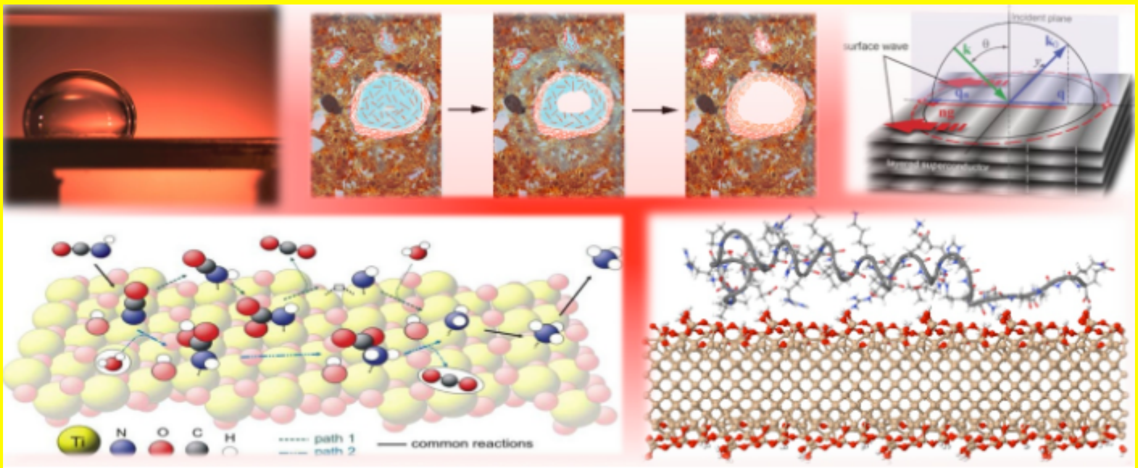

Fourth Annual Niels Bohr International Academy Workshop on ESS Science: Surface Interactions

Copenhagen, November 10-14

This year our workshop-school is intended to be a forum of discussion of how the use of X-ray and neutron reflectometry tells us about the binding of molecules to a surface and of how the characteristic frequencies of motions of surface-bound molecules can be detected by inelastic neutron scattering, and finally, how such experimental results can be interpreted by molecular dynamics simulations.

Organizers

Heloisa N. Bordallo
Juergen Eckert
Hanna Wacklin

Sponsors

Niels Bohr International Academy
Niels Bohr Institute
PhD School of the University of Copenhagen
European Spallation Source
Institut Français du Denmark
ISIS, Science&Technology Facilities Council
BDEW Bundesverband der Energie- und Wasserwirtschaft e.V.

Invited Speakers

Jens Als Nielsen (Denmark)
Dimitri N. Argyriou (Sweden)
Heloisa N. Bordallo (Denmark)
Niels B. Christensen (Denmark)
Stuart M. Clarke (UK)
Juergen Eckert (USA)
Michael Fitzsimmons (USA)
Henrich Frielinghaus (Germany)
Jason Gardner (ROC)
Himanshu Khandelia (Denmark)
Virginie Marry (France)
Des McMorrow (UK)
Thomas Schrøder (Denmark)
Neal Skipper (UK)
Mark Telling (UK)
Robert K. Thomas (UK)
Hanna Wacklin (Sweden)
Eugen Weschke (Germany)

Fourth Annual NBIA Meeting on ESS Science – Practical information

Access

The main door of Building C will be unlocked from 8 am to 4 pm each day of the workshop. The door to Building A, which is to the right, is also unlocked during the same period.

Lectures & Posters

All lectures will be held in Auditorium A of Building C of the Niels Bohr Institute.

Please try to be respectful and do not use your computers during the lectures.

All posters will be exposed in auditorium C. Afternoon refreshments will be served by the posters.

Work space

Down the hall in the B building, which houses the Niels Bohr International Academy, there is a lounge with a chalkboard and a free espresso machine. If you are looking for a quite place the library is ideal.

Wireless connectivity

The local network is named "**Conference".**

To connect, you need to specify a password. This is "**Bohr2013**".

The network "**Eduroam"** is also available for those who have access to this service.

Computers have been stolen from the Institute. **Please never leave your computer unattended.**

Lunch

Lunches are provided free of charge to the registered participants at the NBI canteen. On Thursday and Friday we will provide delicious homemade sandwiches.

Guided tour at the NBI

A guided tour of the Niels Bohr's Office will take place on Thursday, November 13 from 10:15 to 10:45 for the invited speakers.

Round Table with ESS Scientists

Tuesday, 11 of November 14:00 – 16:00

This parallel section is aimed as a brainstorming meeting between the invited speakers and ESS scientists.

Social Program

Wednesday, 12 14:00 – 22:00

Guided tour of the Maritime Museum of Denmark followed by the conference dinner at Strand- & Badehotel Marienlyst.

Thursday, 13 June 13:30 – 16:00

Guided tour of the Den Hirschsprungske Samling followed by coffee and cake at the NBI for the invited speakers.

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Fourth Annual Niels Bohr International Academy Workshop on ESS Science:

Surface Interactions

Scientific Program

Final Program for the Fourth NBIA Meeting on ESS Science, November 10-14, 2014		
Only 20 students will take part on the hand on exercises. "ESS Science: Opportunities & Ideas" session is intended to give the participants an opportunity to discuss on what they think is most important to develop a good neutron facility, including instrumentation, sample preparation laboratories, software, hardware, etc..		
Day/Time	*Lecturer*	*Topic*
Monday, 1st day		
8:00 am - 9:00 am	**Registration & Posters placement**	
9:00 am – 9:15 am	Robert Feidenhans'l (NBI Director)	Welcome!
9:15 am - 9:30 am	Andrew Jackson (NBIA)	Very short history of the Niels Bohr Institute
9:30 am – 10:15 am	Robert K Thomas (University of Oxford)	Neutron Reflection: History, basis and applications
10:15 am - 10:45 am	Coffee break	
10:45 am - 11:30 pm	Jason Gardner (Science Park Taiwan)	Measuring the inelasticity of materials by neutron scattering
11:30 am - 12:15 pm	Virginie Marry (Université Pierre et Marie Curie)	Water in clays: Combining neutron scattering to molecular dynamics simulations
12:30 pm – 1:30 pm	Lunch	
1:30 pm - 2:15 pm	Hanna Wacklin (ESS)	Studying biological surfaces using neutron reflectometry
2:15pm - 3:00 pm	Mark Telling (ISIS)	Quasi-Elastic Neutron Scattering: A tool for the study of molecular dynamics
3:00 pm - 3:30 pm	*Posters* Coffee Break	
3:30 pm - 5:30 pm	Hanna Wacklin (ESS)	***Reflectometry Tutorial*** - Students chose project, hands on exercises
Tuesday, 2nd day		
9:00 am - 9:45 am	Stuart M. Clarke (University of Cambridge)	Neutron Scattering: Structure and dynamic at interfaces
9:45 am - 10:30 am	Thomas Schrøder (Roskilde University)	Molecular Dynamics (MD) simulations of liquids
10:30 am - 11:00 am	Coffee break	
11:00 am - 11:45 am	Des McMorrow (University College London)	Collective Excitations: are photons and neutrons really complementary?
11:45 am - 12:15 pm	Dimitri Argyriou (ESS)	ESS Science: Opportunities & Ideas
12:30 pm - 2:00 pm	Lunch	
2:00 pm – 4:00 pm	Mark Telling (ISIS)	***QENS Tutorial*** - Students chose project, hands on: Data analysis etc
2:00 pm – 4:00 pm	ESS Scientists	Round Table with ESS Scientists
4:15 pm - 5:00 pm	Students clip presentations: 3 minutes clip to show their research work	
5:00 pm - 6:30 pm	Beer party and posters	

Wednesday, 3rd day		
9:00 am - 10:30 am	**2 Students: Working groups together with tutors**	
10:30 am - 11:00 am	Coffee Break	
11:00 am - 11:45 am	Himanshu Khandelia (SDU)	MD simultaions in the biological regime
11:45 am -12:15 pm	Henrich Frielinghaus (JCNS)	Neutron reflectivity and grazing incidence methods applied to microemulsions adjacent to planar walls
12:30 pm - 2:00 pm	Lunch	
2:00 pm -	Excursion Maritime Museum of Denmark (http://mfs.dk/en/) & Conference dinner (Strand- & Badehotel Marienlyst A/S - http://www.marienlyst.dk) Sponsored by the ESS	
Thursday, 4th day		
9:00 am - 10:45 am	**2 Students: Working groups together with tutors**	
10:45 am - 11:15 am	Eugen Weschke (HZB)	Opportunities and challenges of soft X-ray resonant elastic scattering
11:15 am - 12:00 pm	Niels Bech Christensen (DTU)	Distinguishing lattice vibrations and magnetic excitations with neutrons
12:00 am - 12:45 pm	Juergen Eckert (USF)	Surface vibrational spectroscopy with neutrons
12:45 pm - 1:45 pm	Lunch	
1:45 pm - 4:00 pm	**2 Students: Working groups together with tutors**	
1:45 pm - 4:00 pm	Guided Tour for the senior scientists: Den Hirschsprungske Samling (http://www.hirschsprung.dk/default.aspx)	
4:00 pm - 4:30 pm	Coffee break	
4:30 pm - 6:00 pm	**2 Groups of Students (30 minutes each group)**	Students presentations on their results
Friday, last day		
9:00 am - 9:45 am	Michael Fitzsimmons (Los Alamos National Laboratory)	Probing large-scale structures with polarized neutron beams
9:45 am - 10:30 am	Neal Skipper (UCL)	Dynamics of molecular hydrogen in layered materials
10:30 am - 11:00 am	Coffee break	
11:00 am - 11:45 pm	Heloisa N. Bordallo (NBI-KU)	Molecules in confinement: Structure and Dynamics
11:45 am - 12:30 pm	Jens Als Nielsen (NBI)	Final remarks
12:30 pm - 2:00 pm	**Lunch and Good Bye**	

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Fourth Annual Niels Bohr International Academy Workshop on ESS Science:

Surface Interactions

Invited Talks

Neutron Reflection: History, Basis and Applications

Robert Thomas

University of Oxford

Neutron reflection is now known as a method of studying interfaces. It is especially effective as a non-invasive technique for the study of liquid surfaces because there is a shortage alternative techniques with sufficient sensitivity.

The phenomenon of total neutron reflection was demonstrated in 1944 and was used mainly by two separate groups through the 50s, 60s and 70s for determining accurate values of nuclear scattering lengths, before its value for the study of interfaces was recognized. It is now widely used in interfacial studies.

The basis of the technique is relatively simple compared with other scattering methods but the systems it studies are generally correspondingly more difficult. This creates a situation where bringing together molecular dynamics and neutron reflection, as opposed to just comparing the results, could have distinct advantages, although it has been little exploited.

The basis of neutron reflection will be explained and examples used to illustrate the strengths and limitations of neutron reflection on its own.

Measuring the inelasticity of materials by neutron scattering

Jason Gardner

Science Park Taiwan

The properties of the neutron make it an ideal prove for studying the internal motions within samples in condensed matter research. Over the week many speakers will explain how this is done. In my talk I will introduce you to neutron scattering, focusing on how you measure the dynamics in the sample rather than the spatial arrangement of objects in the sample.

This will include an introduction to spectrometers that measure inelastic modes and those that measure relaxation processes. These tools combine to allow neutron scientists to measure processes within their samples with energy scales from μeV to eV (or sub 1 K to 1000's K).

Water in clays: combining neutron scattering and molecular dynamics simulations

Virginie Marry

Université Pierre et Marie Curie

The study of transport properties in materials such as clays, which are a main component of soils, is crucial for environment and industry.

Properly understanding the interactions between water and clay minerals and their consequences on transport phenomena is of prime importance in the framework of the remediation of contaminated environments as well as for predicting the long-term functioning of geological nuclear waste repository sites and CO2 storage in aquifers.

Swelling clay minerals or smectites are lamellar negatively charged alumino-silicates whose charge is compensated by exchangeable interlayer cations, the amount, nature and valence of which govern both hydration and colloidal behavior. They are considered as hydrophilic minerals, although neutral clays have hydrophobic properties in the absence of hydrated cations.

At the clay layer scale, quasielastic neutron scattering is the choice technique to measure water dynamics in this type of systems. On the other hand, molecular dynamics simulations allow a direct comparison with the experiments. The interest is double: first, molecular simulations offer a detailed description of water behavior in clay pores depending on the interlayer cations and the hydration level. Thus simulations can help in the neutron data interpretation and the choice of the relevant models of analysis. Second, the validity of the force-fields used in the simulations can be improved from the quantitative comparison with experimental results.

Studying biological surfaces using neutron reflectometry

Hanna Wacklin

European Spallation Source

Cell membranes, surfaces formed by lipids, are an important part of the biological environment that mediate biochemical reactions and regulate biomolecular functions. As cell membranes lack long range molecular order in plane, and require an aqueous environment, structural studies are not necessarily simple. In this talk I will describe the use of neutron reflectometry to elucidate the structure of lipid membranes, to probe their interaction with proteins, enzymes and pharmaceuticals.

Quasi-Elastic Neutron Scattering: A Tool for the Study of Molecular Dynamics

Mark Telling

Science & Technology Facilities Council (ISIS)

The spatial and temporal ranges accessible using the technique of quasi-elastic neutron scattering (QENS) are ideally matched to the vibrational displacements and diffusive motions encountered in molecular systems. The QENS method has been successfully applied to a diverse range of problems which encompass, for example, the mechanical integrity of concrete, improvements in dental care, spider silk formation and food preservation.

In addition, while beyond the immediate scope of this talk, the
times and length scales accessible using Molecular Dynamic (MD) simulations can be directly related to those probed experimentally by QENS.

In this introduction, the basic principles of the QENS method pertinent to the study of dynamic processes in soft matter systems will be presented. An overview of the neutron instrumentation required for such studies will be given as will be the experimental methodology; from sample preparation and optimization to data reduction. To conclude, the most common data analysis procedures will also be discussed.

Neutron Scattering: Structure and Dynamic at Interfaces

Stuart M. Clarke

University of Cambridge

The talk outlines the use of a combination of elastic and inelastic scattering methods (such as reflectometry, quasielastic and inelastic neutron scattering (QENS and INS) to address the structural and dynamic properties of interfacial materials relevant to lubrication, oil recovery and making ice-cream. Generally these are complex systems and so a combination of neutron/synchrotron and other complementary methods are required to piece together their behaviour.

In this talk, I propose to highlight what advantages neutrons in particular can provide as well as an outline a few other recent approaches

Molecular Dynamics (MD) simulations of liquids

Thomas Schrøder

Roskilde University

Molecular Dynamics (MD) simulation is a valuable tool when trying to understand the dynamics of liquids. I will give examples of how we use this simulation method in the "Glass and Time" group (glass.ruc.dk) where we focus on the dynamics of viscous liquids. In particular I will put emphasis on the connection between theory, simulation, and experiment, exemplified by the development and testing of the so-called "isomorph theory". I will also give a very short introduction our own open source MD code (rumd.org), which is optimized to utilize state of the art GPU hardware.

Collective magnetic excitations: are photons and neutrons really complementary?

Des McMorrow

University College London

The study of collective magnetic excitations is central to a number of fields ranging from attempts to understand the mechanism of novel superconductors through to foundational aspects of many-body quantum mechanics.

For most of the last fifty years or so neutrons have reigned supreme in this endeavour. Within the last five years resonant X-ray techniques have emerged that rival and in some cases exceed the capabilities of neutron experiments.

The extent to which X-rays complement or compete with neutrons will be illustrated with recent examples. Some perspectives on future possibilities will also be presented.

Looking into the future of neutron scattering with ESS: Current status and scientific opportunities

Dimitri Argyriou

European Spallation Source

The European Spallation Source (ESS) is on track to be build in Lund, Sweden and co-hosted by both Denmark and Sweden. The ESS will offer an order of magnitude greater peak neutron flux than what is currently available in the world. These unprecedented bright neutron beams will enable new science and allow us to examine matter with a clarity that is not attainable with current neutron sources. With accelerator and target station currently under detailed design considerations, ESS is focusing on the neutron instrumentation suite. In the talk I will discuss the status of the ESS project and focus on the proposed neutron scattering instrumentation, its capabilities and the processes we have put in place to identify and pursue scientific opportunities.

MD simulations in the biological regime

Himanshu Khandelia

University of Southern Denmark

Biological phenomena are today described on the basis of the underlying fundamental physical and chemical interactions. Non-covalent forces drive the development of complex biomolecular assemblies; which form the ultimate basis of life along with the covalent chemical reactions that lead to destruction and creation of new biochemical entities and energy. Computer modeling and simulation of complex systems consisting of many interacting particles is one of the most powerful methods to investigate the behavior of such complex molecular assemblies, and this is particularly true for biological systems. We use molecular dynamics (MD) simulations and related methods to investigate the self-assembly, phase behavior and interaction networks of a range of soft-matter biological systems.

I will illustrate how MD works in the biological regime using three distinct examples. First, the formation of lipid droplets inside lipid bilayers, and investigation of the internal structure of 25-nanometer sized lipid droplets. Second, I will also talk about the investigation of the dynamics and conformations of complex proteins, such as ion pumps. Finally, I will show how MD can predict self-assembly of mixtures of surfactants into flat lipid bilayers. For each of the three cases, diffraction promises to be a very useful complementary technique.

Neutron Reflectivity and Grazing Incidence Methods Applied to Microemulsions Adjacent to Planar Walls

Henrich Frielinghaus

Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH

The features that different neutron scattering methods reveal are discussed in the context of bicontinuous microemulsions exposed to a planar hydrophilic silicon surface. We found an induced lamellar ordering close to the surface while the bulk does not have any anisotropy. The reflectivity experiments displays the laterally averaged order parameter, and therefore ideally identifies the lamellar order, but is completely insensitive to the bicontinuous structure. A typical decay length is obtained. The GISANS experiments distinguish the two different structures, and the separating depth is obtained by this method. Computer simulations complete the picture and help to interpret the obtained length scales. Grazing incidence neutron spin echo spectroscopy aims at the dynamics of the surfactant membranes. Two different relaxation times are obtained for the bulk and the near surface structure. The intermediate relaxation times can be interpolated by the structural information obtained from GISANS. Theoretical models are presented to support the experimental findings. Amphiphilic diblock copolymers, which are the most suitable polymeric additives to microemulsions, are presented as a summarizing example to wrap up the presented methods in a coherent manner.

Opportunities and challenges of soft x-ray resonant elastic scattering

Eugen Weschke

Helmholtz-Zentrum Berlin für Materialien und Energie

Resonant elastic x-ray scattering combines the information about spatial correlations with the spectroscopic information about the related electronic states via the resonance process. While the method is sensitive to spin and orbital ordering, the contrast mechanism is purely electronic, different to the interaction of neutrons with matter. Resonant x-ray scattering is thus at the heart of the electronic origin of ordering phenomena in materials.

Despite severe limitations in terms of the accessible momentum transfer and particular experimental challenges, the soft x-ray energy range between 250 eV and 1500 eV has gained particular interest, as it covers strong dipole-allowed resonances of relevant materials including 3d and 4f transition elements as well as core-level excitations of oxygen, nitrogen and carbon.The sensitivity introduced by a huge resonant enhancement of the form factor paves the way to studies of subtle ordering phenomena in materials, such as complex magnetic order in ultrathin films or tiny single crystals, or charge order in 3d transition metal oxides [1].

The talk will shortly introduce the method and discuss two recent important applications, namely the appearance of antiferromagnetic order in two unit cells of nickelate films [2], and the role of charge order in superconducting high-Tc cuprates [3]. A short outlook will touch further applications, such as the study of organic molecule films using bond-selective reflectivity measurements at the carbon K-edge resonance, and time-resolved experiments.

References

[1] J. Fink, E. Schierle, E. Weschke, J. Geck: Resonant elastic soft x-ray scattering, Rep. Prog. Phys. 76, 056502 (2013).
[2] A. Frano et al., Phys. Rev. Lett. 111, 106804 (2013).
[3] G. Ghiringhelli et al., Science 337, 821 (2012).

Distinguishing lattice vibrations and magnetic excitations with neutrons

Niels Bech Christensen

Department of Physics, Technical University of Denmark

Neutron scattering is sensitive to both lattice vibrations and magnetic excitations. Using practical examples and with reference to theory, I will describe how one can in practise distinguish lattice and magnetic excitations by exploiting their characteristic dependence on temperature and momentum-transfer or by analyzing the polarization state of the neutron.

Surface Vibrational Spectroscopy with Neutrons

Juergen Eckert

University of South Florida

Among the many important properties of neutrons as a scattering probe of the structure and dynamics of condensed matter systems are their nondestructive nature and high penetrating power, both the result of their weak interaction with most atomic nuclei. It would therefore seem impossible to employ neutrons effectively in surface science, We can, however, utilize scattering contrast to dramatically improve this situation by selecting systems where the outermost layer of interest scatters neutrons much more strongly than the support. In the case of molecular spectroscopy this would normally be a layer of hydrogen containing molecules. The relatively low intensities of neutron beams, however, make it necessary to utilize materials with high surface areas. Vibrational spectroscopy by inelastic neutron scattering (INS) can thereby be utilized to study a number of important topics in surface science and catalysis particularly when combined with advanced computational modeling. These include the binding of sorbate molecules by physisorption and chemisorption, the nature of the interaction with the surface and the attendant the potential energy surfaces, intermolecular interactions as well as details of catalytic reactions.

Along with work on such equilibrium properties we have also been developing the use INS vibrational spectroscopy performed directly on quenched reaction intermediates and products in a catalytic reactor, in which the reaction was carried out either ex-situ, or in-situ. Examples of our ongoing studies to be described may include the synthesis of propylene carbonate on ceria-zirconia catalysts, propylene epoxidation by aqueous hydrogen peroxide in TS1, and on Au/TiO2 by reaction with H2 and O2, and ammonia synthesis over molybdenum nitride, along with computational analysis of the reaction steps using vibrational frequencies of reaction intermediates and products for comparison with experiment.

The work reported herein is the result of collaborations with many investigators including Luke Daemen, Panchapakesan Ganesh, Ivana Matanovic, and the late D.W. Goodman.

Probing large-scale structures with polarized neutron beams

Michael Fitzsimmons

Los Alamos National Laboratory

In this talk I will describe applications of polarized neutron reflectometry (PNR) and polarized beam small angle neutron scattering (pSANS) with polarization analysis. Examples include: the influence of bending stress or electric fields on the magnetism of epitaxial (La0.4Pr0.6)0.67Ca0.33MnO3 (LPCMO) and La0.8Sr0.2MnO3 (LSMO) films, use of polarization analysis to identify pinned uncompensated magnetism in an exchange bias system, use of PNR as a probe of nuclear polarization in GaAs, and use of pSANS to understand the role of 100's nm size magnetic domains on the coercivity and exchange bias of magnetic films. In fact, recent advances in thin film preparation offer new opportunities to further exploit interface magnetism in films with coherent interfaces perpendicular to the growth surface. Such samples are not amenable to study with reflectometry. Rather, I suggest the next blue ocean opportunity for neutron scattering will involve application of SANS with polarized neutron beams and polarization analysis to studies of interface magnetism. Finally, I briefly describe an application of polarized neutron beams to measure large scale structures in soft matter.

The Structure and Dynamics of Molecular Hydrogen in Layered Materials

Neal Skipper

University College London

The properties of molecular H2 physisorbed in solid-state nanoporous media are currently highly topical, with applications including gas adsorption and nuclear waste containment. In the context of hydrogen storage, physisorption of H2 offers the advantages of rapid kinetics, reversibility and stability of the host to long-term recycling. Strategies for achieving such interaction energies with porous substrates include: provision of open metal (Kubas) binding sites; creation of strong electrostatic fields within the cavity through a charged framework and counterions, and; reduction of the pore size towards the adsorbate diameter (around 2.9 Å for H2) to allow contact with more than one sorbate surface. With these factors in mind, 2-dimensional graphene-based nanostructures have been identified as potential targets for hydrogen storage. These materials allow metal (and solvent) intercalation with concomitant tunability of the layer-layer spacing. An alternative class of tunable 2-dimensional materials are the swelling 2:1 clays. This group of phyllosilicates, which includes smectites and vermiculites, are comprised of negatively charged mica-like sheets held together by charge-balancing counter ions, such as Na+ and Ca2+. Water molecules readily diffuse into the interlayer region of these clays causing lattice expansion, and thereby provide an ideal pillar to facilitate H2 intercalation. Moreover, the hydration state of the interlayer cations of clays can be controllably reduced by thermal treatment, leaving them exposed for direct binding to multiple H2 molecules.

Here we will discuss how neutron scattering and DFT calculations have been used to reveal the structure and dynamics of molecular H2 physisorbed into the two-dimensional pores of the graphite intercalate KC24 and sparingly hydrated Ca-laponite clay. For KC24 High-resolution inelastic neutron data show spectral features consistent with a strong pinning of H2 along a single axis. First-principles calculations provide novel insight into the nature of H2 binding in intercalates but fail to account for the symmetry of the H2 orientational potential deduced from experiment. The above discrepancy disappears once the H2 center of mass is allowed to delocalize in the quantum-mechanical sense across three vicinal adsorption sites. For Ca-laponite quasielastic neutron scattering experiments conducted at 40 – 100 K reveal two populations of H2 within the clay. First, we find molecules that are localized close to the partially hydrated Ca2+ cations. Second, we identify a more mobile liquid-like population whose motion is captured by jump diffusion.

References

[1] Quantum delocalization of molecular hydrogen in alkali-graphite intercalates. Lovell, A.; Fernandez-Alonso, F.; Skipper, N.T.; Refson, K.; Bennington, S.M.; Parker, S.F. Phys. Rev. Lett. 101, 126101 (2008). DOI: http://dx.doi.org/10.1103/PhysRevLett.101.126101

[2] Structure and Dynamics of Molecular Hydrogen in the Interlayer Pores of a Swelling 2:1 Clay by Neutron Scattering. Edge J.S., Skipper N.T., Fernandez-Alonso F., Lovell A., Gadipelli S, Bennington S.M., Garcia Sakai V., Youngs T.G.A. J. Phys. Chem. C, Article ASAP (2014).DOI: 10.1021/jp5082356

Molecules in confinement: Structure and Dynamics

Heloisa N. Bordallo

Niels Bohr Institute

Why in a barren and hot desert, clays can contain a significant fraction of water? Why does concrete crack? How can we demonstrate that complexation of a drug does not alter its conformation in a way that affects its functionality?

In this talk I will present results on various studies using Quasi-Elastic Neutron Scattering aimed at clarifying these questions. To allow for a better understanding of how neutrons can help, experimental results dealing with the effects of confinement on the water dynamics caused by the interfaces in clays and the nano- and micro-pores of concrete will be reviewed in detail. In addition, recent Quasi-Elastic Neutron Scattering investigations on the complexation of the local anesthetics Bupivacaine (BVC.HCl) and Ropivacaine (RVC.HCl) into the cyclic β-cyclodextrin oligosaccharide are presented. To conclude, the perspectives of the combination of X-rays and neutrons for the develpment of a drug carrier for cancer treatment will be discussed.

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Fourth Annual Niels Bohr International Academy Workshop on ESS Science:

Surface Interactions

Posters

Aspirin Reorganizes the Lipid Membrane

Richard Alsop, Maikel Rheinstadter

McMaster University

Non-specific interactions of drugs and pharmaceuticals within the body are believed to contribute to the occurrence of side-effects. Understanding these interactions has been a challenge. We use X-ray and neutron scattering experiments in synthetic, biomimetic tissue to better understand the non-specific interactions of these small molecules. My research to date has focussed on potential interactions between the common analgesic Aspirin and cholesterol. Aspirin is often prescribed as a secondary treatment for patients with diseases of high cholesterol, such as atherosclerosis, in a regimen known as the Low-Dose Aspirin Therapy. Cholesterol leads to an increase in membrane stiffness and stimulates the formation of functional domains, known as rafts, at physiological cholesterol concentrations. At high concentrations, atherosclerotic plaques are observed. To test an interaction between Aspirin and cholesterol within membranes, we prepared synthetic membranes containing cholesterol, and incorporated Aspirin into the tissue. We observed using X-ray diffraction that aspirin incorporates into membranes and increase lipid membrane fluidity, countering the effect of cholesterol [1]and dissolving atherosclerotic plaques [2]. Using neutron diffraction, we recently observed that aspirin suppresses cholesterol raft formation [3]. I will discuss these results, and our current plans to develop our scattering techniques into a platform to detect non-specific drug interactions.

References

[1] MA Barrett, S Zheng, G Roshankar, RJ Alsop, et al (2012). Interaction of Aspirin (Acetylsalicylic acid) with Lipid Membranes. PLOS ONE 7, e34357, 2012.
[2] RJ Alsop et al. (2014) Aspirin Increases the Solubility of Cholesterol When Incorporated in Lipid Membranes. Soft Matter (24).
[3] RJ Alsop et al. Aspirin Inhibits the Formation of Cholesterol Rafts in Fluid Lipid Membranes. Submitted to BBA-Biomembranes

Surface Dynamics and Rheology of Thin Polymer Films

Christian Appel, Martins Kraska, Bernd Stühn

TU Darmstadt

We investigate thin polymer films consisting of homo and diblock copolymers (main constituent: poly(2 - vinyl pyridine), P2VP)) and their mechanical behavior as thin films. For this we prepare monolayers of polymer at the air/water interface by the Langmuir technique and probe them by mechanical stress. By this we found that P2VPs dynamical behavior is a reptation-like motion in the so-called semi dilute surface regime. We present first experiments on the mechanical response of diblock copolymers, where P2VP is combined with two different organometallic ferrocene polymers: A semi crystalline (poly(ferrocenyl silane), PFS) and an amorphous (poly(vinyl ferrocene), PVF) block. The structure of the thin polymer films of P2VP-PFS and P2VP-PVF is particular important for the mechanical response and is therefore investigated by X-Ray reflectometry and Brewster angle microscopy. While the mesoscopic (in the µm scale) structure of P2VP-PVF is rather homogeneous, P2VP-PFS shows interesting quasi two dimensional crystallites when prepared in thin films being mainly responsible for the tremendous change in surface pressure isotherms.

Porosity Evolution of Geopolymers: a Multi-technique Study

Virginie Benavent, Prune Steins, Fabien Frizon, Arnaud Poulesquen

CEA Marcoule, LP2C

Geopolymers are amorphous aluminosilicate materials with low calcium content. They are made from a highly alkaline solution containing silicate precursors, in which an aluminosilicate source is added. As the aluminosilicate source dissolves, silicate and aluminosilicate species are formed in the solution phase until polycondensation begins. Eventually, a 3D solid network is formed, constituted by AlO4 and SiO4 tetrahedrons, and the remaining water is trapped in the porous phase of the material (interstitial solution). The durability of geopolymers represents a burning issue for the following years. Nowadays, geopolymers are studied because they represent an alternative solution to calcium silicate cements for low and intermediate level waste conditioning in the nuclear industry, as well as new materials for the building industry. The evolution of porosity with time and the chemistry of the pore solution are keys parameters to have a better understanding of their durability.

In this study, Na-Geopolymers and K-Geopolymers were synthesized using metakaolin as the aluminosilicate source. They were kept under 100% HR at 20°C during all the cure period before experiments to prevent drying. We have studied the influence of composition on porosity by adsorption-desorption of N2 and Small-Angle Neutron Scattering (SANS), by changing the molar ratios SiO2/M2O and H2O/M2O (M = Na or K). It was shown that the water ratio had the bigger influence on pore volume and pore size: the bigger the water ratio, the higher the open pore volume and the pore size. The evolution of porosity with time was also investigated on geopolymers aged between 7 days and 6 months. We have demonstrated by N2 adsorption-desorption an increase in pore size and a decrease in pore volume with time. Neutron scattering with contrast matching by isotropic exchange was used to highlight the presence of closed porosity and to determine the scattering length density of the geopolymers. The samples were immersed in H2O or in D2O in order to exchange the interstitial solution. In the first case, water was present in both open and closed porosity because the interstitial solution is mainly composed of water. In the second case, heavy water could only access to the open porosity. The difference of scattered intensity between the two curves revealed the presence of closed porosity. The isotopic mixture H2O/ D2O corresponding to the extinction of the geopolymer solid network was of 30/70%. This allowed calculating the scattering length densities of the geopolymers. Finally, both N2 adsorption-desorption and SANS techniques demonstrated a partial closure of porosity with time. The next step of our work will be the understanding of the evolution of porosity by the study of the interstitial solution, and the reactivity at the interface pore wall/solution. The structure and the dynamics of the confined solution will be studied by NMR and QENS techniques. The first 1H NMR and spin-lattice relaxation time T1 measurements showed that the half width at half height of the 1H signals were much higher for the interstitial solutions in the porosity than for the bulk solutions, extracted from the geopolymers thanks to high pressure device. Therefore, the molecular motions of H2O would be affected by the confinement. T1 was around 5 ms for all geopolymer compositions, while T1 was about 2.8 s for the bulk solutions.

Theoretical studies of the magnetic and superconducting properties of super-oxygenated $La_{2-x}Sr_xCuO_{4+y}$

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This work presents a theoretical study and brief review of La_2CuO_{4+y} (LCO+O), $La_{2-x}Sr_xCuO_4$ (LSCO) and $La_{2-x}Sr_xCuO_{4+y}$ (LSCO+O). In these types of cuprates, stripe order has been experimentally observed. The occurrence of high temperature superconductivity in cuprates is due to the CuO planes. In LCO the Cu atoms form strongly hybridized bonds with oxygen, which can be approximately explained by assuming there is one hole in the d-bond per Cu atom. The Cu sites can interact via the oxygen atoms through the super exchange mechanism and thereby forming an AFM-insulator (Mott insulator) best described by the one band Hubbard model. The excess oxygen will be described by a Thomas Fermi screening added to the one-band Hubbard Hamiltonian. By self-consistent calculations, we have stabilized stripe order in a 2D and 3D model. The calculations show that the spin settles in periodicity of 8 in the layers and anti-parallel between the layers. This type of calculation does not seem to work for compound with intermediate oxygen with modulations in the c-axis since the system stabilizes homogeneously.

Analysis of the confined cation-exchange process via XRD and EDS experiments

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Clays have shown potential for application as molecules capture, storage and delivery carriers. Due to the clay properties, as swelling capability, layer electrically charged, among others, atoms and even molecules can be intercalated into clay particles through a process called cation-exchange, which is as process usually performed in the time-scale of days. In this poster is presented some results recently published concerning the cation-exchange process of a synthetic clay mineral from Lithium-Fluorohectorite to Nickel-Fluorohectorite, as well as the reverse process from Nickel-Fluorohectorite to Lithium-Fluorohectorite and also from Lithium-Fluorohectorite to Sodium-Fluorohectorite. Using X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDS) the dynamics of these cation-exchange processes was investigated and it was observed that these processes can be faster than 1 minute, with results comparable with the standard cation-exchange process.

3D Neutron Diffraction

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Various natural materials, like sand or minerals, and almost all metals are formed by a number of crystals. 3D Neutron Diffraction is a new neutron-based microscopy technique for analyzing polycrystalline materials in 3D. The method enables non-destructive 3D reconstruction of the morphology and orientation of the grains present in millimeter to centimeter sized samples. The technique also allows to investigate complex samples environments.

We performed virtual and real experiments using polychromatic and time-resolved beams. The data have been analyzed with algorithms based on software developed for 3DXRD (3D X-ray Diffraction) microscopy. The methodology, algorithms and examples are presented along with potential applications.

Structure and dynamics of binary liquid mixtures in nanoconfinement

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Heterogeneous systems under nanoconfinement have been studied extensively so far in different domains of interest owing to their broad range of applications such as catalysis, drug delivery, fuel cells, petrochemical industry and others. Soft matter such as liquids, macromolecules and gels under certain selective conditions could undergo a self-assembly and structuration at the nanoscale, giving rise to novel properties which are non-existent in their bulk state. The balance between hydrophobic and hydrophilic interactions is a major driving force of such self-assembly in the liquid state. We address here the question of the nanostructure and molecular dynamics of model binary liquids in a variety of situations of nanoconfinement, at thermodynamic equilibrium or under flow.

In our experiments, we study the binary mixture of tert-butanol and toluene confined inside hydrophilic silica matrices (MCM-41 and SBA-15). The mixture is homogenous at a macroscopic scale. Small Angle Neutron Scattering (SANS) experiments on confined MCM-41 provide evidence for self-assembly and structuration occurring at the nanoscale giving rise to a core-shell structure.

PFG-STE NMR performed on confined MCM-41 provided dynamical information on the diffusion coefficients of the molecular groups present in the pores at equilibrium.Dynamics of these liquid mixtures in confinement under non equilibrium conditions have been investigated by spontaneous imbibition into nanoporous Vycor glass. In addition to PFG-STE NMR, adsorption-isotherm experiments are conducted on MCM-41 to derive more information at equilibrium.

Transport in and out of Extruded ER Formulations

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Low water solubility continues to be a major challenge when developing oral formulation strategies for several drug compounds. The poor ability of the drug compound to dissolve within the gastrointestinal system prevents it from reaching its intended target. Due to patient compliance and industrial scalability orally administered formulations are nevertheless desired. A promising technique to raise aqueous solubility and thereby the bioavailability through oral administration is the formulation of the Active Pharmaceutical Ingredient (API) in the amorphous state due to the improved dissolution characteristics compared to that of the crystalline state.

The on-going master thesis project investigates the manufacture of amorphous solid dispersions using Hot Melt Extrusion (HME). Amorphous solid dispersions are commonly referred to as an API in the amorphous state dispersed within a polymer network that is either amorphous or semi-crystalline. HME is an industrial processing technique used and developed in plastic industry and has increasingly been applied for pharmaceutical purposes.

The aim of this master thesis is to probe molecular mobility and physical structure within solid dispersions, and to connect this with long-term stability and storage properties. The influence of moisture upon mobility and structure will also be investigated. Dissolution properties of the solid dispersions in buffer solutions that mimic the gastrointestinal environment will be tested. This poster is a presentation of the current progress and puts emphasis on the physical characterization on single components performed so far.

Magnetic High-Field Phases of Magnetoelectric LiNiPO4

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In this work the magnetic high-field phases and magnetoelectric properties of LiNiPO 4 are studied up to 30T.

LiNiPO4 is a member of the family of lithium orthophosphates which are of orthorhombic structure and exhibit the magnetoelectric effect [1]. LiNiPO4 is a quasi-2D system with long range antiferromagnetic order below TN=21.8T in zero-field. The magnetic phase diagram of the material has previously been studied up to 17.3T [2,3] and pulsed-field magnetization measurements up to 23T show several additional phase transitions [4].

Here LiNiPO4 is investigated for fields up to 30T by pulsed high magnetic field time-of-flight Laue neutron diffraction and by magnetization and electric polarization measurements. Two high-field phases were found in agreement with the previous observations. The ordering vectors were determined and possible spin structures were suggested. The polarization measurements show a re-entrance of the magnetoelectric effect for μ 0 H≈19−21T, which points towards a commensurate ferrimagnetic state. However, the behavior of the effect is not fully understood. The effect vanishes above 21T where either a linearly polarized spin structure or a spin spiral is present.

The experimental technique using pulsed high magnetic fields in connection with neutrons is relatively new [5]. Nevertheless, the results displayed here show that the technique presents a future possibility to study high-field phases of certain magnetic materials.

References

[1] M. Mercier, J. Gareyt, and E. F. Bertaut, C. R. Acad. Sci. Ser. B 264, 979, 1967

[2] T. B. S. Jensen, N. B. Christensen, M. Kenzelmann, H. M. Rønnow, C. Niedermayer, N. H. Andersen, K. Lefmann, J. Schefer, M. Zimmermann, J. Li, J. L. Zarestky, and D. Vaknin, Phys. Rev. B, 79(092412), 2009

[3] R. Toft-Petersen, J. Jensen, T. B. S. Jensen, N. H. Andersen, N. B. Christensen, C. Niedermayer, M. Kenzelmann, M. Skoulatos, M. D. Le, K. Lefmann, S. R. Hansen, J. Li, J. L. Zarestky, and D. Vaknin, Phys. Rev. B, 84(054408), 2011

[4] V.M. Khrustalyov, V.N. Savitsky, and N.F. Kharchenko, Czechoslovak Journal of Physics, 54, 2004

[5] S. Yoshii, K. Ohoyama, K. Kurosawa, H. Nojiri, M. Matsuda, P. Frings, F. Duc, B. Vignolle, G. L. J. A. Rikken, L.-P. Regnault, S. Michimura, and F. Iga, Phys. Rev. Letters, 103(077203), 2009

Synthesis of Strained Alkenes with Low-Valent Titanium Reagents

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Steric strain in alkenes can lead to a change of standard geometries of the molecule.[1] The most known effect of this kind, described as deviation from the planar geometry of double bond, has been observed in many olefins, for which the structure was deduced by different experimental and theoretical methods.[2] In general, these deviations from planarity have been explained by the “effect of strain” on alkene structure and this phenomenon undoubtedly has significant impact on reactivity of carbon-carbon double bonds. Using low-valent titanium reagents for McMurry reaction to combine two ketones is a very convenient way to prepare these strained alkenes.

It was confirmed that using potassium to prepare the needed titanium species for the strained alkene synthesis gave better results than using zinc.

The effect of strain on the reactivity of the strained alkene was further analyzed by its gas-phase basicity measurements. From these measurements it could be concluded, that strained alkenes prepared this way are significantly more reactive than ordinary planar alkenes.

AOT based microemulsions: Structure and dynamics in bulk and at the air interface

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We investigate microemulsions based on the anionic surfactant AOT. Such systems, especially in the droplet phase, are well suited as model system with a soft confining geometry. In order to use them for confinement studies the structural as well as the dynamical features of the pure microemulsion system have to be known in detail. For all these aspects various scattering methods are well suited. The bulk structure is investigated by small angle neutron and X-ray scattering. Close to the air interface this structure might be strongly influenced which is analysed in terms of specular and off- specular X-ray reflectometry. Finally the system dynamics are explored with neutron spin echo spectroscopy being sensitive to form fluctuations of the surfactant shell. By the combination of static and dynamic scattering experiments it is possible to deduce the bending modulus of the surfactant shell, being a crucial parameter for the system stability. Furthermore, first results on the influence of water soluble polyethylene glycol on the microemulsion system are shown.

Towards Safer Sodium-Ion Batteries Via Ionic Liquids As Electrolyte Additives

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Our society is in urgent need of more efficient, affordable and environmentally friendly energy storage technologies. While lithium-ion batteries (LIB) is undeniably the main track of development and outstanding at present, complementary technologies are needed for managing applications such as renewable energy integration. One particularly appealing alternative is to explore the feasibility of a technology analogous to LIB – sodium ion batteries (SIB) – using the basic LIB know-how and with sodium being more abundant and less expensive.

As in any battery technology, the electrolyte choice is as important as that of the electrodes to ensure successful operation. Considering both safety and "environmental impact" ionic liquids (ILs) have emerged as an interesting option for LIB. ILs exhibit both non-volatility and non-flammability, but unfortunately their high viscosities and comparatively low conductivities are expected to considerably limit the rate performance. Mixed electrolytes, i.e. with ILs as additives to an organic electrolyte, are a compromise suggested to improve the safety – while still providing an appreciable conductivity. Here, the possibility of expanding this strategy also to the SIB technology has been explored.

We here present a systematic study of several electrolytes consisting of a sodium salt (NaTFSI) dissolved in mixtures of ILs and organic solvents, using electrochemical techniques (cyclic voltammetry, chronopotentiometry) coupled to various safety tests (e.g. self-extinguishing time (SET) and flash point (FP)). Imidazolium (BMImTFSI/EMImTFSI) and pyrrolidinium (PYR13TFSI) ILs were used as additives to optimized ethylene carbonate: propylene carbonate (EC:PC) electrolytes, while Hard Carbon (HC) and Na3V2(PO4)3 (NVP) were used as anode and cathode, respectively. Electrochemical tests were performed on half cells to evaluate the cycling abilities and the electrochemical stability of each electrolyte/electrode combination. HC tested with the BMImTFSI-EC:PC electrolytes exhibit specific capacities of ca 250 mAhg-1 and 140 mAhg-1 at C/5 and 1C rates with capacity retentions of 95% and 98%, respectively. For PYR13TFSI-EC:PC ~150 mAhg-1 at C/10 rate a Coulombic efficiency of ca 98% was achieved. The NVP electrode, exhibits capacities of ~80 mAhg-1 with the BMImTFSI-EC:PC electrolytes at C/10 rate, and of 80, 75 and 46 mAhg-1 at C/10, C/5 and C, respectively with the PYR13TFSI-EC:PC electrolyte. A successful full SIB cell was assembled based on the best choices of the above materials as a proof of concept. As a major argument for the use of ILs is an increased safety, it was encouraging that the safety tests, carried out in air for many different compositions, unambiguously proved the addition of ILs to decrease the SET, as well as the flame intensity, and simultaneously raise the FP.

Impact of pi(3,4,5)p3-mediated beta-arrestin-1 recruitment on structure of asymmetric lipid bilayers

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The membrane spanning G-protein coupled receptors (GPCRs) facilitate crucial physiological responses to a variety of extracellular ligands, such as hormones, neurotransmitters, ions, photons, and other stimuli1, thus 50% of drugs available in the market today target GPCRs2. The biological mechanisms behind GPCR-signaling involves several other biomolecules, including the key protein group of β-arrestins. These cytosolic adaptor proteins regulate signaling through several different pathways, classically by removing receptors from the plasma membrane via clathrin-mediated endocytosis3.

In membrane binding experiments using both confocal fluorescence microscopy and quartz crystal microbalance, we found that β-arrestin-1 binds specifically to supported lipid bilayers (SLBs) containing phosphatidylinositol trisphosphate lipids, PI(3,4,5)P3. We have consistently shown, using both methods, that such binding is lipid specific and not driven by membrane charge. We have also shown that the membrane-protein interaction depends on protein concentration and membrane composition, and that β-arrestins can induce membrane curvature, which may play a role in the endocytic pathway. This is for the first time quantified with respect to dynamics and respective contributions of specific vs non-specific binding.

Having established an assay for PI(3,4,5)P3-mediated recruitment of β-arrestin-1, we conducted a series of neutron reflection experiments to study the protein-lipid interaction on a structural level. Both hydrogenated and deuterated protein was used in reflectometry experiments with diverse contrast matching of the bulk media. We present here the detailed structures of asymmetric lipid bilayers containing PI(3,4,5)P3, and demonstrate that β-arrestin-1 not only binds but also reorganizes the membrane structure.

References

[1] Rosenbaum, D. M. et al. Nature. 459(7245), 356-363 (2009).
[2] Gudermann, T. et al. J Mol Med-Jmm. 73(2), 51-63 (1995).
[3] DeWire, S. M. et al. Annu Rev Physiol. 69, 483-510 (2007)

Structure of water and glycerol/2PGME in confinement by neutron diffraction and structural modeling

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The study of hydrogen-bonded liquids in confinement yields insights into how complex structures in liquids form, which in turn may elucidate how we think about similar systems in all different fields of science.

In this study we have performed measurements on solutions of glycerol or di-propylene glycol methylether (2PGME) and water confined in 24 Å pores of MCM-41 by neutron diffraction. All samples contained 50 wt% water and 50 wt% glycerol or 2PGME, but several isotopically different samples were measured of each composition in order to be able to establish all the different structural correlations. The neutron data were used to create a molecular model of the system using an empirical potential structural refinement (EPSR) technique.

The preliminary result indicates that the solutions partly phase-separates inside the pores due to water preferring to bond to the hydrophilic surface of the silica. Thus, the water molecules seem to form a shell between the inner pore surface and the glycerol/2PGME water mixture in the centre of the pore.

Self-assembled systems in Deep Eutectic Solvents

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Deep eutectic solvents (DES) are promising solvents for many application areas. The formation of the solvent relies on an important depression of the freezing point due to a high hydrogen bounding interaction between the constituents1. DES have common properties with ionic liquids such as (i) a melting point near or below room temperature, which generally demonstrates negligible vapour pressure, (ii) high thermal and chemical stability and (iii) wider liquid temperature range than molecular solvents. In addition, DES can be made from non-toxic species, avoiding the usage of highly toxicity precursors found in ionic liquids2. These major features suggest they are a favourable solvents for multiple processes. Prior studies have shown the self-assembly of amphiphile systems in ionic liquids, which can also themselves present self-aggregation properties. Until the last few years, the number of solvents with self-assembling properties had been quite limited. Nevertheless, the emergence of the design solvents to this field has promoted the control over these systems3, 4. So far, in reviewing literature, DES have been used as solvents for nucleation of inorganic materials5 and for synthesis of zeolite analogues6, but very little was found on DES solvent for micelle-based templating systems.

The present study was designed to test two different choline chloride-based DES, in order to determine whether self-assembly of amphiphiles, including surfactants and phospholipids, occurs in these systems. The structural behaviour was studied using small angle X-Ray and neutron scattering, while surface pressure-area measurements were carried out using a Langmuir trough for insoluble lipids. The obtained systems were also characterized both thermally and physically by means of DSC –differential scanning calorimetry- in order to deduce the glass transition temperatures and contact angle method for the surface tension determination. The findings indicate the ability of DES to stabilise the self-assembly phenomena and a significantly different behaviour from the systems studies so far, which opens many possibilities ahead in this field.

References

[1] Abbott, A. P., et al., Chem. Soc. 2004, 126 (29), 9142-9147.
[2] Dai, Y.; et al., Anal. Chim. Acta 2013, 766, 61-68.
[3] Araos, M. U.; Warr, G. G., J. Phys. Chem. B 2005, 109 (30), 14275-14277.
[4] Greaves, T. L.; Drummond, C. J., Chem. Soc. Rev. 2008, 37 (8), 1709-1726.
[5] Abbott, A. P. et al., Phys. Chem. Chem. Phys. 2013, 15 (40), 17314-17323.
[6] Cooper, E. R. et al., Nature 2004, 430 (7003), 1012-1016.
[7] Chen, S. et al., Dalton T. 2010, 39 (3), 697-699.

Polarizable Force Field for the study of transport in clays at the molecular scale

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The wide use of clay minerals in industrial applications (catalysis, formulation), energy and ecological engineering (oil recovery, ground water remediation, geological barrier for radioactive waste and CO2) is partly due to their remarkable properties of retention at the mineral surface. In environmental engineering, the role of water on clay permeability and retention properties is crucial. Indeed, the water is the vector of the motion of the species present in the medium, hazardous elements for instance. Clays can show different behaviors towards water, depending in particular on the value of the negative structural charge carried by the mineral layers: although hydrophobic when uncharged, a clay can become hydrophilic when charged. This is partly due to the favorable hydration of the counter-ions located between the layers, which cause the swelling of the clay nanopores.

Simulations at the atomic level can help because they allow a detailed picture of the structure, thermodynamics and dynamics of the fluid at the interface. They are already used to explain the hydrophobic/hydrophilic property of various clays such as: Talc, Pyrophyllite and Montmorillonite [1,2]. Unfortunately, the numerical results do not always reproduce quantitatively the experimental results, which casts, consequently, a doubt on the validity of simulations interpretations[3]. In particular, the polarizability is not taken into account although it can play a significant role especially when an electric field is present at the interface [4]. The PHENIX laboratory is currently developing a polarizable force field to study clay/water systems from DFT calculations. This is the first time that a polarizable force field is used to study the diffusion of cations and water molecules in Montmorillonites. The results are compared to a classical force field CLAYFF and experimental data.

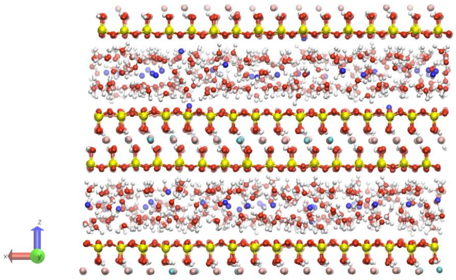

Figure: Structure of Na-Montmorillonite

References

[1] Rotenberg, B. et al., J. Am. Chem. Soc., 2011, 133, 20521
[2] Botan, A. et al., J. Phys. Chem. C., 2013, 117, 978-985
[3] Marry, V. et al., J. Phys. Chem. C., 2013, 117, 15106-15115
[4] Kamath, G. et al., J. Phys.: Condens. Matter, 2013, 25, 305003

Morphology investigation on conjugated diblock copolymer/fullerene BHJ system

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Organic photovoltaic attracts worldwide research interest due to its potential for low-cost fabrication process, lightweight and flexible applications. The inner nanoscale morphology in the donor-acceptor active layer plays important effects on the final device performance. In order to achieve promising energy conversion efficiency, what is required is not a two-phase system, but an interpenetrating bulk heterojunction (BHJ) network between electron donor and electron acceptor. In which the nanoscale morphology is constrained in the same scale of exciton diffusion length (~10 nm), and the interpenetrating network provides larger interface area for exciton dissociation. In the traditional P3HT/PCBM BHJ system, apart from pure PCBM and pure P3HT phase, there also contains a very fast diffusion mechanism of PCBM molecule in the amorphous part of P3HT. In this present work, we want to use conjugated diblock copolymer, P3HT-b-PS as electron donor, and blend it with fullerene derivative PCBM, by applying grazing incidence small angle neutron scattering to investigate the detailed structures, such as phase information, structure length scales and molecular miscibility of the components.

Fourth Annual Niels Bohr International Academy Workshop on ESS Science:

Surface Interactions

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Fourth Annual Niels Bohr International Academy Workshop on ESS Science:

Surface Interactions

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