Dept., University of Tennessee, Knoxville, TN 37996. ²Oak Ridge National Laboratory, Oak Ridge, TN 37831. ³Diamond Light Source, Chilton, Didcot, OX11 0DE, UK. ⁴Institut Laue-Langevin, Grenoble Cedex 9, France. ⁵ISIS Neutron Source, Chilton, Didcot, OX11 0DE, UK. Studying molecular adsorption at the gas-solid interface or within porous media sheds light on a wide range of technologically important processes including gas storage and separation, corrosion, lubrication, catalysis and environmental remediation. A first principles description of the forces that govern the formation of molecular films at these interfaces has yet to be realized. We will present recent measurements of the wetting and dynamical properties of monolayer and multilayer molecular films of methane, hydrogen and ethylene adsorbed on the (100) surface of MgO and discuss how the rotational motion of the molecules within the film evolve as the films thicken. We will also present the results of recent modeling efforts that provide additional insight into the physics that governs the dynamical behavior and indicates what the observed molecular motion says about the physical and chemical properties.

Si backscattering spectrometer at the pulsed neutron source of J-PARC. Nobuaki Takahashi¹, Kaoru Shibata¹, Yukinobu Kawakita^{1, 2}, Taku J. Sato^{1, 3}, Itaru Tsukushi^{4, 5}, Hiroshi Nakagawa⁵, Satoru Fujiwara⁵, Kenji Nakajima¹, Masatoshi Arai¹. ¹J-PARC Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan. ²Department of Physics, Kyushu University, 810-8560, Japan. ³Institute for Solid State Physics, University of Tokyo, Tokai, Ibaraki 319-1106, Japan. ⁴Department of Physics, Chiba Institute of Technology, 275-0023, Japan. ⁵Quantum Beam Science Directorate, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan. A time-of-flight Si-analyzer backscattering spectrometer (BSS) DNA is proposed for construction in the Materials and Life Science Facility (MLF) of Japan Proton Accelerator Research Complex (J-PARC) [1] located in Tokai, Ibaraki, Japan, in order to research on the dynamics of bio-molecules and proteins. Si(111) and Si(311) analyzers will be mounted in a vacuum vessel on both sides located at 43 m (L_1) away from a coupled moderator [2] to enjoy the highest peak intensity among moderators at the target station, viz. coupled, decoupled and decoupled-poison. On the other hand, there is a demerit that the pulse-shape of the coupled moderator is broad and has a long tail. Then, the instrument is designed to utilize a pulse-shaping device, which is high speed counter rotating disc choppers, staying on the beamline as far away from the sample position as possible (at 7.8 m from the source) to sharpen the pulse-shape. Optimizing the components of the instruments and tuning the pulse-shaping device, we can receive the benefit of 1 μeV energy resolution with $\pm 35 \mu\text{eV}$ energy band, obtained by analytical calculations and Monte-Carlo simulations. This is almost comparable to BSSs at reactor sources. Additionally we can obtain valuable energy resolution by tuning the pulse-shaping device (1 ~ 13 μeV). And also

when measuring inelastic part, we can easily broaden the limitation of such narrow energy band (± 35 μ eV) by phasing the pulse-shaping device. A novel efficient measurement technique, so-called Repetition Rate Multiplication (RRM) [3] is also planned, i.e., measuring inelastic part is efficiently achievable by using a multi-slit pulse-shaping chopper. In this presentation we will show conceptual design of the instrument. The expected performance will be compared with BSSs at reactor sources as well as BSSs at spallation neutron sources. [1] <http://j-parc.jp>. [2] N. Takahashi *et al.*, J. Chem. Phys. Sol., **68**, 2199 (2007). [3] N. Takahashi *et al.*, J. Neutron Res., **15**, 61 (2007). Corresponding to: Nobuaki Takahashi, Materials and Life Science Division, J-PARC Center, Japan Atomic Energy Agency, e-mail: nobuaki.takahashi@j-parc.jp, tel: +81-(0)29-284-3888. fax: +81-(0)29-284-3889

Structure and dynamics of weak polyelectrolyte layer-by-layer films. Eugenia Kharlampieva^{#*}, John F. Ankner[§], Michael Rubinstein[&] and Svetlana A. Sukhishvili[#]. [#]Department of Chemistry, Chemical Biology and Biomedical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030. [&]Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599. [§]Oak Ridge National Laboratory, Spallation Neutron Source, Oak Ridge, TN 37831. ^{*} current address: Department of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332. Controlling polymer-polymer interactions lies in the heart of engineering polyelectrolyte multilayers (PEMs) fabricated by layer-by-layer (LbL) technique. Applications of such materials as optically active coatings, or as platforms for sequential release of chemical and biological molecules strongly rely on their internal layering. With examples of polyelectrolyte pairs of opposite charge and pairs of neutral hydrogen bonding polymers, we show how the choice of polymer-polymer pairs and self-assembly conditions determines dynamics of polymer chains and controls polymer intermixing within temperature- and pH-responsive multilayers. The degree of ionization of carboxylic groups in self-assembled weak polyelectrolytes was quantified using *in situ* Fourier transform infrared spectroscopy in attenuated total reflection (FTIR-ATR), and the degree of layering within LbL films was probed by neutron reflectivity. In the case of hydrogen-bonded polymer multilayers, neutron reflectivity studies show that the degree of interpenetration of polymer layers expressed as the interlayer roughness was strongly correlated with strength of intermolecular interactions between the adjacent layers, and that polymer layers became more diffuse with a distance from the surface. In the case of a polycation assembled with poly(methacrylic acid) (PMAA) at low pH, we show that the polycation/PMAA films selectively release the polyacid in response to an increase of external pH. Studies of the kinetics of PMAA release reveal that the characteristic time of PMAA chain release, τ , scales with molar mass, M_w , as $M_w^{1.1 \pm 0.1}$. We present a theoretical model of the “sticky gel electrophoresis” of polyacids with excess charge which predicts a release time proportional to the molecular weight of released polyions and to the film thickness, in agreement with experimental results. Neutron reflectivity studies show explicitly that PMAA release results in disordering of the PEM film structure.

Swell or not swell? An improved Dreiding III molecular dynamics study on PAMAM dendrimer in aqueous solution.

Yi Liu, V. Bryantsev, M. Diallo, and W. A. Goddard III, Materials and Process Simulation Center, California Institute of Technology, Pasadena, California. Consensus is yet to be reached on the conformational change of PAMAM dendrimer upon pH conditions: SANS experiments indicate that the radius of gyration (R_g) of dendrimer is essentially independent of pH levels, while all previous computational studies showed the significant increase of R_g when pH decreases. Our study aims to develop a novel first-principles based multi-scale simulation approach to solve the contradictory discrepancy between experiments and theory, and give further insights on structure and dynamics that are complementary to experiments. The previous force fields (FF), generic Dreiding II, is found to overestimate the binding of counter ion (Cl⁻) to water, but underestimate the counterion-dendrimer binding and intramolecular interaction of dendrimer. Recently we develop a full atomistic classical force field - Dreiding III to describe PAMAM dendrimer at high accuracy by deriving parameters from quantum mechanics density functional theory (QM-DFT) studies. The improved Dreiding III is able to reproduce QM energies and geometries of all key interactions that are critical to characterize PAMAM conformation in aqueous solution, including 24 cases in fitting process and 11 cases for validation. The large scale Dreiding III MD simulations show that the R_g of PAMAM G4 is ~ 21.3 Å on average, and remain essentially invariant upon various pH conditions, which is in quantitative agreement with SANS experiment. Solvent accessible surface area and volume as well as shape tensor were evaluated to further characterize the conformation of dendrimer. Segmentation density distribution and radial distribution function are used to study counterion condensation, water solvation and intramolecular interaction of dendrimer. It is found that PAMAM backfolds locally at the periphery of dendrimer rather than to the center of dendrimer core, and expose large hollow interior region to solvent through open surface. Counterions reside mostly at vicinity of protons indicating their strong association with dendrimer. The electrostatic screening owing to counterions thus prevents effectively protonated dendrimer from swelling.

Understanding ion transport in ionomers using dielectric spectroscopy. U Hyeok Choi¹, Sharlene R. Williams², Timothy E. Long² and Ralph H. Colby¹. ¹ Materials Science and Engineering, Penn State University, University Park, PA 16803. ² Chemistry Department, Virginia Tech, Blacksburg, VA 24061. The future use of electrical energy demands development of the next generation of batteries. Existing battery technologies have limited energy storage capacity of individual battery cells

and for automotive applications are severely limited by slow ion transport. To provide the major breakthroughs, a fundamental understanding of ion transport in these complex systems must be obtained. In order to deduce the mechanism of ion conduction in ion-containing polymers, not only the conductivity needs to be measured but also the number density and mobility of charge carrying ions must be determined. Our group has studied the basic mechanism of ion transport on single-ion conductors in a broad frequency and temperature range. To obtain a transference number of unity, one ionic charge is covalently bonded to the polymer so that only the counterions can contribute to ion conduction. In this study, we also attempt to produce mechanically stable single-ion conducting polymers. Microphase separating polymers are attractive due to the combination of a high-T_g phase for good mechanical properties and a low-T_g phase for facile ion transport. Ions can associate into pairs and larger aggregates. The degree of ion pairing can be estimated from the temperature dependence of the dielectric constant and knowledge of the dipole moment of the ion pair, through the 1936 Onsager equation. Using the 1953 Macdonald model makes it possible to separately determine mobile ion concentration and ion mobility, from analysis of electrode polarization in dielectric spectroscopy. This talk will present these results on single-ion conducting polymers synthesized from ionic liquid monomers with bromide counterions.

Weakening ion interactions in ionomers using ionic liquid Counterions. Gregory J. Tudryn and Ralph H. Colby, Materials Science and Engineering, Penn State University, University Park, PA 16803. Anionic ionomers based on poly(ethylene oxide), (PEO) are single-ion conductors that are candidate electrolyte materials for advanced electro-active devices due to the ability of the ether oxygen in PEO to solvate conducting cations. Conventional cations (Na⁺ and Li⁺) in sulfonated PEO-ionomers are replaced with ionic liquid counterions and electrical and mechanical properties are measured by dielectric spectroscopy and linear viscoelastic characterization via oscillatory shear. Ion exchange from sodium counterions to ionic liquid counterions such as tetramethyl ammonium and tetrabutyl ammonium show on the order of 10⁴ X larger conductivity than the same ionomers with sodium counterions. Electrode polarization is used in conjunction with the 1953 Macdonald model to determine the number density of conducting counterions and their mobility. Conductivity and mobility exhibit Vogel-Fulcher-Tammann (VFT) temperature dependences and both increase as the counterion size increases. Conducting counterion concentrations show Arrhenius temperature dependences, with activation energy notably reduced as counterion size increases. Linear viscoelastic response reveals two important features. Time-temperature superposition works, suggesting that ions do not microphase separate. The ionomer with tetramethyl ammonium counterions has higher plateau modulus than the ionomers with larger counterions, suggesting that TMA allows formation of stable quadrupoles. Improvements observed in this study show favorable results for fundamental design of single-ion conductors for actuators, as ionic liquid counterions can provide both larger and faster strains, which such electro-active devices require.

7:00 Poster Session ends

Surfaces Session
Saturday, December 6, 2008
Sheraton Hotel – 3rd floor – Fairfax A/B
Ian Anderson, Chair

8:00 am

Role of interfaces on the long-time dynamics of polymers. Peter F. Green, University of Michigan. Nearly four decades ago it was recognized that in a highly entangled melt of linear chains, a chain undergoes translational motion within a virtual tube, formed due to its entanglements with neighboring chains (Reptation). The resistance this moving chain experiences is assumed to be distributed uniformly along its contour, so each monomer experiences an average frictional drag, $\zeta(T)$. $\zeta(T)$ determines the time scales of chain diffusion and the viscosity of homogeneous melts in a predictable manner. Today, there is significant interest in understanding the effect of interfaces on the transport of chains in thin films and in polymer nanocomposites. Interfaces contribute to the local heterogeneity not only of the chain dynamics, but also to the local heterogeneity of the glass transition. A comprehensive picture of the manner in which the mechanisms of flow, time-scales of dynamics, and T_g are affected in these systems remains elusive. In this presentation we will describe experiments involving incoherent elastic neutron scattering and quasi elastic neutron scattering, complimented by dielectric spectroscopy, rheology and scanning transmission electron microscopy, to illustrate new insights into fundamental processes that control dynamics and T_g in thin films and nanocomposites. Specific systems include thin supported polystyrene and poly teramethyl bisphenol polycarbonate homopolymers, as well as PS based nanocomposite systems. This presentation will also identify new directions and outstanding challenges where neutrons will play a critical role toward the development of an overall understanding of the structure and properties of these technologically important material systems.

8:45

Polymer dynamics under quasi-uniaxial confinement: the case of PEO in porous alumina. K. Lagrené¹, M. Daoud², J.-M. Zanotti¹. ¹Laboratoire Léon Brillouin (CEA-CNRS), CEA Saclay, 91191 Gif-sur-Yvette, France. ²CEA/Service de Physique de l'Etat Condensé, CEA Saclay, 91191 Gif-sur-Yvette, France. Thanks to numerous theoretical developments, it is now possible to draw a close relationship between polymer rheology in the bulk and chain dynamics at the molecular level. Nevertheless, the peculiar properties of polymers in interfacial situations or deep confinement are not completely understood. For instance, recent NMR relaxometry results suggest that the confinement of a polymer melt in a nanoscopic isotropic porous matrix leads to a chain dynamics that is dramatically different from the bulk behavior: the reptation tube diameter under confinement would be one order of magnitude smaller than in the bulk (for PEO: $d_{\text{conf}} = 0.6 \text{ nm} \ll d_{\text{bulk}} = 7 \text{ nm}$). This phenomenon has been called the “corset effect” [1]. The aim of the present work is to extend the relaxometry study reported in the literature to the case of PEO confined in an anisotropic matrix. We probe the polymer dynamics using a technique that measures simultaneously the time and space correlations: inelastic neutron scattering. The confining materials are custom-made Anodic Aluminum Oxide (AAO) membranes [2]. The porosity of the AAO matrices is made of micrometers long, macroscopically highly oriented cylindrical pores. We analyze this structure in details by a concurrent small angle scattering (SANS) and microscopy (SEM) analysis [3]. We show how to take advantage of the macroscopic orientation of AAO pores to evidence orientational dynamical effect – namely radial or longitudinal with respect to the highly anisotropic pore geometry. At large time and spatial scales (300 ms and 10^{-4} \AA^{-1}), we observe a highly anisotropic dynamics. However at a semi-local scale (1 ns and 0.6 \AA^{-1}), we do not observe any corset effect. [1] N. Fatkullin, E. Fischer, C. Mattea, U. Beginn and R. Kimmich, Chem. Phys. Chem., 5, 884 (2004). [2] H. Masuda and K. Fukuda, Science, 268, 1466 (1995). [3] K. Lagrené and J.-M. Zanotti, Eur. Phys. J. ST, 141, 261 (2007).

9:15

Dynamics of soft matter and complex fluids in confined geometry. D. Morineau¹, R. Lefort¹, R. Busselez¹, Q. Ji¹, R. Guégan², G. Chahine^{1,3}, M. Guendouz⁴, J.-M. Zanotti³ and B. Frick⁵. ¹Institut de Physique de Rennes, CNRS-Université de Rennes 1, Rennes France; ²Institut des Sciences de la Terre, Orléans, France; ³Laboratoire Léon Brillouin, CEA-Saclay, Gif-sur-Yvette, France; ⁴Laboratoire d'Optronique, Université de Rennes 1, Lannion France; ⁵Institut Laue-Langevin, Grenoble, France. The manipulation of fluids in nanochannels has become a crucial issue for many foreseen applications in advanced nanomaterials and biotechnology. Fundamental questions arise from the unexpected behaviors of fluids confined in capillaries of nanometric dimension, which rule out the validity of some approaches derived from the physics of liquids at the macro or microscopic scale. Intensive experimental studies of molecular liquids have shown that confinement on a nanometric scale considerably modifies the structure, phase behavior and molecular dynamics. Recently, much effort has focused on the unusual dynamic properties of low-molecular weight liquids and glassforming systems in mesoporous solids. It reveals a complex entanglement of low dimensionality, finite size and surface effects. In this field, a current challenge is to extend the knowledge of nanoconfined liquids to more complex fluids such as soft matter or solutions of biological interest. The aim of the present contribution is indeed to present some original features that are observed, when the confined system is tuned from pure globular liquids to anisotropic mesogenic molecules or multi-component glassforming bioprotectant solutions. (1) R. Busselez et al., Int. J. of Nanotechnology. 5, 867-884 (2008). (2) See recent reviews : C. Alba-Simionesco et al., J. Phys.: Condens. Matter 18, R15 (2006); M. Alcoutlabi and G. B. McKenna, J. Phys.: Cond. Mat. 17, R461 (2005). (3) R. Guégan et al., Phys. Rev. E 73 (1), 011707 (2006); R. Guégan et al., J. Chem. Phys. 126 (6), 1064902 (2007); D. Morineau et al., ILL Annual Report Scientific Highlights (2007).

9:45 Break

10:15

The dynamics of simple organic molecules in aqueous solution and confined in swelling clays. Neal Skipper, Univ. College, London. The interlayer pores of swelling 2:1 clays such as smectite and vermiculite provide an ideal 2-dimensional host in which to study confined aqueous and organic fluids. In addition, understanding and predicting the diffusion of simple organic molecules in clay-rich soils and rocks is extremely important in environmental and earth sciences, and is also a key for locating and extracting oil and natural gas. Quasi-elastic neutron scattering is a very powerful method for studying the dynamics of organic molecules such as methanol and phenol, both in the bulk and under confinement as a function of temperature and pressure. In all the cases we have so far studied, we have found that the confined organic molecules remain relatively mobile when compared to those in the bulk liquids, even when the interlayer pore dimensions are reduced to a few ångströms. This conclusion has important implications in areas such as the trapping and immobilization of organic pollutants.

10:45

Neutron and x-ray scattering experiments on stable molecular glasses. Mark D. Ediger, University of Wisconsin, Madison, Wisconsin. In contrast to the dominant view in the literature, we have recently shown that physical vapor deposition can prepare high density, low enthalpy, highly stable organic glasses. We estimate that a typical glass formed by cooling the supercooled liquid would have to be aged for more than 1000 years to achieve similar enthalpies and densities. Here we present experiments characterizing the structure and kinetics of these stable glasses. Neutron reflectivity, in conjunction with SIMS measurements, shows that when stable glasses are heated above T_g they transform to a supercooled liquid by a constant-velocity growth front. Wide-angle x-ray scattering, in conjunction with calorimetry, indicates that stable glasses can adopt different local packing arrangements than ordinary glasses. Physical vapor deposition thus represents a powerful tool for preparing unique materials that could fruitfully be investigated by a range of neutron methods.

11:15

Near-surface structure and dynamics explored by grazing incidence neutron scattering. Marco Walz¹, Max Wolff², Peter Falus³, Nicole Voss¹, Hartmut Zabel², and Andreas Magerl¹. ¹Chair for Crystallography and Structural Physics, University of Erlangen-Nürnberg, Erlangen, Germany. ²Ruhr-University Bochum, Bochum, Germany. ³Institut Laue-Langevin, Grenoble, France. Even in simple fluids the conventional non-slip boundary condition becomes microscopically void. Surface slip characterized by the slip length may become macroscopic, and a large slip length implies a pronounced anomaly in the shear flow adjacent to a solid surface, where the anomaly itself is only present in a thin layer next to the solid interface within the order of nanometers. For an understanding of boundary slip, the anomalies in the structural and dynamical properties in the interface layer need to be understood. Neutron grazing incidence diffraction techniques can be tuned to become surface sensitive and are thus ideally suited for this question. The high contrast of neutrons on hydrocarbon chains combined with a surface sensitive setup make neutron scattering techniques to a particularly suitable method for the investigation of the near-interface polymer structure and dynamics. To highlight the properties of the boundary layer we carried out Grazing Incidence Small Angle Neutron Scattering (GISANS) and, for the first time, a Neutron Spin-Echo experiment under condition of Grazing Incidence (GINSE). Our investigation of a concentrated tri-block copolymer solution shows that the local structure depends on the distance to the interface and the chemical termination of the solid boundary. However, the key for the understanding of slip may also be related to a change in the local dynamics of a liquid at an interface and under flow. GINSE appears to be the appropriate technique to access the relevant internal relaxation next to an interface. We have verified that the investigation of the dynamics of the sample with the GINSE technique is well feasible, and we present first data taken near the critical angle of total reflection. It appears that the diffusive motion of micelles at the hydrophilic (attractive) interface is reduced in comparison to a hydrophobic (repulsive) interface. The authors gratefully acknowledge the financial support by the DFG grants MA801/12-2 and ZA161/18-2 within the DFG priority program (SPP) 1164 and the BMBF grant ADAM 03ZA7BOC.

11:30

Shear induced relaxation of polymer micelles at the solid-liquid interface. Max Wolff^{*,1}, Roland Steitz², Philipp Gutfreund¹, Nicole Voss³, Stefan Gerth³, Marco Walz³, Andreas Magerl³, Hartmut Zabel¹. ¹Institute for Experimental Physics/Solid-State Physics/EP IV, Ruhr-University Bochum, Bochum, Germany. ²Helmholtz Centre Berlin for Materials and Energy, Berlin, Germany. ³Crystallography and Structural Physics, University of Erlangen-Nürnberg, Erlangen, Germany. ^{*}present address: Institute Laue-Langevin, Grenoble, France. Mixtures of amphiphilic block copolymers with a selective solvent are known to form various structures. At moderate and high concentrations micelles develop and may crystallise in face centered cubic (fcc) or hexagonal (hex) structures with unit cells in the range of several up to hundreds of nanometres. Applying external fields such as shear can dramatically change the overall structure of the sample. In most cases crystallites become aligned. Also secondary Bragg peaks are detected that were explained by a finite coherence of the crystalline structure. A second possibility to introduce anisotropy is by bringing a solution in contact with a solid wall. Well suited methods for monitoring the near surface region over many orders of magnitude in length scales (from nm up to μm) are small angle scattering and reflectometry. A 20 % aqueous solution of (ethylene oxide)₉₉ - (propylene oxide)₆₅ - (ethylene oxide)₉₉, F127, was investigated by combining rheology in a cone/plate-geometry and surface sensitive grazing incident neutron scattering. The crystalline structure formed by the polymer micelles becomes less pronounced for low shear rates but correlations increase for higher shear rates. After stopping shear a slow relaxation of the micelles is found in the vicinity (50 μm thick layer) of a hydrophilic silicon wall (strong micelle-wall interaction), while a fast relaxation is observed in the boundary layer against the hydrophobic silicon wall (weak micelle-wall interaction). The results show that in the vicinity of the interface wall-particle interactions compete heavily with the shear force acting on the liquid.

11:45 Break

Summary Session

Rob McGreevy, Chair

Noon

Lunch and Instrumentation Current Capabilities and Future Needs

Ken Herwig, Oak Ridge National Laboratory

1:00

Panel Discussion to Summarize Workshop

Christiane Alba-Simionesco

Sow-Hsin Chen

Victoria Garcia Sakai

2:30 Session and Workshop End

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