Fifth Annual Niels Bohr International Academy Workshop-School on ESS Science: Condensed Matter Theory and Advanced Software Copenhagen, November 9 - 13

The goal of this workshop-school is to describe the manner in which static and dynamic processes in materials give rise to their neutron scattering profiles. The school will demonstrate how current data treatment and computational analysis can effectively be used to improve the scientific understanding derived from data obtained on current and next generation of neutron scattering instruments.

## **Organizers:**

Heloisa N. Bordallo Pascale P. Deen Juergen Eckert

## Local support:

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## **Sponsors**

PhD School of the University of Copenhagen Niels Bohr International Academy European Spallation Source Institut Français du Denmark Helmholtz-Zentrum Berlin für Materialien und Energie GmbH Knud Højggrds Fond

## **Invited Speakers:**

Arantxa Arbe - Spain Dimitri N. Argyriou – Sweden Ferdi Arvasetiawan - Sweden Heloisa N. Bordallo – Denmark Jeroen van den Brink – Germany Stefano Carreta – Italy Pascale P. Deen – Sweden Juergen Eckert – USA Gerald Kneller – France Charles M. Marcus - Denmark Maxim Mostovoy - The Netherlands Poul Nissen - Denmark Thomas Proffen – USA Thomas Rod - Sweden Stéphane Rols – France Neal Skipper – UK Jernej Stare - Slovenia Sandor Toth - Switzerland



# Fifth Annual Niels Bohr International Academy Workshop-School on ESS Science:

Condensed Matter Theory and Advanced Software

**Scientific Program** 

Program for the Fifth NBIA Meeting on ESS Science, November 9-13, 2015						
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 labo	pratories, software, hardware, etc	<del>.</del> .				
Day/Time	Lecturer	Горіс				
Monday, 1st day						
8:00 am - 9:00 am	Registration & Welcome					
9:15 am – 9:20 am	Poul Henrik Damgaard (NBIA Director)	Welcome!				
9:20 am -9:45 am	Andrew Jackson (NBIA)	The Niels Bohr Legacy				
9:45 am – 10:30 am	Charles M. Marcus (NBI)	Topological States in Nanowires: Experimental status and prospects				
10:30 am - 11:00 am	Coffee break					
11:00 am - 11:45 am	Gerald Kneller (Centre de Biophysique Moléculaire)	Simulation-based modeling of neutron scattering data				
11:45 am - 12:30 pm	Stéphane Rols (ILL)	Measuring and simulating the vibrational density of states of carbon nano- structures				
12:30 pm – 2:00 pm	Lunch					
2:00 pm - 2:45 pm	Posters and coffee break					
3:00 pm - 5:00 pm	Jernej Stare (National Institute of Chemistry)	Molecular Dynamics tutorial: Students chose project, hands on exercises				
3:00 pm - 5:00 pm	Visit if the QDev laboratory for the invited speakers (Charles Marcus invitation)					
Tuesday, 2 <sup>nd</sup> day						
9:00 am - 9:45 am	Maxim Mostovoy (Zernike Institute)	Magnetic Superstructures: Crystallization of Topological Magnetic Defects				
9:45 am - 10:30 am	Stefano Carreta (Università di Parma)	Unravelling the Spin dynamics and Microscopic Properties of Molecular Nanomagnets by Neutron Scattering				
10:30 am - 11:00 am	Coffee break					
11:00 am - 11:45 am	Sandor Toth (PSI)	Strong magnon decay in a triangular lattice antiferromagnet				
11:45 am - 12:30 pm	Thomas H. Rod (DMSC-ESS)	Data Analysis and Modeling software for the future ESS users				
12:30 pm - 2:00 pm	Lu	nch				
2:00 pm – 2:30 pm	Dimitri Argyriou (ESS)	ESS Science: Opportunities & Ideas				
2:30 pm – 4:00 pm	Sandor Toth (PSI)	Spin wave tutorial: Students chose project, hands on exercises				
2:30 pm – 4:00 pm	ESS Scientists	Round Table about ESS				
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, 3 <sup>rd</sup> day			
9:00 am - 10:30 am	2 Students: Working groups		
10:30 am - 11:00 am	Coffee Break		
11:00 am - 11:45 am	Thomas Proffen (Oak Ridge National Laboratory)	The road from collecting neutron data to scientific result	
11:45 am -12:30 pm	Pascale P. Deen (ESS)	Emergent magnetic order and topologically complex structures	
12:30 pm - 2:00 pm	Lunch		
2:00 pm – 2:45 pm	Jeroen van den Brink (Institute for Theoretical Solid State Physics)	Resonant Inelastic X-ray Scattering on high Tc cuprates and magnetic iridates	
2:45 pm – 3:30 pm	Neal Skipper (UCL)	The structure of simple aromatic liquids by neutron scattering and Empirical Potential Structure Refinement (EPSR)	
	Museum visit (The David Collecti	on (https://www.davidmus.dk/en))	
4:30 pm -	& Conference dinner (Sponsored by the ESS) at Restaurant Brdr. Price (http://rosenborggade.brdr-price.dk/content/info)		
Thursday, 4 <sup>th</sup> day			
9:00 am – 11:00 am	2 Students: Working groups		
11:00 am - 11:45 am	Ferdi Aryasetiawan (Lund University)	First-principles approach to the electronic structure of strongly correlated systems	
11:45 am - 12:30 pm	Arantxa Arbe (CSIC-UPV/EHU)	Neutron scattering and molecular dynamics simulations: synergetic tools to unravel structure and dynamics in polymers	
12:30 pm – 2:00 pm	Lunch		
2:00 pm - 4:00 pm	2 Students: Working groups		
2:00 pm - 3:00 pm	Guided tour of the Niels Bohr's Office for the senior scientists		
4:00 pm - 4:30 pm	Coffee break		
4:30 pm - 5:30 pm	2 Groups of Students (30 minutes each group)	Student presentations on their results	
Friday, last day			
9:00 am - 9:30 am	Jernej Stare (National Institute of Chemistry)	Computational enzymology by Empirical Valence Bond simulations: amine oxidation catalyzed by monoamine oxidase	
9:30 am - 10:00 am	Juergen Eckert (USF)	Dynamics of Pharmaceutical Molecules	
10:00 am - 10:30 am	Coffee	e break	
10:30 am - 11:00 am	Heloisa N. Bordallo (NBI)	Neutrons and X-ray scattering applications on systems of biological relevance	
11:00 am - 11:45 am	Poul Nissen (Aarhus Univeristy)	A biological view of neutrons	
12:00 pm - 12:45 pm	Lunch		
12:45 pm – 5:30 pm	Visit to the ESS site in Lund, including lunch at the ESS and return to Copenhagen with a stop at the airport (Trip sponsored by the Institut Français)		

## <u>Access</u>

The main door of Building A, which is to the right, will be unlocked from 8 am to 4 pm each day of the workshop. The main door of Building C will be unlocked 30 min before the beginning of the activities of the workshop and at lunchtime.

## Lectures & Posters

All lectures will be held in Auditorium A at the Niels Bohr Institute. Please try to be respectful and do not use your computers during the lectures.

The practical exercises will take place in rooms **BK-2 (MD-tutorials** on Monday, Wednesday and Thursday) and **FA10 (Spin Wave-tutorial** on Tuesday, Wednesday and Thursday).

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 networks are Eduroam and KUGuest network.

If you need to use the KUGuest network you will be guided by the website in how to get access.

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

## <u>Lunch</u>

Lunches are provided free of charge to the registered participants at the NBI cantine. On Friday we will provide delicious homemade sandwiches before our trip to Lund.

## **Guided tour at the NBI**

A guided tour of the Niels Bohr's Office will take place on Thursday, November 12 from 14:00 to 15:00 for the invited speakers.

## **Round Table with ESS Scientists**

Tuesday, 10 of November 14:00 – 16:00 This parallel section is aimed as a brainstorming meeting between the invited speakers and ESS scientists.

## Social Program

Monday, 915:00 – 17:00Charles Marcus will take the invited speakers to visit the Center for Quantum Devices where he is the<br/>director (http://qdev.nbi.ku.dk).Wednesday, 1116:30 – 22:00Guided tour of the The David Collection (https://www.davidmus.dk/en) followed by the conference<br/>dinner at Restaurant Brdr. Price (http://rosenborggade.brdr-price.dk/content/info).Friday, 1312:45 – 17:30Guided tour of the ESS construction site in Lund. On the way back the bus will stop at Kastrup airport at<br/>17:00h and then at the Wake-Up hotel.



## Fifth Annual Niels Bohr International Academy Workshop-School on ESS Science:

Condensed Matter Theory and Advanced Software

**Invited Talks** 

## Topological States in Nanowires: Experimental status and prospects

Charles Marcus

Niels Bohr Institute

### Simulation-based modeling of neutron scattering data

#### Gerald Kneller

#### Centre national de la recherche scientifique / Univ. Orléans

The lecture focuses on the use of Molecular Dynamics (MD) simulations as an essential tool for the analysis of neutron scattering data from complex molecular systems. In this context, the basics of neutron scattering will be shortly reviewed, emphasizing the virtues and the limits of the classical Van-Hove theory. Another important subject is the calculation of space and time correlation functions and their Fourier spectra, such as neutron dynamics structure factors, as well as the decomposition of such spectra into contributions from different motion types. The treatment of unwanted effects, such as multiple scattering, will also be briefly presented from the point if view of virtual experiments.

## Measuring and simulating the vibrational density of states of carbon nanostructures

#### Stephane Rols

### Institut Laue Langevin

In this communication, I will present different results obtained using inelastic neutron scattering on the dynamics of selected carbon nanostructure. The results are interpreted based on DFT simulations, using either lattice dynamics methods or molecular dynamics simulations. The basis of the principles of the neutron time of flight technic and atomistic simulations will be introduced.

## Magnetic Superstructures: Crystallization of Topological Magnetic Defects

#### Maxim Mostovoy

### Zernike Institute for Advanced Materials, University of Groningen

Some magnetic materials show surprisingly complex spin orders, e.g., cycloidal and helical spirals incommensurate with the crystal lattice, stripe and labyrinth domains, and multiply periodic non-coplanar spin textures such as skyrmion crystals. Low symmetry and non-trivial topology of these magnetic superstructures lead to interesting and unconventional phenomena, e.g., magnetically-induced ferroelectricity and the Topological Hall Effect. I will give an introduction to incommensurate magnetic states and discuss their microscopic origins, phenomenological description and some physical properties. I will discuss unusual stripe domains in TbFeO<sub>3</sub> and PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> with the coupled rare earth and transition metal magnetic subsystems, which are arrays of topological defects (domain walls) in the rare earth magnetic ordering kept at large distances from each other by magnon exchange. Finally, I will show how a combination of magnetic frustration, applied magnetic field and magnetocrystalline anisotropy can give rise to a plethora of multiply periodic states, including the triangular skyrmion lattice.

[1] S. Artyukhin et al., Solitonic lattice and Yukawa forces in the rare-earth orthoferrite TbFeO3, Nature Materials 11, 694–699 (2012).

[2] A. O. Leonov and M. Mostovoy, Multiply periodic states and isolated skyrmions in an anisotropic frustrated magnet. Nat Commun 6:8275 DOI: 10.1038/ncomms9275.

## Unravelling the Spin dynamics and Microscopic Properties of Molecular Nanomagnets by Neutron Scattering

## Stefano Carretta

## Università di Parma

Molecular nanomagnets (MNMs) are molecules containing a core of magnetic ions whose spins are strongly coupled by superexchange interactions. They form crystals which behave like ensembles of non-interacting magnetic units. Being among the first examples of finite-size spin systems, MNMs are promising for applications and have been test beds for addressing several important quantum phenomena. The combination of neutron scattering experiments and microscopic theoretical modeling has played a key role in the understanding of the spin dynamics and of the properties of MNMs.

In this talk I review some investigations of MNMs combining neutron scattering and theoretical modeling, exploiting microscopic spin Hamiltonians and a recently-developed ab-initio scheme to build many-body models for MNMs [1]. In addition, I show that the determination of the four-dimensional inelastic-neutron scattering function in vast portions of the reciprocal space enables the spin dynamics to be determined directly [2], without the need of a model Hamiltonian. This allows us to determine how quantum fluctuations propagate along antiferromagnetic rings, to test the degree of validity of the Néel-vector-tunnelling framework and to investigate the presence of entanglement in a dimer of  $Cr_7Ni$  molecular qubits. At last, I discuss the quantitative study of the microscopic spin structure of finite spin chains by polarized neutron diffraction [3]. The results reveal finite-size effects depending on the boundary condition and the parity of the chains.

[1] A. Chiesa, et al, Phys. Rev. Lett. 110, 157204 (2013); [2] M. Baker et al, Nature Physics 8, 906 (2012); [3] T. Guidi et al., Nature Communications 6, 7061 (2015).

### Strong magnon decay in a triangular lattice antiferromagnet

#### Sándor Tóth

#### Paul Scherrer Institut

Quasiparticles are collective excitations emerging from a strongly interacting system. Generally, magnons are regarded as weakly interacting quasiparticles with lifetime long enough to be detectable only by high-resolution resonant neutron spin echo technique. The first class of system where dynamics significantly differs from conventional semi classical approximation is the antiferromagnetic chain, where the fundamental excitations are spinons. However, recent theoretical results revealed surprisingly strong magnon-magnon interactions in non-collinear magnets at zero temperature that causes spontaneous decay of magnons and finite lifetime [1]. The simplest model system with non-collinear ground state is the triangular lattice antiferromagnet where the spontaneous decay is predicted even for S=3/2 systems. Beside the large body of experimental data on triangular lattice compounds, there is no compelling experimental evidence for the predicted broadening. We show that LiCrO<sub>2</sub> is an almost ideal spin -3/2 triangular lattice antiferromagnet and present our experimental evidence of strong magnon decay at the zone boundary.

[1] M. E. Zhitomirsky, et al., Rev. Mod. Phys. 85, 219 (2013).

## Data Analysis and Modelling software for the future ESS users

## Thomas Rod

## **European Spallation Source**

Data analysis and modeling is vital for generating value from the huge investments into neutron sources, and for the individual scientist, for generating high impact scientific papers. This importance of data analysis and modeling was recognized from the outset when planning for the European Spallation Source (ESS) and therefore a Data Analysis and Modelling group was formed with the responsibility of delivering analysis and modeling software for the neutron instruments and user programme at ESS and which is an integral part of the ESS Data Management and Software Centre (DMSC) located in Copenhagen.

In this presentation I will describe our plans and challenges for delivering data analysis and modeling software for the instruments at ESS, integration of atomic-scale modeling and simulations, as well as ideas for analysis software that will enable new and better experiments to be performed at ESS.

# 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 built 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.

## The road from collecting neutron data to scientific result

## Thomas Proffen

## Oak Ridge National Laboratory

Neutron scattering enables simultaneous measurement of structural and dynamic properties of materials from the atomic scale (0.1 nm, 0.1ps) to the meso scale (1 $\mu$ m, 1 $\mu$ s). These ranges are remarkable complementary to current capabilities of computational modeling and the simplicity of the scattering cross section allows the prediction of neutron scattering data straight forwardly from computer modeling results.

Oak Ridge National Laboratory is home to two world leading neutron facilities, the Spallation Neutron Source (SNS) and the High Flux Isotope Reactor (HFIR) as well as the Oak Ridge Leadership Computing Facility. Turning these ORNL's unique strengths into the highest impact science is not without challenges. In this talk I will discuss challenges and opportunities and present recent advances at the SNS towards linking materials simulation and neutron scattering and towards real time feedback between experiment and simulation.

#### Emergent magnetic order and topologically complex structures

Pascale P. Deen<sup>1,2</sup>, N. d'Ambrumenil<sup>3</sup>, O. A. Petrenko<sup>3</sup>, H. Jacobsen<sup>2,1</sup>, O. Florea<sup>4</sup>, E. Lhotel<sup>4</sup>, J. A. M. Paddison<sup>5</sup>, A. L. Goodwin<sup>5</sup>, M. T. Fernandez<sup>6</sup>, H. Mutka<sup>6</sup>.

<sup>1</sup>European Spallation Source <sup>2</sup>Nanoscience Center, Niels Bohr Institute, University of Copenhagen. <sup>3</sup>Department of Physics, University of Warwick <sup>5</sup>Institut Laue-Langevin <sup>6</sup>Department of Chemistry, University of Oxford

The search for new states of matter is a fundamental theme of condensed matter science. Frustrated magnetic materials are promising candidates for new states because lattice geometry suppresses conventional magnetic dipole order. Frustration thus drives novel emergent states. Classical spins on the 3D triangular hyperkagome lattice have long been considered ideal for novel states yet have provided few examples.

Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub> is the canonical frustrated magnet since the compound does not order via the pervasive "order by disorder" mechanism down to the lowest temperatures probed, 25 mK [1 and ref. therein]. Short-range correlations, determined via neutron diffraction, have long been assumed to originate from near neighbour short-range interactions [1]. However in recent work an emergent spin state of decagon looped structures at the lowest temperatures has been uncovered [2,3]. These emergent decagon spin loops remain dominant when attempting to polarise the spin structure by a large applied magnetic field [4]. Neutron inelastic scattering shows a dominant contribution at large momentum transfers from a band of almost dispersionless excitations that correspond to the spin waves localized on ten site rings, expected on the basis of nearest neighbor exchange interaction [4]. These result illustrate the richness and diversity that arise from frustrated exchange on the three-dimensional hyperkagome lattice.

[1] O. A. Petrenko, C. Ritter, M. Yethiraj, D. McK Paul, Phys. Rev. Lett. 80, 4570 (1998).

[2] J. A. M. Paddison, A. L. Goodwin, Phys. Rev. Lett. 108, 017204 (2012).

[3] P. P. Deen, O. Florea, E. Lhotel, and H. Jacobsen, Phys. Rev. B 91, 014419 (2015)

[4] N. d'Ambrumenil, O. A. Petrenko, H. Mutka, and P. P. Deen, Phys. Rev. Lett. 114, 227203 (2015)

## Resonant Inelastic X-ray Scattering on high Tc cuprates and magnetic iridates

### Jeroen Van Den Brink

## Institute for Theoretical Solid State Physics

Resonant Inelastic X-ray Scattering (RIXS) provides direct access to elementary charge, spin and orbital excitations in complex oxides. As a technique it has made tremendous progress with the advent high-brilliance synchrotron X-ray sources. From the theoretical perspective the fundamental question is to precisely which low-energy correlation functions RIXS is sensitive. Depending on the experimental RIXS setup, the measured charge dynamics can include charge-transfer, phonon, d-d and orbital excitations [1]. The focus of this talk will be on RIXS as a probe of spin dynamics and superconducting gap of high-Tc cuprates [2-4] and the combined magnetic and orbital modes in strongly spin-orbit coupled iridium-oxides [5-10].

[1] L. J. P. Ament, et al., Rev. Mod. Phys. 83, 705 (2011).
 [2] L. Braicovich, et al., Phys. Rev. Lett. 104, 077002 (2010).
 [3] M. P. M. Dean, et al., Nature Materials 11, 850 (2012).
 [4] P. Marra, et al., Phys. Rev. Lett. 110, 117005 (2013).
 [5] L. J. P. Ament, et al., Phys. Rev. B 84, 020403 (2011).
 [6] V. M. Katukuri, et al., Phys. Rev. B 85, 220402 (2012).
 [7] N. A. Bogdanov, et al., Phys. Rev. B 85, 235147 (2012).
 [8] J. Kim, et al., Phys. Rev. Lett. 108, 177003 (2012).
 [9] H. Gretarsson, et al., Phys. Rev. Lett. 110, 076402 (2013).
 [10] A. Lupascu, et al., Phys. Rev. Lett. 112, 147201 (2014).

## The structure of simple aromatic liquids by neutron scattering and Empirical Potential Structure Refinement (EPSR)

Neal Skipper

## Universitry College London

In this tutorial we will discuss how the application of neutron scattering in conjunction with isotopic labelling can be used to determine the structure of molecular liquids, with the simple aromatic molecules benzene and toluene being taken as examples. In addition to covering briefly the instrumentation and primary data reduction, we will also examine how a 3-dimensional model of the system can be obtained by using methods such as Empirical Potential Structure Refinement (EPSR) [1-3]. In this technique a Monte Carlo computer simulation of the liquid system is constrained by the experimental diffraction data, via modification of a set of trial intermolecular potential functions. In the case of benzene and toluene this approach enabled us to identify a new and rather unexpected motif within the liquids, in which molecules direct two hydrogen atoms towards the p-orbitals of a neighbouring molecule [4]. The data and EPSR files that are referred to in [4] can be downloaded from [2].

[1]http://www.isis.stfc.ac.uk/groups/disordered-materials/software/empirical-potentialstructure-refinement6157.html

[2] Delight in Disorder: https://www.facebook.com/disord.matt

[3] Empirical potential Monte Carlo simulation of fluid structure. Soper AK. Chem. Phys. 202, 295-306 (1996). http://dx.doi.org/10.1016/0301-0104(95)00357-6 [4] The structure of  $\pi$ - $\pi$  interactions in aromatic liquids. Headen TF, Howard CA, Skipper NT, Wilkinson MA, Bowron DT, Soper AK. J. Am. Chem. Soc. 132, 5735-5742 (2010). DOI: 10.1021/jp8083502.

# First-principles approach to the electronic structure of strongly correlated systems

### Ferdi Aryasetiawan

#### Lund University

In the last few decades, materials science has witnessed numerous discoveries and syntheses of new compounds with unusual properties which are not only highly interesting from fundamental point of view but also have an enormous potential for technological harness. These materials are characterised by the presence of 3d or 4f elements with partially filled shells for which mean-field approximation is not reliable. For these systems, it is imperative to consider explicitly the electron-electron interactions, which in interplay with the spin and orbital degrees of freedom as well as lattice distortions give rise to new phenomena not observed in conventional materials whose conduction electrons are dominated by s and p electrons. Unconventional superconductivity, multiferroicity, colossal magnetoresistivity, and frustrated magnetism are among these new emergent phenomena. One of the major challenges in condensed matter physics is to develop accurate first-principles theories for calculating the electronic structure of strongly correlated materials. In this talk, an overview of the electronic structure methods from density functional theory to many-body methods based on the Green's function technique is presented.

# Neutron scattering and molecular dynamics simulations: synergetic tools to unravel structure and dynamics in polymers

## Arantxa Arbe

## Materials Physics Center (CSIC-UPV/EHU)

We present a methodology based on the tandem neutron scattering / fully atomistic molecular dynamics simulations that allows unraveling structural and dynamical features of polymer melts at different length scales, mainly in the intermolecular and monomeric range [1]. Its particular success rests on that (i) both techniques cover approximately the same length and time scales and (ii) the classical van Hove formalism allows easily calculating the magnitudes measured by neutron scattering from the simulated atomic trajectories. So, direct comparison with experimental results provides a demanding test for validating the simulated cell. Once validated, the information of the simulations can be exploited, calculating magnitudes that are not experimentally observable or extending the parameters range beyond the experimental capabilities. We present some examples to illustrate the application of this strategy.

[1] A. Arbe, F. Alvarez and J. Colmenero, Soft Matter 8, 8257-8270 (2012)

## Computational enzymology by Empirical Valence Bond simulations: amine oxidation catalyzed by monoamine oxidase

#### Jernej Stare

#### National Institute of Chemistry

Despite enormous efforts, elucidation of chemical reactivity in enzymes remains a challenge for theoretical treatments, requiring both accuracy of quantum methods and long timescales of classical simulations. Perhaps the most efficient multiscale protocol in this regard available to date is the Empirical Valence Bond (EVB) method. The basic idea is that the reactive subsystem is described on the level of a classical reactive force field augmented by the quantum treatment of the valence states representing the reactants and products. The method facilitates the modeling of chemical reactions (bond breaking and making) in a complex macromolecular environment while enabling simulation timescales sufficient for thermal averaging. The power of EVB has been demonstrated for numerous enzymatic reactions and led to significant development in the understanding of the functionality of enzymes.

Our research in computational enzymology is focused on the oxidation of primary amines, catalyzed by monoamine oxidase enzymes (MAO). The biogenic substrates of MAO are neurotransmitters such as dopamine and serotonin present in the central nervous system and other tissues. A detailed information of (pharmaco)kinetics of these systems on the molecular level is a key toward understanding of nerve signal transduction, function, pathology and pharmacological treatment of the central nervous system. The origin of neurodegenerative disorders such as Alzheimer and Parkinson disease can be traced to the metabolism of biogenic monoamines. The most crucial task required for a detailed understanding of the metabolism of monoamines is the characterization of the mechanism of oxidative deamination catalyzed by MAO, including the reaction free energy profile. Using EVB in conjunction with quantum chemical methods, various aspects of amine oxidation have been investigated, both in the isolated state as well as in the enzyme active center. The research includes detailed mechanistic studies, calculation of free energy profiles, elucidation of point mutation effects, and investigation of the role of protonation states and tunneling. In general, the EVB approach yields reliable results that are in good match with the experimental kinetic data on amines decomposed by MAO.

The presentation will include an overview of EVB and the related simulation methods applied to the MAO-catalysed decomposition of biogenic amines and their nonbiogenic analogs. Factors governing the catalysis will be presented and critically discussed.

- [1] J. Åqvist, A. Warshel, Chem. Rev. 1993, 93, 2523-2544.
- [2] R. Vianello, M. Repič, J. Mavri, Eur. J. Org. Chem. 2012, 7057-7065.
- [3] M. Repič et al., Proteins 2014, 82, 3347-3355.
- [4] R. Borštnar et al., J. Chem. Theory Comput. 2012, 8, 3864-3870.
- [5] J. R. Miller, D. E. Edmondson, Biochemistry 1999, 38, 13670-13683.

#### **Dynamics of Pharmaceutical Molecules**

Heloisa Bordallo<sup>1,2</sup> and <u>Juergen Eckert<sup>3</sup></u>

## <sup>1</sup>Niels Bohr Institute, University of Copenhagen <sup>2</sup>European Spallation Source <sup>3</sup>Department of Chemistry, University of South Florida

Interactions of drug molecules with proteins and their binding to receptor sites are typically viewed in a static picture, where the inherent flexibility and dynamics of the molecules are not explicitly taken into account. We have therefore undertaken a series of studies of the low frequency dynamics of several classes of pharmaceutical molecules using quasi- and inelastic neutron scattering techniques coupled with computational modeling and analysis. Neutrons and computers may be said to be a nearly ideal match since the simplicity of the interaction of neutrons with atomic nuclei in matter greatly facilitates computational modeling of neutron scattering experiments. These can cover both structure and dynamics, the latter on an enormous range of time scales, and hence types of molecular dynamics ranging from reptation in polymers to the stretching mode of the hydrogen molecule. The joint neutron scattering and computational studies to be described include drug molecules of increasing size, and hence likely flexibility, from paracetamol to local anesthetics to antipsychotic drugs, including the effects on the dynamics of encapsulation for drug delivery.

### Neutrons and X-ray scattering applications on systems of biological relevance

#### Heloisa N. Bordallo

## Niels Bohr Institute, University of Copenhagen European Spallation Source

Neutrons, similarly to X-rays, penetrate matter. However, unlike X-rays, neutrons interact with matter in a different manner, thus allowing the identification of elements with very low molecular weight, including hydrogen. While X-rays allow the characterization of the micro-structure of materials, neutron imaging provides information on proton distribution within the structure. For this reason, both X-rays and neutron imaging, complemented by neutron spectroscopy, which brings information about hydrogen mobility, can contribute for better understanding of complex structures.

In this talk I will discuss on this promising approach. I will present two specific examples. The first is related to the investigation of the highly intricate pore structure of dental cements [1] and the second to a recent study of the encapsulation of the HBsAg protein, used in the Hepatitis B vaccine, into the SBA-15 adjuvant [2].

[1] A.R. Benetti, J. Jacobsen, B. Lehnhoff, N.C.R. Momsen, D.V. Okhrimenko, M.T.F. Telling, N.Kardjilov, M. Strobl, T. Seydel, I. Manke and H.N. Bordallo (2015) How mobile are protons in the structure of dental glass ionomer cements? Sci. Rep. 5, 8972 (8 pages)

[2] Martin Kjærulf Rasmussen, BSc thesis: "Localization of hepatitis B vaccine in SBA-15: A new method of delivery".

#### A biological view of neutrons

Poul Nissen

Aarhus University, Dept. Molecular Biology and Genetics Danish Research Institute of Translational Neuroscience – DANDRITE, Nordic-EMBL Partnership for Molecular Medicine Centre for Membrane Pumps in Cells and Disease – PUMPkin, Danish National Research Foundation

Biological systems and molecules are challenged by immense complexity, chaos and feed-back at many time and length scales and yet show overall predictive behavior. Classically, biological sciences have often followed a descriptive approach aiming for qualitative network models of molecular physiology, but currently, the biological sciences and in transition with aims to obtain quantitative data on the structure, activity, localization and dynamics of cellular structures to help formulate and incorporate proper biophysical models of the cell. A good starting point is a focus on biological membranes that can be analyzed in many different ways using e.g. X-ray and neutron scattering and diffraction techniques, electron microscopy techniques, fluorescence microscopy, mass spectrometry, and NMR. In the talk I will point to the major challenges we are facing in studies of biomembranes and neuroscience and where neutrons can provide game-changing possibilities in studies of biomolecular and cellular structure, dynamics and function.



## Fifth Annual Niels Bohr International Academy Workshop-School on ESS Science:

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**Posters** 

#### Intercalation of Ciprofloxacin into Lithium-Fluorohectorite at different pHs

### Éverton Carvalho dos Santos

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Over the last decade, different porous materials have been used as hosts for drug encapsulation, and recently, due to its swelling properties and cation-exchange capacity, clays have been added to this list. Additionally to its swelling properties and cation-exchange capacity, clays have been shown to be non-toxic for trans-dermal application and oral administration.

In this poster are presented an initial analysis of the intercalation of Ciprofloxacin (CIPRO,  $C_{17}H_{18}FN_3O_3$ ), a broad-spectrum antibacterial agent, into the layers of the synthetic smectite Lithium – Fluorohectorite (LiFh, Li<sub>1.2</sub>[Mg<sub>4.8</sub>Li<sub>1.2</sub>]Si<sub>4</sub>O<sub>10</sub>F<sub>2</sub>) at different PHs. TG experiments together with Infrared spectroscopy confirms that the CIPRO molecules are at least mixed with the clay particles and indicates that the intercalation process might change the Clay/water interactions. X-ray measurements indicates the presence of CIPRO into the clay layers and shows that this intercalation process is strongly dependent of the PH, being more effective at lower than higher PHs.

#### Synthesis, characterization and application of Luminescent Nanomaterials

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Luminescent nanomaterials, in particular upconverting nano-crystals, are widely studied to be employed in several technological applications, ranging from technological screens [1] to solar cells [2] and optical fibers, to bio-medical and theranostics (= therapy and diagnostics) fields [3].

The latter field is where these luminescent nano-materials, due to their bright emission, coupled with the deep tissue penetration of the NIR light source, find broader applications, therefore drawing the attention of the scientific community in studying and improving drug delivery, biological imaging, photo-thermal and photodynamical treatments [3]. Furthermore, since they show low cito-toxicity, they are interesting to the bio-medical and pharmacological industrial market.

Our research's interests lay in the synthetic development of highly luminescent nanomaterials with up-or down-converting properties. Normally these non-linear optical effects are carried out through doping a host crystal with suitable atomic concentrations of Terrae Rarae ion pairs.

In particular, we focuses in the spatial (distance, angles) relation between lanthanide ion pairs and understand the emission transfer between sensitizers ( $Yb^{3+}$  or  $Ce^{3+}$ ) and emitters (Ln=La-Lu, not Gd(III)) in relation to the crystal structure of the host materials (NaYF<sub>4</sub>, BaYF<sub>5</sub>, ZrO<sub>2</sub>, YTZ,YAG, Y<sub>2</sub>O<sub>3</sub>, etc...) and evaluation of their luminescent properties; furthermore, we are interested in their employability in various technological fields such as nano-technology, energy devices fabrication, solar cells, luminescent hybrids, supra-molecular (hybrid) fluorescent (organo and hydro) gels, bi-modal nanomaterials, photochemistry and photocatalysis, water splitting, bio-medical application such as photothermal therapy or theranostics and so on.

Our interest in the school resides in the opportunity to be hands on the understanding of the interaction between neutron and matter and how can we apply this interaction to our materials, as well as to learn how to compile and run programs or scripts which will enable us to analyze data and understand the interaction of the material with neutrons.

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#### Time dependent magnetic transition in the near Ising chain CoCl<sub>2</sub>·2D<sub>2</sub>O

#### Ursula B. Hansen

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Low dimensional magnetism has been a subject of fundamental interest since these materials provide a unique possibility to study the ground and excited states of quantum models, possible new phases of matter and the interplay of quantum fluctuations and thermal fluctuations.  $CoCl_2 \cdot 2D_2O$  can be considered as a one dimensional Ising system where the dominant magnetic interactions are ferromagnetic and couple nearest neighbor spins lying on chains oriented along the crystallographic c-axis. Weaker inter-chain interactions gives rise to an antiferromagnetic ordering below TN=17.2 K [1].

When a magnetic field is applied along the easy axis  $CoCl_2 \cdot 2D_2O$  has two metamagnetic transitions at  $H_{c1}$ =3.1 T and at  $H_{c2}$ =4.5 T. The transition at  $H_{c1}$  is from the antiferromagnetic state (AF) to a ferrimagnetic state (FI) and the transition at  $H_{c2}$  is to a ferromagnetic state (FE) [2]. The first order transition between the two states are characterized by a large hysteresis. Here we have studied the time dependent magnetic transition from one long-range magnetically ordered state to another. The change in intensity of the AF-peak (1 0 1) and the FI-peak (2/3 0 1) were measured as a function of time at different fields close to the boundary between the FI-phase and AF-phase. Depending on the combination of field and temperature we measure characteristic relaxation times in the range of seconds to hours.

## Water dynamics in neural tissue, living cells and phantom system by neutron scattering.

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Scientists from biophysics, biology and medicine fields are interested in exploring and characterizing topologically cerebral tissue in order to diagnostic different diseases which affect brain in many patients [1-3]. One of the most diffuse diagnostic techniques is dMRI (diffusion magnetic resonance imaging) which extracts information about heterogeneity and asymmetries in brain tissue studying water diffusion dynamics (~80% mass constituent of tissues). The experimental limit of this technique is related to the acquisition time, TA, of the order of milliseconds. Water molecules diffuse within micrometer distance using TA as diffuse time (Eistein equation  $D\sim2<x^2>TA$ ). Cells have micrometric size and they consist in many organelles surrounded by water molecules essentially, therefore dMRI lose information concerning interaction between water molecules and extra/intra cellular Such limit, from physical point of view, means that dMRI gets out material. information on an average diffusion coefficient, losing information of local motions. Nevertheless, many works show that the diffusion properties of water molecules in brain tissue are not in agreement with classical free-like diffusion (Fick law). Although, several models have been proposed to describe such a discrepancy, an univocal physical interpretation of water dynamics in brain is still not achieved [4-13].

#### Aims of PhD project

Neutron scattering technique gives access to space scale of the order of interatomic distances and dynamics in ps-ns time scale. It is particular sensitive to highly enriched H macromolecules, such as water. Thus, neutron scattering may offer a unique tool to overcome the dMRI experimental limit. Recently studies of quasielastic neutron scattering (QENS) on cerebral tissue of bovine and mice have shown that it is possible to distinguish two water pools in cerebral tissues: the first one having a behaviour similar to bulk water (called free-like water) with a diffusion coefficient similar to free water (Dw= $2.3.10^{-5}$  cm<sup>2</sup>/s) and a second one showing a reduced diffusion coefficient probably due to interactions with intra and extra cellular material [14-15]. The project aims at addressing the following points:

· Joint complementary QENS and dMRI investigation;

• Proton dynamics of water at different degrees of confinement. Comparison of dMRI and QENS on phantoms;

• Proton dynamics in glioma at different degrees of malignancy.

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## Studies of proton conductors by combining neutron spectroscopy and computer simulations

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One of the current objectives of fuel cell research is to develop a stable and efficient ion conducting electrolyte for intermediate temperature applications. Solid oxides present an interesting and more sturdy alternative with many advantages compared to the other candidates. In these materials oxide ion conductivity usually occurs via oxygen vacancies. Protonic defects, responsible for proton conduction, can be incorporated from humid atmosphere into the oxygen vacancies. Recently attention has been moving towards oxides containing tetrahedral moieties, because they exhibit improved properties. Fundamental mechanisms acting on atomic scale determine the macroscopic behavior of materials, and therefore understanding of the atomic scale processes is essential. We have studied a material consisting of tetrahedral network of GaO<sub>4</sub>, i.e. La<sub>1-x</sub>Ba<sub>1+x</sub>GaO<sub>3- $\delta$ </sub> and its hydrated form. We combine neutron spectroscopy and computer simulation to study this material. We show that this approach allows us to reveal structural and dynamical information that has not been available before, and cannot be readily obtained through other commonly used methods.

#### Dynamic rotor mode in antiferromagnetic nanoparticles

#### Henrik Jacobsen

#### Niels Bohr Institute

We present experimental, numerical, and theoretical evidence for an unusual mode of antiferromagnetic dynamics in nanoparticles. Elastic neutron scattering experiments on 8-nm particles of hematite display a loss of diffraction intensity with temperature, the intensity vanishing around 150 K. However, the signal from inelastic neutron scattering remains above that temperature, indicating a magnetic system in constant motion. In addition, the precession frequency of the inelastic magnetic signal shows an increase above 100 K. Numerical Langevin simulations of spin dynamics reproduce all measured neutron data and reveal that thermally activated spin canting gives rise to an unusual type of coherent magnetic precession mode. "rotor" mode can be seen as a high-temperature version This of superparamagnetism and is driven by exchange interactions between the two magnetic sublattices. The frequency of the rotor mode behaves in fair agreement with a simple analytical model, based on a high-temperature approximation of the generally accepted Hamiltonian of the system. The extracted model parameters, such as the magnetic interaction and the axial anisotropy, are in excellent agreement with results from Mössbauer spectroscopy.

#### Superconductivity in the heavy-electron superconductor TINi2Se2

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TINi<sub>2</sub>Se<sub>2</sub> is a very new Type-II superconductor, discovered in 2013 [1]. It is a Nichalcogenide similar to KNi<sub>2</sub>Se<sub>2</sub> and KNi<sub>2</sub>S<sub>2</sub>, with a tetragonal structure and no structural transitions below 300K, like the Ni-pnictides. In the normal state it is a Pauli paramagnet, becoming superconducting at  $T_c = 3.7K$  with an easily accessible upper critical field of  $H_{c2} = 0.802T$ . Previous results by Hong et al. [1] and Wang et al. [2] demonstrate that the material has a heavy-electron mass of m<sup>\*</sup> = (14-20)m<sub>e</sub>, making the material comparable to the heavy-fermion superconductors. Hong et al. found that the material is likely nodeless, with two gaps. The thermal conductivity results by Hong et al. indicate that this material doesn't conform to a d-wave interpretation, however it may not be strictly s-wave either. Additionally the penetration depth has only been estimated so far to be <200nm. This needs to be determined more accurately.

In order to better characterise this superconductor, a SANS study will be conducted at PSI in November 2015 in order to measure the form factor of the vortex lattice. In doing so we can extract the penetrations depth, the superfluid density and a more accurate calculation of the coherence length. This kind of invesitgation will also probe any structural phase changes in the vortex lattice and highlight any flux lattice anisotropy.

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#### Following the formation of CaCO3 polymorphs in solution

#### Anders Christian Solberg Jensen, Zhaoyong Zou, Luca Bertinetti, Yael Politi, Peter Fratzl, Wouter Habraken

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Calcium carbonates form some of the most common minerals found in biology and Geology. However, its solution chemistry is still poorly understood. It has been showed that amorphous calcium carbonate (ACC) transforms into vaterite and calcite by a discrete set of steps [1, 2]. ACC is first dehydrated, then crystallized to vaterite which undergoes Ostwald ripening and finally it transforms into calcite by a dissolution reprecipitation mechanism depending on the surface area of calcite. In our study most of our findings are consistent with these finding. By using rietveld refinement we additionally observed that vaterite is nucleated in a strained state that relaxes to it more crystalline state over time. We also find that calcite and vaterite can form simultaneously and we see a much longer lifetime of the vaterite phase along with nucleation event of calcite is limited by the number of nucleation events and not the growth rate as suggested in previous studies [1, 2].

To understand this system we need to examine the nature of the amorphous precursor and the solution chemistry to determine the mechanisms at play. The solution chemistry can be probed by in situ time resolved PXRD as presented in this study but this is a poor probe to study the ACC.

ACC has been studied by combining X-ray PDF work with RMC and MD simulation which has opened the questions about the dynamic of the ions and water inside the ACC [3, 4]. Here we plan to use combined neutron and X-ray PDF with EPSR refinement to study the structure of ACC, this will give us the sensitivity to include the water in the model while also taking force field and charge in account. We plan to probe the dynamics of water with inelastic Neutron scattering where we are highly sensitive to hydrogen in the sample.

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## Novel incommensurate peaks in high temperature superconductor $La_{2-x}Sr_xCuO_4$

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The interplay between magnetism and high temperature superconductivity has been a subject of fundamental interest since the rise of this new state of matter in these materials is still not understood. The understanding can help direct the way to improvements in todays superconducting materials, and furthermore to numerous technical developments. We have investigated the under-doped La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>.

Under-doped La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> allows the study of magnetic order in the superconductor, in which incommensurate (IC) antiferromagnetic stripe order has been observed[1], with the incommensurability ( $\delta$ ) close to the doping (x), for 0.06<x<0.12. The magnetic diffraction intensity from the IC magnetic signal is found [2] to increase upon application of a magnetic field along the c-direction.

We aimed at investigating the field dependence of the IC magnetic peaks at  $(1\pm\delta\pm\delta)$  and  $(\pm\delta \ 1\pm\delta \ 0)$  by means of neutron diffraction on single crystal. We will here present data from measurements on La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> with two different doping, x=0.06 and x=0.07, which revealed a forbidden central peak (1 0 0) or (0 1 0) in the orthorhombic space group (Bmab) and peaks on the diagonals at  $(1\pm\delta,\pm\delta,0)$  or  $(\pm\delta,1\pm\delta,0)$ , where  $\delta = x/2$ . The intensity of these peaks was ten times stronger than what we were expecting. From Yamada et al. [1] we expect to see the peaks in a different position peak at  $\delta = x$ . We measured the signal at different temperatures and observed that the shape and position of the peaks were changing.

In this presentation we will present the latest findings in this vastly studied compound.

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## Vibrational study of the hybrid material: Photo-active molecule encapsulated inside Single-Walled Carbon Nanotubes

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Due to their hollow space, nanotubes NT can host molecules giving rise to new hybrid molecule@NT systems. A possible class of molecules that can be hosted by nanotubes are  $\pi$ -conjugated oligomers which are attractive due to their electronic and optoelectronic properties[3]. Its drawback are brittleness and low electric conductivity[4]. Encapsulation of dimethyl-quaterthiophene (4TCH<sub>3</sub>) inside SWCNTs gives rise to a hybrid material, expected to combine the protection of the confining matrix to the photo-physical properties of the encapsulated unit. This hybrid material will be referred hereafter as  $4TCH_3@NT\phi$  (where  $\phi$  is the nanotube diameter in Å). The first recent experimental study, based on Raman spectroscopy, brought the proof that the number of encapsulated molecules depend on the size of the confining matrix[5]. Some influence of the diameter of the nanotube on the confinement state of the molecule as well as their interaction with the nanotube is expected. Inelastic neutron scattering, mostly sensitive to the confined molecule, due to the strong cross-section of hydrogen atoms, probes wide Q vector range, which is a very interesting tool in order to obtain a complete picture of the vibrational properties of such system.

We are interested on the confinement properties of two hybrid systems:  $4TCH_3@NT09$  and  $4TCH_3@NT14$ . Those materials were studied by means of inelastic neutron scattering (INS) at two instruments at the Institute Laue-Langevin, time-of-flight IN4C and Triple Axis IN1-Lagrange spectrometers. The resulting experimental HPDOS can be compared to the DFT-simulated HPDOS, allowing thus the assignment of main vibrational modes. We show that specific vibrational modes undergo to modifications upon a change of the size of the confining matrix, evidencing the influence of encapsulation in such molecules.

## Study of covalent grafting of Fluorescein Isothiocyanate on double-walled carbon nanotubes.

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Over the past decades the popularity of Carbon nanotubes (CNTs) rose drastically and made them the subject of an intense research effort. Nowadays, new applications for CNTs are found each year, leading to foresee an increase of their production and their use for new nanomaterials. Therefore, it became not only legitimate but also necessary to study their toxicity and environmental impact.

The use of those CNTs always requires their dispersion which is generally obtained through their functionalization. In the case of covalent grafting, the question of the competition between real grafting and simple adsorption (also likely to happen) is very relevant and has never been really investigated in a rigorous way. This question is however a central one in many current debates, and especially in the field of nanotoxicology and biomedical applications [1a-11] of CNTs, where their functionalization by fluorophores is used to track the latter inside cells. The visualization of the fluorescence is then naturally associated to that of the CNTs. However, fundamental questions are raised as there is no simple evidence that a fluorescent molecule simply adsorbed onto a CNT will indefinitely stay there once inside a cell.

In order to answer those questions we chose to deeply investigate the covalent grafting of the Fluorescein Isothiocyanate (FITC, fluorophore commonly used for toxicity studies) onto Double-walled carbon nanotubes (DWCNTs) [2]. The aim of the work presented here is to fully understand the mechanisms involved behind the three steps of the functionalization process (1- Carboxylation of the DWCNTs, 2- Grafting of 1,4-diaminobutane as a linker, 3- Grafting of FITC) [3][4], by using different experimental techniques such as Transmission Electronic Microscopy, Raman spectroscopy, X-ray Photo-electron Spectroscopy and Neutron Vibrational spectroscopy. The preliminary results obtained with XPS and Neutron spectroscopy already seem to indicate that both covalent and non-covalent grafting happen while the functionalization process. In addition to the combination of those techniques, DFT calculations will be performed as a further step, expecting deriving quantitative information and distinguish between simple adsorption and covalent grafting for a given molecule.

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#### **Modification of Glass ionomer cements**

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Glass ionomer cement (GIC) is used in dentistry as a restorative material due to its adhesion to tooth surfaces, good biocompatibility and ability to release fluoride. However the mechanical properties makes it un- desirable for use in load bearing areas, such as for example in large cavities in the molar region. Therefore the aim of this work was to modify a commercial GIC (Voco Ionofil Molar AC) to improve the mechanical and chemical properties of this GIC. The idea was to substitute part of the glass particles with hydroxyapatite of different particle sizes and in different concentrations.

The testing methods used to evaluate the properties of the experimental material were compressive fracture strength (CFS), thermogravimetric analysis (TGA) and X-rays Tomography.

The results from the CFS tests seem to indicate that a 1wt% substitution is the most desirable. Moreover a trend towards improved mechanical properties seems to be observed for larger hydroxyapatite particle sizes (average 5 microns). The results also seems to indicate that the hydroxyapatite-modified GIC reaches early strength faster than the commercial GIC.

## Hydrogen bond dynamics, conformational flexibility and polymorphism in antipsychotics

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The market related to drugs for central nervous system is the second largest in the therapy industry, with the segment of antidepressants, antipsychotics and antiepileptics holding the highest percentage. However due to their mode of action, antipsychotic drugs, used for the treatment of central nervous system disorders generate a wide range of undesirable side effects.

Last year, most of the brand-name antidepressant drugs on today's market went off patent, opening a door to the pursuit of development of derivatives that are more effective. However, because of its marketing importance, pharmaceutical companies seem to have withheld significant information on this type of drugs. In fact, even the data of X-ray of polymorphs are generally only in patents, and very few academic papers can be found on the subject [1]. This is no less true of the characterization by vibrational spectroscopy (infrared, Raman and neutron scattering) of antipsychotics, and even less on the optical characterization (optical absorption and luminescence). In conclusion, there is a general lack in the understanding of the conformational habit of these molecules.

This work is related to the investigation of three different antipsychotics, one of each generation: haloperidol ( $C_{21}H_{23}CIFNO$ ), Seroquel ( $C_{21}H_{25}N_3O_2S$ ) and aripiprazole ( $C_{23}H_{27}Cl_2N_3O_2$ ) using a combination of inelastic neutron scattering (INS) and density functional theory (DFT). These substances were selected because their crystalline structure and the concerns related to their polymorphism have been already reported in the literature [2].

Here we will report on data obtained using the spectrometers PELICAN and TOSCA located at the Bragg Institute (Australia) and ISIS (UK), respectively. Polymorphic transformations and purity of the studied samples were determined by calorimetric studies, while their structure was verified by X-rays diffraction. Furthermore, the origin of each of the observed modes will be discussed with the support of theoretical data provided by Density Functional Theory calculations (DFT).

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## Attractive lateral interactions between chemisorbed oxygen atoms on aluminum surfaces

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When electronegative atoms adsorb on a more electropositive metal surface, charge transfer occurs and adsorbed atoms become negatively charged. Because of this accumulated charge, repulsive lateral interactions are expected between the adatoms. According to the classical method of images the lateral repulsion between negatively charged adatoms can be treated as a dipole-dipole interaction that scales as  $\Theta^{3/2}$ , where  $\Theta$  is the surface coverage of adatoms. Such dependence is typical for chemisorbed atomic oxygen on transition metal surfaces. However, in the case of O on Al(111) and Al(100) surfaces the opposite occurs and the binding energy magnitude increases with increasing coverage. Although this anomaly has been noticed [1,2], no sound explanation as to why this occurs has been given in the literature. Hence, we attempted to explain this anomaly on a molecular level by means of DFT calculations. We found that the attractive interactions are a consequence of a simple electrostatic stabilization. Namely, at full monolayer coverage the O adatoms are located close to the surface and together with positively charged surface AI atoms form an interlaced layer of anions and cations, which is electrostatically stable. We conclude that the attractive interactions between negatively charged O adatoms at high-coverage stem from an interplay between Coulombic interactions and geometric effects, which depend on the height of adatoms above the surface.

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## High magnetic field studies of the vortex lattice structure in Y0.96Ca0.04Ba2Cu3O7

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Small-angle neutron scattering (SANS) measurements of the vortex lattice structure as a function of field and temperature make it possible to extract information such as the penetration depth, coherence length and the superconducting gap structure of a given superconductor. In YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-5</sub> (YBCO) SANS can reveal the effective mass anisotropy, the vortex lattice melting, the vortex lattice pinning [1] and the fieldinduced non-locality [2]. In YBCO the oxygen doping level alters the population of oxygen atoms in the 'chain' layers where Cu-O chains lie along the b-axis. Varying the amount of oxygen changes the number of available holes and this tunes the superconductivity. An alternative to oxygen doping in  $YBa_2Cu_3O_{7-5}$  is doping the yttrium sites with calcium whilst leaving the compound fully oxygenated ( $\delta = 0$ ). We present a SANS study of Y<sub>0.96</sub>Ca<sub>0.04</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> [3] at magnetic fields up to 17 T. The calcium doping increases the whole concentration in the copper-oxide planes beyond that found in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, so this material is overdoped. We find differences between the two compounds in the vortex lattice structure and coordination at base temperature as a function of applied magnetic field that indicate changes in the superconducting order parameter, and we also find that non-local effects become important at high fields. We also investigate the perfection of the vortex lattice and the variation of the SANS signal at higher temperatures. The vortex lattice form factor and structure provide evidence that the inclusion of calcium into  $YBa_2Cu_3O_{7-5}$ increases the strength of pinning of the vortices.

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## Hydration of triblock copolymers and stabilization of semiconductor nanoparticles

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Ternary polyether are block ABA copolymers consisting of poly(ethyleneoxide) (PEO) (A) and poly(propylenoxide) (PPO) (B). Ternary polyether or poloxamers change their hydrophilic/hydrophobic balance dramatically with their temperature and their concentration in water. This change causes a micelleisation of the poloxamers where the hydrophobic block will form the inner part of the micelle and the hydrophilic block the outer part of the micelle. In small angle x-ray scattering analysis form/shape models have to be used to determine the size, scattering length densities (SLD) and the volume fraction of a material. For micelles an appropriate model is the core-shell model where shell mostly consists of PEO and the core mainly of PPO. In this model the SLD's for core and for shell heavily depend on each other. A new parameter  $\kappa$  is introduced to describe the change of the conformation and hydration of the micelle while including the radii of shell and core. It shows that the SLD of the core decreases and thus dehydrates with increasing temperature.

For producing Cadmiumsulfide (CdS) semiconductor nanoparticles two solutions are required: Cadmiumchlorid (CdCl<sub>2</sub>) and Natriumsulfid (Na<sub>2</sub>S). During the precipitation reaction the CdS nanoparticles will agglomerate because of their hydrophobic nature. To stabilize those hydrophobic nanoparticles usually EDTA is used, where only small concentrations of the solution can be used. In our

approach poloxamers will be used to stabilize those nanoparticles, which can be caught in the micelle cores. Varying the parameters of the stabilization process, different sizes of nanoparticles will be produced. CdS nanoparticle show special properties if the size of the particle is smaller then the exciton radius. The Wannier-Exciton consist of an electron and a hole. If the radius of the particle is in the range of 15 Å to 50 Å the exciton radius is artificially reduced and thus affects the semiconductors bandgap.



# Fifth Annual Niels Bohr International Academy Workshop-School on ESS Science:

Condensed Matter Theory and Advanced Software

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