Dynamics in Confinement

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CONFIT 2022

Monday 10 October 2022 - Thursday 13 October 2022
Institut Laue Langevin, Grenoble

Book of Abstracts

5th International Workshop on
DYNAMICS IN CONFINEMENT
11-13 Oct 2022

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Talks on

Tuesday, 11 October 2022

Invited Talks / Tuesday, 11 October 2022, 08h50

Confinement effects and multiple glassy dynamics for a homologous series of triphenylene-based columnar liquid crystals – A study by broadband dielectric spectroscopy, advanced calorimetry and neutron scattering

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Hexakis(n-alkyloxy)triphenylene) (HATn) consisting of an aromatic triphenylene core and alkyl side chains are model discotic liquid crystal (DLC) systems forming a columnar mesophase. In the mesophase, the molecules of HATn self-assemble in columns, which has one-dimensional high charge carrier mobility along the columns. Here, a homologous series of HATn with different length of the alkyl chain (n=5,6,8,10,12) is investigated using differential scanning calorimetry (DSC), broadband dielectric spectroscopy (BDS) and advanced calorimetric techniques including fast scanning calorimetry (FSC) and specific heat spectroscopy (SHS). The investigation of the phase behavior was done utilizing DSC experiments and the influence of the alkyl chain length on the phase behavior was revealed. By the dielectric investigations a γ-relaxation due to localized fluctuations as well as two glassy dynamics the αcore and αalkyl relaxation were observed in the temperature range of the plastic crystalline phase. Moreover, the observed glassy dynamics were further studied employing advanced calorimetry. All observed relaxation processes are attributed to the possible specific molecular fluctuations and discussed in detail. From the results a transition at around n=8 from a rigid constrained (n=5,6) to a softer system (n=10,12) on a molecular lenght scale was revealed with increasing alkyl chain length. A counterbalance of two competing effects of a polyethylene like behavior of the alkyl chains in the intercolumnar domains and self-organized confinement is discussed in the context of a hindered glass transition. The results were confirmed by in- and quasielastic neutron scattering.

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Contributed Talks / Tuesday, 11 October 2022, 09h20

Confinement induced relaxations and phase behavior of a nanoconfined ionic liquid crystal

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Liquid crystalline mesophases in nanoconfinement exhibit intriguing phase transition behaviors and relaxation dynamics. Here in, we investigate the molecular dynamics and electrical conductivity of a linear shaped guanidinium based ILC confined in self-ordered nano porous alumina oxide membranes of pore size ranging from 180nm down to 25nm by employing broadband dielectric spectroscopy (BDS) and calorimetry. Calorimetric investigation reveals a complete suppression of the columnar – isotropic transition, while the plastic crystalline – columnar transition temperature decreases with inverse pore size and deviates from the Gibbs – Thomson equation.
For the bulk case, BDS detects two relaxation modes in the crystalline phase, the ☒ relaxation and the $\alpha1$ relaxation, and two relaxation modes in the columnar phase, the $\alpha2$ and $\alpha3$ relaxation. For the confined case, all relaxation modes slow down compared to the bulk. However, for the least pore size (25 nm), the $\alpha2$ relaxation is absent. We discuss the possible molecular origins of the different relaxation modes observed. For the bulk ILC, a clear jump of 4 orders of magnitude in the absolute values of DC conductivity occurs at the transition from the plastic crystalline to hexagonal columnar phase, for the confined ILC, this transition is smooth. DC conductivity is reduced for the confined case, except for the 25nm, where the values is similar to the bulk.

Contributed Talks / Tuesday, 11 October 2022, 09h40

Layers of ionic liquids with nitrate ions enclosed between micrometer-spaced glass plates

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Ionic liquids (ILs) have been widely used in a range of applications due to their unique physico-chemical and electrochemical properties. For many of their practical applications, for example, in mechanical devices, supercapacitors, batteries, and catalytic reactors, etc., understanding the properties of ILs close to a solid surface or in confinement has crucial importance. Some protic and aprotic ionic liquids with nitrate anion (ethylammonium nitrate, ethyl methyl imidazolium nitrate and their mixtures with nitrate salts, being enclosed between a micrometer-spaced glass or quartz plates, demonstrates unusual dynamics of cations, which is different from that in bulk and in nano-confinement of these systems [1-3]. The dynamics of the ions is also reversibly changes during the exposure of the ILs in a static magnetic field [4]. These phenomena were analysed and interpreted as a results of intermolecular structure transformations occurring in the enclosed ILs. Conditions of the transformations were investigated by NMR-diffusometry and NMR-relaxometry. Nature and mechanisms of the transformations are under discussion.

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Invited Talks / Tuesday, 11 October 2022, 10h30

How the behavior of cations within interfacial layer can influence the water dynamics in confined media

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The investigation of the processes taking place at the solid/aqueous solution interface in nanoconfinement media is an important key parameter to understand and predict the behavior of nanoporous materials. Indeed, understanding the water and ions behavior in such media can help to clarify the processes and chemical reactions occurring at this level of confinement. Recently, we highlighted how the dynamics and the structure of confined water in the presence of ions drive the alteration of mesoporous silica materials and glass [1−3]. This change of water properties is mainly due to the ions adsorption at the pore surface that structures water molecules [4−5].
In order to clarify this point, we investigated the impact of ions such as Li^+, Na^+ and Cs^+, on the structural and dynamical properties of water confined in silica materials (d_p=2.6 nm). To reach this goal, we studied the structural properties of the confined water using total X-ray scattering (ID15-A at ESRF) coupled with pair distribution function analysis. In addition, we performed empirical simulations to access the density profile in the pores [6]. Furthermore, we characterized the water dynamics at picosecond timescale using Quasi-Elastic Neutron Scattering (IN5 time-of-flight at ILL). The results clearly support the existence of ion-specific effects under confinement.
From such analysis, we will be able to propose an accurate structural description to understand the ions behavior and their impact on the structure and diffusion of water into silica confined space.

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Contributed Talks / Tuesday, 11 October 2022, 11h00

Dynamics of water inside boehmite suspensions probed by NMR techniques

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γ-Alumina is a widely used heterogeneous catalytic support. To perfect the optimization of its catalytic performance, the accessibility of the molecules to active sites and more generally the molecular transport inside the support need to be fully assessed. As γ-alumina is obtained through a topotactic transformation, most of its properties are inherited by the boehmite and its process [1]. The peptization, where the agglomerates of the raw boehmite powder break into aggregates and then reorganize themselves, is one of the key steps for the final structure and properties of the support.

In this work, we perform a multi-scale analysis of the water dynamics inside boehmite suspensions. Diffusion is assessed on a second-to-millisecond time scale by PFG-NMR while confined dynamics at the interface and particularly bulk mediated surface diffusion is probed by Fast-Field Cycling NMR (NMRD) on a microsecond time scale. We especially study the influence of the aggregates organization on the solvent dynamics. To this aim, several boehmite suspensions have been prepared by varying the ionic force and the volume fraction of boehmite. Whether it arises from the topological structure or the strong interactions to the surface, the water dynamics appears to undergo confinement effects. For instance, at the microsecond time scale, the prepared boehmite suspensions display almost identical NMRD profiles. It means that the long-range geometry of the system does not seem to influence the dynamics. Furthermore, we were able to prove that the observed water dynamics comes from a confined area: the adsorption layer (first few water monolayers from the surface). At this scale, the water dynamics seem to be controlled only through strong interactions with the surface of aggregates. Hence, we found that surface diffusion of water in boehmite is slow. QENS experiments could bring a deeper understanding of this surface diffusion.

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Contributed Talks / Tuesday, 11 October 2022, 11h20

Heterogeneous Microscopic Dynamics of Intruded Water in a Superhydrophobic Nanoconfinement: Neutron Scattering and Molecular Modeling

Julie Wolanin; Loïc Michel; David Tabacchioni; Jean-Marc Zanotti[1] ; Judith Peters; Inhar Imaz; Benoit Coasne[2] ; Marie Plazanet[2] ; Cyril Picard[3]

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With their strong confining porosity and versatile surface chemistry, Zeolitic Imidazolate Frameworks - including the prototypical ZIF-8 - display exceptional properties for various applications. In particular, the forced intrusion of water at high pressure (around 25 MPa) into ZIF-8 nanopores is of interest for energy storage. Such a system reveals also ideal to study experimentally water dynamics and thermodynamics in ultra-hydrophobic confinement. Here, we report on neutron scattering experiments to probe the molecular dynamics of water within ZIF-8 nanopores under high pressure up to 38 MPa. In addition to an overall confinement-induced slowing down, we provide evidence for strong dynamical heterogeneities with different underlying molecular dynamics. Using complementary molecular simulations, these heterogeneities are found to correspond to different microscopic mechanisms inherent to vicinal molecules located in strongly adsorbing sites (ligands) and other molecules nanoconfined in the cavity center. These findings unveil a complex microscopic dynamics, which results from the combination of surface residence times and exchanges between the cavity surface and center. We believe that our findings represent an important step forward in the understanding of complex dynamical behavior in superhydrophobic systems, which are relevant to many industrial applications.

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Contributed Talks / Tuesday, 11 October 2022, 11h40

Translational diffusion of a fluorescent tracer molecule in nanoconfined water

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Diffusion of tracer dye molecules in water confined to nanoscale is an important subject with a direct bearing on many technological applications. It is not yet clear however, if the dynamics of water in hydrophilic as well as hydrophobic nanochannels remains bulk-like. Here, we present diffusion measurement of a fluorescent dye molecule in water confined to nanoscale between two hydrophilic surfaces whose separation can be controlled with a precision of less than a nm. We observe that the fluorescence intensities correlate over a fast($\sim$ 30 μs) and slow ($\sim$ 1000 μs) time components. The slow timescale is due to adsorption of fluorophores to the confining walls and it disappears in presence of 1 M salt. The fast component is attributed to diffusion of dye molecules in the gap and is found to be bulk-like for sub-10 nm separations and indicates that viscosity of water under confinement remains unaltered up to confinement gap as small as $\sim$ 5 nm. Our findings contradict some of the recent measurements of diffusion under nanoconfinement, however they are consistent with many estimates of self-diffusion using molecular dynamics simulations and measurements using neutron scattering experiments.

Invited Talks / Tuesday, 11 October 2022, 13h30

The effect of surface conditions on the glass-transition dynamics of poly(phenylmethylsiloxane) confined in cylindrical nanopores

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In this contribution, we demonstrate the results of the study on the effect of surface conditions on the polymer glass-transition dynamics in nanopore confinement. The tested material is poly(phenyl methyl siloxane) (PMPS) embedded in alumina nanopores with modified surface properties. The main experimental techniques used are dielectric spectroscopy, differential scanning calorimetry, and contact angle measurements. Two different strategies were used to modify the character of the inner surface of the pores: (i) functionalization with the use of highly polar phosphoric acid units separated from each other by non-polar triethoxysilane groups (N= number of spacers N changes from 0 to 24) and via (ii) atomic layer deposition technique. Changes in the surface conditions dramatically affect interactions between the polymer and the confining surface as reflected in the values of the interfacial free energy changing from 0.5 mN/m up to 18.7 mN/m. Surprisingly we found that the characteristic "two glass transitions event" seen in nanopore confinement does not vanish, even in the absence of strong interfacial interactions. In this way, changes in the glass-transition behavior of the tested polymer in confined geometry cannot be rationalized in terms of the differences in polymer/substrate interfacial energy. Eliminating strongly adhered surfaces does not eliminate the puzzling two-Tgs effect seen in cylindrical nanopores.

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Contributed Talks / Tuesday, 11 October 2022, 14h00

Block Copolymer Assembled Mesoporous Materials Architectures for Biosensing Applications

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Block copolymer self-assembly provides effective routes for the precise structural arrangement of inorganic materials architectures, either via templating or co-assembly. In my talk, I want to provide an overview of how we exploit formation principles in 2D and 3D to tailor mesostructured electrodes for biosensing applications.

We have recently developed an approach, based on quartz crystal microbalance with dissipation monitoring (QCM-d), for the stepwise functionalisation of surfaces immobilisation and subsequent uptake and release of binding partners.[1] This is an ideal platform to study extracellular vesicles (EVs), with the potential to be used biomarkers for disease diagnostics via liquid biopsies from readily accessible bodily fluids.[2,3] To this end, we studied the effect of nanostructured gold arrays compared to flat sensing surfaces.[4] Crucially, we find that the nanostructuration significantly enhances the detection sensitivity, and that gold islands matched to the lengthscale of the binding partners outperform smaller arrays. We hypothesise that the creation of such confined sensing regions interspersed by non-binding silica, provides optimal spatial orientation with reduced steric effects and negative cooperativity of grafted antibodies.

In a separate line of research, we are exploiting the capability of block copolymers to structure-direct inorganic films for electrochemical biosensing within mesoporous architectures. The integration of mesoporous films with finely controllable pore characteristics allows to detect target analytes by immobilisation within the mesoporous network, where trapping events and associated pore blockage can be conveniently read out by electrochemical means. Herein, the formation of tailored inverse opal-type pore arrangements enabled the reliable detection of E. coli DNA.[5,6]

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Contributed Talks / Tuesday, 11 October 2022, 14h20

Mechanics of buried thin polymer films revealed by a combined full analy-sis of the off-specular and specular neutron reflection

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In this work we show the power of the off-specular scattering (OSS) technique applied simultaneously with the specular reflection (SR) to probe the thermal capillary-type wave spectrum of buried interfaces between immiscible polymer layers. The combined SR and OSS data analysis performed using a quick and robust originally developed algorithm, includes a common absolute scale normalization of both types of scattering, which are intrinsically linked, constraining the model to a high degree [1,2]. This, particularly, makes it possible to extract the spectral wavelength cut-offs and ampli-tudes of the interlayer roughness between the two polymers. By a systematic study of these pa-rameters as a function of polymer layer thickness in the range from nano- to sub-micrometer we show that it is possible to show deviations from Newtonian viscosity of the buried polymer layer and that viscoelastic effects have to be taken into account. By using an appropriate model suggest-ed for polymer brushes we are able to extract the shear modulus of a buried thin polymer film supported on a solid substrate without applying external forces. The example presented here consists of polystyrene and polymethyl-methacrylate bi-layers annealed above the glass transition temperature and then rapidly quenched to room temperature for the neutron scattering experiment.
On a wider perspective, the here presented method allows, by the use of nominally elastic scattering, to access mechanical material properties of thin buried liquid films by analyzing the thermal fluctuation spectra of their surfaces.

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Contributed Talks / Tuesday, 11 October 2022, 14h40

Dependence of local dynamics on the chain length of grafted molecules

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Nanoparticles can be utilized to induce restricted spatial mobility in the polymer and smaller molecules. However, a simple blend of nanoparticles with the organic molecules leads to phase separation and hence is unsustainable. Grafting the molecules on nanoparticle surface addresses this problem efficiently. The grafting induces significant alteration to the conformation and dynamics of the molecules. We discuss two cases here: polymer molecules grafted on iron oxide nanoparticles i.e. long molecules and oleic acid grafted on iron oxide nanoparticles i.e. short chains. We study these systems using a combination of Quasielastic neutron scattering (QENS) and dielectric spectroscopy. We observe a molecular weight dependent average dynamics in grafted polymers. For lower molecular weight, the dynamics of grafted polymer is decelerated as compared to the pure polymer. On the other hand, for higher molecular weight, the dynamics of grafted polymer is faster. We invoke a detailed analysis method using distribution of relaxation times to fit the data which unearths the presence of both faster as well as slower segments in all the nanocomposites. On the other hand, in case of oleic acid, the dynamics if restricted to uniaxial rotation when grafted on nanoparticles. We show that even below the crystallization temperature of pure oleic acid, rotational dynamics is observed in case of grafted oleic acid. However, there is selective rotation of bonds depending on temperature. A modified uniaxial rotation diffusion model is able to capture these temperature dependent dynamics of the grafted oleic acid system.

Invited Talks / Tuesday, 11 October 2022, 15h30

Structuration, dynamics and diffusion of water in hydrophilic nanotubes

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An emblematic case of nanofluidics is the ultra-low friction of water in hydrophobic carbon nanotubes. But original behaviours of water molecules are also observed in hydrophilic nanotubes, such as imogolite nanotubes (INT), with nominal composition $GeAl_2O_7H_4$ and $SiAl_2O_7H_4$, noted Ge-INT and Si-INT. Inner diameter is 2.9nm for Ge-INT and 1.5nm for Si-INT. Investigations are based on both experimental and numerical approaches, namely X-ray scattering, quasi-elastic neutron scattering (QENS), inelastic neutron scattering (INS) and classical or ab-initio molecular dynamics simulations.

A unique structure of the water layer adsorbed inside Ge-INT is revealed [1]. Water molecules form an ordered triangular lattice on the inner surface of the nanotube. To the best of our knowledge, this structure differs from that of any kind of two-dimensional water. Analysis of the vibrational density of state measured by INS shows that the dynamics of INT and water are strongly interrelated, a fully original result with respect to the available experimental literature. Water dynamics remains harmonic from 10K to 300K, with no phase transition towards a liquid state up to room temperature.

In Si-INT, the adsorbed water layer is no more solid-like but it is structured periodically along the tube axis z. The influence of this structuration on water diffusion properties will be shown based on QENS experiments. Water close to the nanotube wall diffuses along a ring in the (x,y) plane, while water in the central section of the pore diffuses rapidly along the z axis.

The complementarities between the experimental and computational approaches will be underlined. Different behaviours of water in hydrophilic Si-INT and Ge-INT will be discussed.

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Contributed Talks / Tuesday, 11 October 2022, 16h00

Water dynamics in a saponite: coupling molecular dynamics and NSE experiments

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Clays are porous lamellar materials with remarkable properties of adsorption and retention, which make them good candidates for environmental applications such as water pollution control or waste storage (radioactive, CO2). The retention properties of the mobile species are strongly influenced by the behavior of water in the medium.

On one hand, classical molecular simulations make it possible to describe and quantify the diffusion processes in water/clay systems, as soon as the interactions between the atoms are well defined. On the other hand, QENS experiments provide valuable information on water dynamics in this systems, as soon as a reliable model of analysis is found. I will show on an oriented sample of hydrated saponite how the modeling/NSE experiment coupling allows 1) to find the right model of analysis, 1) to interpret the experiments and their evolution with temperature 3) to define the limit of validity of the simulations.

Contributed Talks / Tuesday, 11 October 2022, 16h20

Anomalous ionic transport in subnanometric water films

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In February 2022, the Intergovernmental Panel on Climate Change (IPCC) report has been published by the UNO, which stated the critical situation and the environmental emergency to reduce greenhouse gases emissions to keep the global warmth below 1.5℃. Thus, an effort has to be made to be able to harvest energy with a minimal CO2 emission. Nanofluidics (fluidic transport in nanoconfined liquids) appears to be a promising field to address this challenge. At such scales, the surface to volume ratio is extremely large and transport properties are mainly governed by interactions at interfaces.

Whereas macroscopic continuous models for electrostatics and hydrodynamics predict well ionic transport for 1-10 nm thick nanochannels, some anomalous properties have been reported in the regime of ultraconfinement, such as dielectric anomalies in confined water. An effort has to be made to precisely understand such behaviors in ultraconfined system, with the ultimate goal to enhance the harvesting of energy in nanofluidic systems.

In the present work, this regime of ultraconfinement is investigated. For that, the conductance of water soft films, that condense spontaneously from undersaturated vapor on hydrophilic silica surfaces, is measured as a function of their thickness. This thickness is modulated by the relative humidity above the substrate. To our knowledge, this experiment is one of a kind to control continuously the confinement down subnanometric scales. A regime of surface conductivity is recovered for large humidity, i.e. for thickness above 1 nm but fails below. A model based on a hindered diffusion layer close to the interface is developed to explain the measurements below the hydrodynamic limit (1 nm). Molecular dynamic simulations have been carried out to confront these results and fully understand the new transport processes. These experimental results open the way to new transport descriptions in ultraconfinement.

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Contributed Talks / Tuesday, 11 October 2022, 16h40

Experimentally probing ionic solutions in single-digit nanoconfinement

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Understanding transport and behavior of ionic solutions in single-digit nanoconfinement is crucial to explain the behavioral transition of confined solutions. This is particularly the case when the system length scale crosses the classical key length scales describing energetics and equilibrium of ionic solutions next to surfaces. Experimentally probing nanoconfinement would open large perspectives to test modelling or theory predictions. Here, using a new test vehicle that consists in 3 and 5 nm-height silica nanochannels associated with an original characterization technique based on the interface hard X-ray reflectivity analysis, we directly probed the transport of solutions containing cations having increasing kosmotropic properties (XCl_2 with X: Ba < Ca < Mg) and obtained their distributions inside the nanochannels. We observed that cation adsorption decreases with the size of the confinement and that small cation adsorption is favored. In addition, nanochannel clogging occurs when ions tend to form ion pairs. These ion pairs may play the role of nano-sized prenucleation clusters leading to phase precipitation. These results evidence the specific ion effect in single-digit nanoconfinement that may result in dramatic changes of solution transport. In this line, our new method opens new perspectives for the characterization of ionic solutions and of interfaces in single-digit nanoconfinement.

Talks on

Wednesday, 12 October 2022

Invited Talks / Wednesday, 12 October 2022, 08h30

Smart membranes for energy conversion: a neutron approach

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Ion conducting polymer membranes are designed for applications ranging from separation and dialysis, to energy conversion and storage technologies. A key application is in fuel cells, where the semi-permeable polymer membrane plays several roles. In a fuel cell, the polymer membrane permits the selective transport of H+ or OH- to enable completion of the electrode half-reactions, plays a major role in the management of water that is necessary for the conduction process and is a product in the reactions, and provides a physical barrier against leakage across the cell. All of these functions must be optimised to enable high conduction efficiency under operational conditions, including high temperatures and aggressive chemical environments, while ensuring a long lifetime of the fuel cell. Polymer electrolyte membranes used in current devices only partially meet these stringent requirements, with ongoing research to assess and develop improved membranes for a more efficient operation and to help realise the transition to a hydrogen-fuelled energy economy. A key fundamental issue to achieving these goals is the need to understand and control the nature of the strongly coupled dynamical processes involving the polymer, water and ions, and their relationship to the conductivity, as a function of temperature and other environmental conditions. This can be achieved by using neutron scattering techniques that give access to information across a wide range of timescales. Here we apply QENS, applied over a wide range of timescales to disentangle the water, polymer relaxation and ion dynamics, using the concept of serial decoupling of relaxation and diffusional processes to analyse the data. The insights provided by these data [1-3] offer a guide for the design of new devices, where tuning the membrane nanostructure would result in activation of the anionic hopping mechanism, providing improved performance over a wide range of operational conditions.

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Contributed Talks / Wednesday, 12 October 2022, 09h00

Selective Ion Transport through Ion-Exchange-Membranes for Fuel Cells, Electrolyzers and Flow Batteries: The effect of "Ion Sieving"

Klaus-Dieter Kreuer

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Ion-exchange separator membranes (IEM) in electrochemical energy conversion and storage devices need to conduct a specific type of ion for mediating the electrochemical reactions taking place at anode and cathode while efficiently separating the electrochemically active species. In PEM-fuel cells and electrolyzers and in flow batteries, the conducting ions are mostly H^+ or OH^-, and parasitic transport of gases (H_2 and O_2 in the case of fuel cells and electrolyzers) and ionic species (e.g. vanadium in the case of flow batteries) must be suppressed. Since wanted and unwanted parasitic transport take place along the same pathways (aqueous ionic domains), these must be **chemically** and **morphologically** designed and controlled. **Ionic species** practically keep their hydration shell and their transport is sterically constrained by the width of aqueous pathways while non-interacting **gas molecules** utilize the accessible dynamic free volume for diffusion. In this presentation, I will discuss the tradeoff between selectivity and transport rates and make suggestions for choosing, optimizing and developing membranes with low parasitic transport for **fuel cells, electrolyzers** and **vanadium-redox-flow batteries**.

K. D. Kreuer and A. Muenchinger: *Fast and Selective Ionic Transport: From Ion-Conducting Channels to Ion Exchange Membranes for Flow Batteries*, Annual Review of Materials Research **51**:21-46 (2021)

C. Klose, T. Saatkamp, A. Muenchinger, L. Bohn, G. Titvinidze, M. Breitwieser, K. D. Kreuer, and S. Vierrath: *All-hydrocarbon MEA for PEM water electrolysis combining low hydrogen crossover and high performance*, Advanced Energy Materials **10**, 1903995 (2019).

Contributed Talks / Wednesday, 12 October 2022, 09h20

Wetting/drying mechanisms associated with nanoconfined salt solutions: an optical reflectance study on vapour phase imbibition and adsorption

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The wetting and drying cycles of salt solutions confined in conductive nanoporous electrodes are conceived to generate energy from low-grade waste heat by coupling the pore drying/wetting process with the charging/ discharging cycles of the electrodes. This could be realised by ascertaining the optimal physical conditions that allow a systematic control and manipulation of the electrically charged layers that develop inside the porous host matrices. We realise this objective by (1) carrying out optical reflectance study of water vapour sorption isotherms in nanoporous glass membranes with/without pre-adsorbed salt solutions to unravel the thermodynamics of salt solution cluster evolution, (2) carry out imbibition of water vapour into the nanopores and/or drying of nanopores with/without pre-adsorbed salt solutions to understand the impact of salt concentration and relative humidity on the kinetics of pore-filling and emptying, and (3) conduct vapour sorption and wetting/de-wetting experiments in nanofluidic devices with only a single nano-pore/channel to precisely quantify the kinetics of mass transport. In this regard, CONFIT 2022 gives an excellent platform to learn and evaluate the possibility of employing inelastic neutron scattering methods for gaining rich information on the multitude of dynamic populations of the nanoconfined water and their evolution as a response to factors such as relative humidity and salt solution activity. In particular, to understand the mechanisms associated with the second order pore filling/emptying character in the presence of confined salt solutions, which will be correlated with the information on salt cluster evolution gained through complementary synchrotron experiments. A general agreement between the optical and neutron scattering studies shall pave the way for conducting future experiments with the non-transparent conducting electrodes actually relevant for the energy harvesting process.

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Modulating The Physico-Chemical Properties Of Water By Confinement In Hydrophobic NanoPores

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Water is the solvent of choice whenever hydrophilic substances are involved in a chemical process. However, because of its polar nature, the solubility of non-polar compounds in water is limited. The modulation of water's solvent properties to increase the solubility of non-polar molecules [1] would be ideal for phasing out the necessity of (organic) environmentally unfriendly solvents in the chemical industry.

The solvation power of water is governed by its hydrogen-bonding network. Furthermore, confinement of water in hydrophobic pores modifies its hydrogen bonding structure, making water a tunable solvent (the WATUSO principle [2]). Water intrusion in hydrophobic pores with diameters of 1-10 nm requires pressures from 0.5 to 20 MPa. Increasing the spinning speed of 4 mm NMR rotors in a Magic Angle Spinning (MAS) probe head, the centrifugal force in the sample increases, generating pressure and inducing intrusion of water in the hydrophobic pores. 1H MAS NMR and dielectric shift measurements, in situ in the NMR probe, reveal local level interactions between water molecules induced by the hydrophobic confinement [3].

In this work, we investigated the dielectric and spectroscopic properties of water, gradually forced into hydrophobic pores by increasing the MAS spinning rate. Silicates with different surface treatments have been used as confining media. Pore penetration results in a modified relative permittivity of the water phase, reflected in the dielectric shift observed in the NMR circuit and in the 1H MAS NMR spectra. These changes are related to the modification of hydrogen bonding network of water upon confinement in hydrophobic nanopores.

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Invited Talks / Wednesday, 12 October 2022, 10h30

Equilibrium and non-equilibrium dynamics of polymers confined in nanopores

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The nonequilibrium dynamics of linear and star-shaped *cis*-1,4 polyisoprenes confined within nanoporous alumina was explored as a function of pore size, *d*, molar mass and functionality (f = 2, 6, 64).[1,2] Two thermal protocols were tested; one resembling a quasi-static process (I), and another involving fast cooling followed by annealing (II). Although both protocols give identical equilibrium times, it is through protocol I that it is easier to extract the equilibrium times.[2] Both thermal protocols establish the existence of a critical temperature below which nonequilibrium effects set-in. The critical temperature depends on the degree of confinement, *2Rg/d*, and on molecular architecture. Strikingly, establishing equilibrium dynamics at all temperatures above the bulk T_g requires *2Rg/d*~0.02, i.e., pore diameters that are much larger than the chain dimensions. The non-equilibrium phenomena in pores reflects the nonequilibrium configurations of the adsorbed layer that extent away from the pore walls.[3] The equilibrium times depend strongly on temperature, pore size and functionality. In general, star-shaped polymers require longer times to reach equilibrium because of the higher tendency for adsorption.

Subsequently, we studied the adsorption kinetics of PI by following the evolution of the dielectrically active longest normal mode with *in situ nanodielectric spectroscopy*.[4,5] For a given pore diameter the characteristic adsorption times are some 8 orders of magnitude slower than the terminal relaxation times and more than 12 orders of magnitude slower than the segmental times. The extremely slow kinetics reflect the fact that exchanging chains with the pore surface have to pass through several unfavorable configurations (e.g trains, loops). The molar mass dependence of the characteristic adsorption times was in good agreement with a scaling theory proposed by de Gennes and later refined by Semenov and Joanny. The results from in situ nanodielectric spectroscopy demonstrate the capacity of the technique to provide the imbibition length, the adsorption kinetics and, at the same time, the chain dynamics.

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Contributed Talks / Wednesday, 12 October 2022, 11h00

Metastable Confinement of Molecular Hydrogen in Double Wall Carbon Nanotubes bundles

Carlos Cabrillo[1] ; Ricardo R. Fernández-Perera[2] ; Francisco Javier Bermejo[3] ; Claudia Mondelli[4] ; Miguel Angel González[5] ; Félix Fernández-Alonso[6] ; Eduardo Enciso[7] ; Marie Louise Saboungi[8]

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Carbon nanostructured materials are regarded to have high potential for the storage and management of H2 at cryogenic temperatures. We have observed isothermal large hysteretic hydrogen adsorption in samples made out of Double Wall Carbon Nanotubes bundles at 50 K, 77 K and 150 K and up to 15 bar of pressure. Adsorption metastability opens remarkable possibilities: it can be used to lower the working pressure for a given uptake; to increase the usable capacity; or to facilitate thermal management. Metastable H2 adsorption, however, has been barely explored, mostly in the context of Metal-Organic Frameworks (MOFs) [1]. For nanostructured carbons, hysteresis has been associated with chemisorption in metallic particles [2], characterized by undesirably high desorption energy barriers. To gain physical insight, we made a series of inelastic neutron scattering measurements. The elastic signals at different H2 loads are consistent with the uptake of the H2 within the interstitials of the bundles. The quasielastic signal display an anomalous dependence on momentum transfer which is nicely reproduced by an accurate 1D dimensional diffusion model (as expected from interstitial confinement of the H2 fluid) while the complete inelastic signal precludes the possibility of chemisorption onto the sample metallic impurities. We have developed developed a 2D dimensional model that reproduces the qualitative behaviour of the real system. The metastability emerges as consequence of the hierarchical structure of energy barriers, a structure that is sensitive to the H2 uptake through the expansion/contraction of the bundle configuration. Preliminary neutron diffraction results confirm the appearance of this structural hysteresis validating the proposed microscopic mechanisms responsible for the metastability.

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Contributed Talks / Wednesday, 12 October 2022, 11h20

Insight into friction in carbon nanotubes: guest-host interactions and thermal-driven pinning and unpinning in nanopeapods

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We report a complete neutron scattering investigation of the structure and dynamics of monomer and polymer phases of C_{60} carbon peapods. When the temperature is lowered below 300 K, the temperature evolution of the monomer data reflects a continuous increase of the orientational correlations between adjacent molecules, a signature of the strong rotation-translation coupling in this system. This transition is not observed in the polymer data, the orientation between the confined fullerenes being locked by covalent bridges. Above 200 K, the physics of the confined chain can fully be described without accounting for the nanotube, the latter merely playing the role of a container for a 1D system. As the temperature is lowered below some 200 K, the signature of the chain-tube interaction is observed by the progressive damping of the 1D acoustic phonon measured in both monomer and polymer data. We suggest that this damping originates from the friction between the confined chain and the nanotube host, friction that appears at low temperature due to the pinning of the C_{60} chain onto an incommensurable lattice – the nanotube. These results are supported by molecular dynamics simulations and are discussed within the framework of Aubry's transition by breaking of analycity.

Contributed Talks / Wednesday, 12 October 2022, 11h40

Hydrogen mobility in layered materials: MoS_2 and Carbon

Peter Fouquet; Vitalii Kuznetsov; Leran Lu; Franziska Traeger; Michael Koza; Wiebke Lohstroh; Alexei Nefedov[1] ; Detlef Rogalla[2] ; Hans-Werner Becker[2] ; Thomas Strunkus[3] ; Eva Kovacevic[4]

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The global climate challenges require a rapid suppression of fossil fuel use. Batteries are now widely used to replace petrol in cars, but they still have many disadvantages in terms of elevated price, long charging time, use of rare chemical elements and recycling. Therefore, hydrogen is still considered an important energy carrier for future mobile applications and much recent research efforts are invested in optimising hydrogen storage and catalysis.

Layered materials such as molybdenum sulfide (MoS2) are being studied intensively because they can serve as matrix for hydrogen storage and as catalyst or cat-alyst support in fuel cells thanks to their large surface area [1]. In addition, MoS2 is inexpensive and widely available, in contrast to platinum, which still is the standard catalyst material. MoS2 is a van-der-Waals bonded 2d material that provides a high density of active sites, but little is known about the mobility and the reaction steps of hydrogen and water in MoS2.

In this presentation we will discuss the progress that we achieved in identifying the translational and rotational diffusion in MoS2 [2]. To shed light on the possible pathways for improving the performance of MoS2 and other 2d catalyst materials, we have studied the diffusion of hydrogen and water by means of neutron scattering and XPS combined with nuclear reaction analysis and MD simulations.

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Invited Talks / Wednesday, 12 October 2022, 13h30

Confinement effects on the Slow Arrenhius Processes (SAP) observed in polymer melts

Simone Napolitano[1] ; Erik Thoms; Zijian Song; Kai Wang; Cristian Rodríguez-Tinoco; Allen Mathew

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The rate at which a nonequilibrium system decreases its free energy is commonly ascribed to molecular relaxation processes, arising from spontaneous rearrangements at the microscopic scale. While equilibration of liquids usually requires density fluctuations at timescales quickly diverging upon cooling – known as the α-modes –, growing experimental evidence indicates the presence of different pathways of weaker temperature dependence. Such equilibration processes exhibit a temperature-invariant activation energy on the order of 100 kJ/mol. Based on a large series of molecular dynamics and equilibration experiments, we identified the underlying molecular process responsible for this class of Arrhenius equilibration mechanisms with a slow mode (SAP), universally present in the liquid dynamics [1]. While in bulk samples the SAP can be masked by conductivity and electrode polarization, measurements in thin films permitted us to directly access the relaxation spectra of these slow modes. By analyzing polymer chains of different molecular weight and films of different thickness, we verified that this process is present also in bulk melts and that the activation energy and the characteristic molecular time of the SAP are not affected by either the macromolecular or the sample size. On the contrary, the large sensitivity of the intensity of the SAP dielectric peak to film thickness indicates that this process extends for length scales much larger than those of the α-modes. The SAP, which we show is intimately connected to high temperature flow, can efficiently drive melts and glasses towards more stable, less energetic states. Our results show that measurements of liquid dynamics can be used to predict the equilibration rate in the glassy state.

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Contributed Talks / Wednesday, 12 October 2022, 14h00

Are strongly confined colloids good models for two dimensional liquids?

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Quasi-two-dimensional (quasi-2D) colloidal hard-sphere suspensions confined in a slit geometry are widely used as two-dimensional (2D) model systems in experiments that probe the glassy relaxation dynamics of 2D systems. However, the question of to what extent these quasi-2D systems indeed represent 2D systems is rarely brought up. Here, we use computer simulations that take into account hydrodynamic interactions to show that dense quasi-2D colloidal bi-disperse hard-sphere suspensions exhibit much more rapid diffusion and relaxation than their 2D counterparts at the same area fraction. This difference is induced by the additional vertical space in the quasi-2D samples in which the small colloids can move out of the 2D plane, therefore allowing overlap between particles in the projected trajectories. Surprisingly, this difference in the dynamics can be accounted for if, instead of using the surface density, one characterizes the systems by means of a suitable structural quantity related to the radial distribution function. This implies that in the two geometries the relevant physics for glass-formation is essentially identical. Our results provide not only practical implications for 2D colloidal experiments but also interesting insights into the 3D-to-2D crossover in glass-forming systems.

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Contributed Talks / Wednesday, 12 October 2022, 14h20

Magnetic Colloids Adsorbed At Fluid Interfaces Acting As Interfacial Swimmers And Colloid Adsorption Probes

Fernando Martínez-Pedrero[1] ; José Martín-Roca[1] ; Chantal Valeriani[1] ; Francisco Ortega[1] ; Ramón G. Rubio[1] ; Carles Calero[2]

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Due to the large surface energy reduction linked to the adsorption of colloids at a fluid interface, these micrometer particles are often used as stabilizing units in the formation of highly stable complex interfacial fluids, Pickering emulsions, foams and colloidosomes. In addition, they act as probes in the characterization of interfacial microrheological properties or as model systems in the study of different phenomena, ranging from the study of 2D phase transitions to transport in the low Reynolds number regime under confined geometries. In this presentation, we will show how magnetic microparticles suspended in aqueous solutions can be accurately transported at the fluid interface by developing Stokesian and non-Stokesian strategies. In Stokesian designs, magnetic particles are dynamically assembled on interfacial micromotors or conveyor belts, which are driven by remotely controlled generation of local hydrodynamic flows, while in non-Stokesian counterparts, adsorbed and non-adsorbed particles are driven by itinerant magnetic potentials generated by lattices or rails of adsorbed colloids. In the last part of this talk, we will show how tracking the rotational-translational mechanism undergone by these particles, when under the influence of a rotating field, yields information on the kinetics and dynamics of particle adsorption in the presence of electrolytes or anionic and cationic surfactants.

Contributed Talks *(via videoconference)* / Wednesday, 12 October 2022, 14h40

The ω^3 scaling of the vibrational density of states in quasi-2D nanoconfined solids

Yuanxi Yu[1] ; Chenxing Yang[1] ; Matteo Baggioli[1] ; Liang Hong [1]

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Atomic vibrations play a vital role in the functions of various physical, chemical, and biological materials. The vibrational properties and the specific heat of a bulk material are well described by the Debye theory, which successfully predicts the quadratic ω^2 low-frequency scaling of the vibrational density of states (VDOS) in bulk solids from few fundamental assumptions. However, the corresponding relationships for nanoconfined materials with fewer degrees of freedom, have been far less well explored. The effects of confinement on the VDOS of glasses and amorphous solids have been discussed in several works with particular attention to the fate of the Boson Peak anomaly and glassy relaxation dynamics. Few discussions have been made on the scaling of VDOS of other solids under confinement or its foundations. Learning how GOM modifies the vibrational dynamics of glass formers, is of utmost significance to understand and optimize the phonon-assisted transportation of energy, electron or proton in various electronic devices and biological systems of nano-meter confinement.

In this work, inelastic neutron scattering was used as an experimental method to investigate the VDOS of ice in the sandwich of graphene oxide thin film at different confined sizes. We found that the low frequency scale of the dynamic vibration density of ice in the sandwich changed from ω^2 in Debye's model to ω^3 at a faster rate as the confined size decreased. All atomic molecular dynamics (MD) simulations confirm the experimental results and show that the scale changes are equally applicable to crystal and amorphous ice.

We developed a simple geometric model, deducing that this power comes from the phase space constraints imposed by the unidirectional confinement of the solid. Based on the model, we predicted that the Debye scale would be at a particular frequency. The quantitative prediction was reappeared and validated by MD simulations

Invited Talks / Wednesday, 12 October 2022, 15h30

Dynamics of amyloid fibers and their hydration water as studied by neutron scattering and molecular dynamics simulations

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— N/A —

Contributed Talks / Wednesday, 12 October 2022, 16h00

Confinement due to crowding in biological cells

Judith Peters

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The interior of biological cells corresponds to an environment, which is highly crowded. For instance, the total concentration of protein and RNA inside *Escherichia coli* is in the range 300–400 mg/mL [1]. Crowding can induce the confinement of molecular motions due to the restrictions in space. It is established that diffusion rates [2], but also activities, dynamics, aggregation or protein folding are influenced by crowding [1]. Here, we want to present new insights into the role of crowding and confinement with respect to extreme external conditions as low or high temperature, high hydrostatic pressure or salinity. Crowding influences the environmental viscosity, which in term can provoke confinement on molecular dynamics. Both together have a protective effect against stress induced by extreme conditions. One possibility for such studies is to investigate cells, which are used to live under extreme conditions, in their intact form and after cell lysis to extract the limiting effects on the molecular dynamics of the proteome and of water molecules [3]. Other opportunities are the studies of proteins under (self-) crowding conditions [4].

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Contributed Talks / Wednesday, 12 October 2022, 16h20

Factors governing ferroelectric ordering of water molecules confined in beryl

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Beryl crystals contain structural voids which may be partly occupied by single molecules of water. Due to the local symmetry of the atoms around the voids, the molecules experience sets of potential minima with respect to their angular orientations. The molecules remain fairly independent of the neutral crystal lattice, and they are mutually separated by several Å. Thus, they cannot interconnect by hydrogen bonds, and the dipole-dipole interaction is dominant. In partly hydrated beryl, the water molecules tend to order directionally on cooling. In fact, dielectric spectroscopy has revealed a ferroelectric-like soft phonon in the far-infrared region. However, no ferroelectric ordering appeared, the soft-phonon frequency leveling off below ~10 K. This was explained by quantum fluctuations occurring at low temperatures.

In order to gain a deeper insight into the ordering mechanisms, we conducted a theoretical study by mean-field approximation and Monte Carlo simulations. These have shown that in an ideal ground state, the dipoles are aligned ferroelectrically in the ab planes and antiferroelectrically in the c direction. This order is suppressed by quantum tunneling, as well as by the disorder in the hydration (empty voids).

Using NMR spectroscopy, we studied the molecules' positional geometry and their dynamical behavior. Up to now, it was assumed that in equilibrium, the H-H lines are parallel to the c crystal axis. In contrast, the measured NMR spectra clearly indicate that the H–H lines deviate from the c axis by ~18°. Most probably, the molecules form O–H-O hydrogen bonds with an oxygen atoms near the void. We propose that the O atoms stay in place while the H atoms perform twofold movements: (i) occasional jumps among the 12 possible binding O sites in the void, and (ii) oscillations around the O-H-O bonds. The frequency of the oscillations, as evaluated from our thermodynamic analysis, agrees well with an earlier published theoretical model.

Contributed Talks *(via videoconference)* / Wednesday, 12 October 2022, 16h40

Interplay Between Local Structure and Nuclear Dynamics in Tungstic Acid: a Neutron Scattering Study

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We provide an exhaustive characterization of structural properties and nuclear dynamics in tungstic acid ($\mathrm{WO3{\cdot}H2O}$). To this end, we employ Neutron and X-ray Diffraction (ND and XRD) combined with Inelastic Neutron Scattering (INS) and Neutron Compton Scattering (NCS) experiments, and corroborate the analysis with extensive ab initio modelling. The first step in our analysis is the elucidation of the crystal structure based on the refinement of low-temperature powder ND data, extending the knowledge gained from XRD analysis of a mineral specimen of tungstite. These results are confronted with low-temperature INS experiments and zero-temperature phonon calculations. The analysis reveals an inconsistency in the definition of the structure of confined water with respect to crystallographic data, also showing a concomitant fail of the phonon calculations due to a strongly anharmonic confining potential. Extending the computational route toward ab initio MD (AIMD) simulations allows us to probe different structural configurations and provides an improved description of the vibrational dynamics as compared to high-resolution INS experiments, nevertheless, requiring the use of effective classical temperatures. The analysis of both INS and the NCS data reveals a remarkable similarity to the nuclear dynamics earlier reported for water confined in Single-Wall Carbon Nanotubes (SWNT), which has been qualitatively described as a new phase of ice. Our analysis reveals a strong two-dimensional hydrogen-bonding network, similar to the shell model for water in SWNT. The reported NCS data show narrowing of the hydrogen momentum distribution with respect to the reference ab initio calculations, indicating a great deal of conformational freedom due to spatial delocalisation of protons in the ground state of the system, a clear signature of the quantum character of the nuclei.

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Contributed Talks / Wednesday, 12 October 2022, 17h30

Spectroscopy of C$_{60}$ Endofullerenes

George Bacanu[1] ; Jyrki Rantaharju[1] ; Gabriela Hoffman[1] ; Mohamed Aouane[2] ; Tanzeeha Jafari[3] ; Mark Walkey[1] ; Sally Bloodworth[1] ; Anna Shugai[3] ; Layara Abiko[4] ; Urmas Nagel[3] ; Jeff Armstrong[5] ; Monica Jiménez-Ruiz[2] ; Stephan Grzesiek[4] ; Stéphane Rols[2] ; Toomas Rõõm[3] ; Richard Whitby[1] ; Malcolm Levitt[1]

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Endofullerenes are supramolecular complexes where one small (endohedral) atom/molecule is completely confined within a bigger, fullerene, molecule which acts as an enclosing cage.[1] Endofullerenes offer an ideal "particle in a box" nano-laboratory to observe quantum mechanical phenomena.

The noble gas endofullerenes He@C$_{60}$ and Ne@C$_{60}$ have been investigated using INS (Inelastic Neutron Scattering) and THz (far-Infra Red) spectroscopy. [2] Surprisingly, He@C$_{60}$ is observed to absorb THz light and scatter neutrons, which translationally excite the Helium atom. The atomic translational quantization arising due to confinement is probed using these techniques. Simulating the experimental results delivers the confining interaction potential between the noble gas atom and the confining C$_{60}$ fullerene cage; providing valuable non-covalent interaction parameters, which serve as benchmark for quantum chemistry calculations.
An unexpected NMR (Nuclear Magnetic Resonance) interaction, J-coupling, between ^{3}He and ^{13}C in the C$_{60}$ cage was observed due to confinement, in the ^{3}He@C$_{60}$ endofullerene.[3] This is attributed to a scalar $^{0}\mathrm{J}_{HeC}$-coupling, where the "zero" represents the number of chemical bonds between Helium and Carbon. Indication of similar ^{0}J-couplings between ^{1}H and ^{13}C are also observed in endofullerenes containing endohedral hydrogen.
When the C$_{60}$ molecule is filled with an endohedral species, the C$_{60}$ ^{13}C NMR resonance is shifted downfield, relative to C$_{60}$, depending on the species (endohedral shift). The magnitude of the shift scales proportionally with the size of the endohedral species. The endohedral shift appears to reflect the "pressure" a single atom/molecule exerts on its container, in this case the C$_{60}$ molecule. Solution and solid state NMR measurements together with an interpretation of the endohedral shifts will be presented.

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Contributed Talks / Wednesday, 12 October 2022, 17h50

Dynamics in Confinement: a study of $CH_4@C_{60}$

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Endofullerenes are substances in which small molecules or atoms are encapsulated in highly symmetrical cages of carbon atoms. Each encapsulated atom or molecule behaves as a textbook ex-ample of a quantized particle-in-a-box. The newest and largest member of the endofullerene fami-ly tree, namely $CH_4@C_{60}$, is the first organic molecule trapped inside the cage and the main interest of this abstract. The use of various spectrometers at ILL, namely PANTHER, IN5 and IN1-LAGRANGE, have allowed us to probe a large energy window up from 1 to 100 meV. The goal from these experiments was to probe the rotational and translational states of the confined CH_4 molecule, and observe the coupling between said states due to the confinement. A novel result that we have observed in this endofullerene, was the effect of the I_h symmetry of the C_{60} on the rotational states of the CH_4 using inelastic neutron scattering, an effect that was absent in previous endofullerene studies. We have also performed QENS measurements, using PANTHER, that have allowed us to observe slight differences in the rotational dynamics of both the C_{60} and CH_4, confirming the stronger guest-host coupling that we observed in our INS measurements.

Contributed Talks / Wednesday, 12 October 2022, 18h10

Does Confinement Enable Methane Hydrate Growth at Low Pressures? Insights from Molecular Dynamics Simulations

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Natural methane hydrates are estimated to be the largest source of unexploited hydrocarbon fuel. The ideal conditions for methane hydrate formation are low temperatures and high pressures. On the other hand, recent experimental studies suggest that porous materials, thanks to their confinement effects, can enable methane hydrate formation at milder conditions, although there has not been a consensus on this. A number of studies have investigated methane hydrate growth in confinement by employing molecular simulations; however, these were carried out at either very high pressures or very low temperatures. Therefore, the effects of confinement on methane hydrate growth at milder conditions have not yet been elaborated by molecular simulations. In order to address this, we carried out a systematic study by performing molecular dynamics (MD) simulations of methane water systems. Using a direct phase coexistence approach, microsecond-scale MD simulations in the isobaric–isothermal (NPT) ensemble were performed in order to study the behavior of methane hydrates in the bulk and in confined nanospaces of hydroxylated silica pores. We validated the combination of the TIP4P/ice water and TraPPE-UA methane models in order to correctly predict the behavior of methane hydrates in accordance to their phase equilibria. We also demonstrated that the dispersion corrections applied to short-range interactions lead to artificially induced hydrate growth. We observed that in the confinement of a hydroxylated silica pore, a convex-shaped methane nanobuble forms, and methane hydrate growth primarily takes place in the center of the pore rather than the surfaces where a thin water layer exists. Most importantly, our study showed that in the nanopores methane hydrate growth can indeed take place at pressures which would be too low for the growth of methane hydrates in the bulk.

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Talks on

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Talks dedicated to Bernhard Frick / Thursday, 13 October 2022, 09h00

Physics with Bernhard Frick - a reminiscence on exciting times

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Talks dedicated to Bernhard Frick / Thursday, 13 October 2022, 09h30

Polymers, neutrons and much more: three decades together with Bernhard

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Begins are usually difficult and most of the times the first experience is crucial in determining the long-term development of an incursion in a new field. Our team had the great opportunity of meeting Bernhard Frick as local contact in our first neutron scattering experiments in the late 80's. Since then, the collaboration with Bernhard has resulted in a plethora of exciting investigations mainly centered on polymer dynamics, but covering diverse aspects that include tunneling and rotations of methyl groups, segmental motions, local processes involved in secondary relaxations, etc. With our own ageing, the complexity of the systems investigated has also increased along these years. The joint investigations cover from homopolymers to polymer blends and, more recently, novel materials based on single-chain nanoparticles. This talk will be a journey along the main achievements of our (still living) collaboration with Bernhard.

Talks dedicated to Bernhard Frick / Thursday, 13 October 2022, 10h30

Confined fluids properties by quasi-elastic neutron scattering with Bernhard Frick

Christiane Alba-Simionesco

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In the mid 90's, Neutron Scattering contributed greatly to a better understanding of the phenomena related to viscous slowing down and Glass Transition in many different systems, polymers, molecular liquids, spin glasses, proteins. Quasi-elastic scattering has been instrumental in providing a description of the various relaxation processes involved and in testing theoretical approaches. The heterogeneous character of the structural relaxation was then associated with a possible dynamic correlation length increasing when approaching the glass transition; the interest of imposing a length via a nanoscopic confinement appeared then particularly relevant. The phase transitions of confined systems were already widely studied by many methods but the whole was far from converging both experimentally and by numerical simulations. Then Bernhard Frick, Reiner Zorn and Herma Buttner proposed to organize the first International Workshop on Dynamics in Confinement in January 2000. At that time, I was lucky enough to discover quasielastic neutron scattering, (in particular backscattering) with my friend and fantastic colleague Bernhard. He introduced me to the methods and we worked together on several approaches starting with liquids under high pressure to properties deep into the glassy state. Bernhard introduced several students and colleagues to neutron scattering and to what constitutes the work of an experimentalist, thus contributing to the training of a new generation of scientists. Their work will be presented focusing on the impact of confinement on the behavior of fluids compared to standard conditions.

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Talks dedicated to Bernhard Frick / Thursday, 13 October 2022, 11h00

Views on confined fluids resulting from a 20-year collaboration with Bernhard Frick

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The physics of nanoconfined fluids is complex and must be approached from several complementary angles. Therefore, effective collaboration is undoubtedly the keystone of a successful study in this field. Over the past 20 years, I have benefitted from Bernhard's invaluable expertise in both neutron scattering methods and confinement effects. Besides being a unique personal experience, sharing his path in science has led to significant scientific realizations. This talk aims to summarize the scientific progress achieved through our joint work on a variety of confined systems, encompassing glassforming fluids, liquid-crystals, discotics, binary mixtures, and water.

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Talks dedicated to Bernhard Frick / Thursday, 13 October 2022, 11h30

Quasielastic neutron scattering experiments on confined glass-forming liquids

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The explanation of the dynamics of glass-forming materials is a still unsolved problem in solid state theory. My collaboration with Bernhard Frick started in 1990 when quasielastic neutron scattering (QENS) was beginning to be employed on such systems. At that time, experiments mostly aimed at scrutinizing Mode Coupling Theory (MCT) and were done on bulk systems because this theory does not explicitly include a length scale. After first successes, the limitations of MCT became clearer over the years and alternative concepts were sought. One of these is that of Cooperatively Rearranging Regions (CRR) of the size of some nanometers. An obvious way to test the importance of CRRs is to confine the sample to that size and look for changes in the dynamics. By the mid-90s materials became available with suited pore sizes, Controlled Porous Glasses (CPG). We immediately started the QENS experiments on simple liquids confined in CPGs, later extending them to polymers and liquid crystals in a cooperation with Andreas Schönhals who provided additional methods allowing an enormous increase in dynamical range. The experiments showed that the basic predictions of a CRR model are fulfilled but surface effects modify the dynamics significantly. To reduce these, experiments were done in 'soft confinement', i.e., microemulsions which confine the glass-forming liquid in droplets. These experiments gave a clearer support to CRR ideas but also turned out to be much more complicated in their interpretation because the 'matrix' material is not immobile.

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Poster Abstracts

Poster session / Tuesday, 11 October 2022, 17h00

Methanol diffusion in H-ZSM-5 zeolite catalysts as a function of loading and Si/Al ratio

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Establishing sustainable catalysts and processes to achieve renewable energy sources and reduce environmental impact is a pressing matter for the development of our society. The monetisation of natural gas and the high demand for light olefins has resulted in the zeolite catalysed methanol-to-hydrocarbons (MTH) process becoming of high industrial interest. The mobility of methanol molecules to the active site can be affected by factors including Si/Al ratio and methanol loading, having a significant impact on catalyst activity/selectivity. QENS is a powerful experimental tool to probe the nanoscale mobility of methanol in zeolite catalysts, especially in combination with molecular dynamics (MD) simulations. Previous studies of methanol dynamics in ZSM-5 at Si/Al = 36 and 135, showed that upon increasing temperature, the methanol behaviour changes from rotational to translational motion. The translational diffusion is characterised by jump diffusion within spheres of radii close to that of a ZSM-5 channel (similarly observed in a sample with Si/Al = 25). Methanol diffusion in H-ZSM-5 was studied using classical MD at 373 - 423 K, using loadings of 3 and 5 molecules per unit cell, in frameworks with Si/Al = 15, 47, 95, 191 and a siliceous system. While the lower loading exhibits higher diffusivity, self-diffusivities increase at both loadings between Si/Al = 15 and 95, after which they are independent of composition. The trend in diffusivity with Si/Al ratio is explained in terms of methanol-acid site interactions, while the trend with loading is explained in terms of methanol-methanol interactions and the resulting methanol structure in the catalyst pores. MD simulations of the systems have been used to reproduce QENS observables (EISF and QENS broadenings) to ensuring the validity of the employed MD model.

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Poster session / Tuesday, 11 October 2022, 17h00

Periodic Mesoporous Organosilicas as Model Host-Compounds to Study Water in Nanoconfinement

Stella Gries[1] ; Sophia-Marie Schwake[2] ; Philip Lenz[2] ; Mark Busch[1] ; Markus Appel[3] ; Denis Morineau[4] ; Michael Froeba[2] ; Patrick Huber[1]

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Periodic mesoporous organosilicas (PMOs) have attracted attention in many research fields, for example catalysis, energy storage or light harvesting.
PMO materials are obtained by a sol-gel process from organo-bridged alkoxysilanes ([(R'O)3-Si-R-Si(OR')3]; R: incorporated organic-bridging group), in presence of structure-directing agents (SDAs). This leads to well-ordered inorganic-organic hybrid systems with cylindrical nanopores, whose diameter (usually in the range from approx. 3 to 10 nm) can be easily adjusted by varying the SDAs. If suitable precursors are used (rigid, π electron-rich) crystal-like pore walls are obtained, in which an alternating sequence of inorganic and organic domains parallel to the pore axis are present. These features make PMOs ideal candidates for studying the behavior of water and other liquids in a nanoconfined environment.
Here, we study the behavior of water in these systems using quasi-elastic neutron scattering (QENS), water vapor physisorption, and differential scanning calorimetry (DSC). In particular, the fluorinated systems are of high interest, due to their very hydrophobic nature and because of other well-known anomalous properties of fluorine.

This work was conducted in the frame of the DFG-ANR collaborative project ("Project NanoLiquids") as well as the LFF-project ("water in confinement", LFF-FV68), which is acknowledged. It is a pleasure to acknowledge the Institute Laue Langevin for the allocation of neutron beam time.

Poster session / Tuesday, 11 October 2022, 17h00

Computer simulations of capillarity-driven water flow in nanoporous silica

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Capillarity-driven flows in pores a few nanometers in diameter play an important role in many natural and technological processes, for example in clay swelling, frost heave, catalysis and transport across artificial nanostructures, bio-membranes and tissues [1]. Here we present molecular dynamics simulations modelling the capillary flow of water into oriented silica nano-pores (MCM-41) of around 3 nm diameter pore size. By providing implementations of water-water [2], water-silica [3] and silica-silica [4] forcefields we are able to simulate the spontaneous imbibition dynamics of water into the silica pores. In this work we show that during imbibition in longitudinal and radial pore direction anisotropic strains can be observed that can be classified as two distinct types of strain. At the start and the end of the imbibition process the observed strains are almost instantaneous while during the imbibition process there are continuous changes of strain that scale with the imbibition progress. Overall the results of the simulations should lead to better understanding of capillary-driven flows in nanoporous material and the corresponding imbibition-induced strains of the host material on a single-pore scale.

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Poster session / Tuesday, 11 October 2022, 17h00

Impact of brush morphology on glass transition and glassy state properties of polymer thin films

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Polymer thin films with enhanced stability are highly desired for applications ranging from antifouling coatings for biomedical devices to organic optoelectronics. Depending on the grafting density (σ_p) of a polymer brush, end-grafted chains can adopt a stable arrangement, leading to enhanced thermal stability (i.e., increase in glass transition temperature, or T_g) regardless of polymer-substrate interactions. Confinement effects are expected to make such changes more drastic. Here, we systematically investigate the role of chain packing and confinement on overall film properties using a polymer brush as a model. We employ a synthetic protocol to form ultradense polystyrene (PS) brushes with a grafting density approaching the theoretical maximum limit of $\sigma_{p,max}$ = 1.45 nm^{-2}. We observe that a 5 nm PS brush (σ_p = 1.23 nm^{-2}) exhibits a T_g that is ~75 K greater than a spin-coated film of similar thickness. In addition to studies on glass transition, we are exploring the impact of polymer brush morphology on glassy state properties, specifically physical aging and fragility, in thin films. Complementary techniques for these studies include ellipsometry and fast-scanning calorimetry. Ultimately, we aim to elucidate the complex relationship between confinement and chain packing to design highly stable polymer thin films.

Poster session / Tuesday, 11 October 2022, 17h00

Confinement effects induced by pore surface roughness on Knudsen diffusion in amorphous mesoporous materials: An experimental study

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The roughness of the internal surface of porous media is a form of static geometrical heterogeneity that influences the molecular trajectories of gas molecules moving through them. The perturbations along the pore walls reduce the accessibility of the surface area and cause temporary trapping effects. The surface roughness of the pore walls is responsible for non-negligible confinement effects in amorphous mesoporous materials (2-50 nm pore diameter), such as those used for catalysis and separation processes [1], where Knudsen diffusion is often the limiting transport mechanism in mesopores. In Knudsen diffusion, the interactions between the gas molecules and the pore walls are significant.

The investigation of the effect of surface roughness of porous media on Knudsen diffusion was conducted by Coppens and co-workers [2] and Zschiegner et al. [3] using analytical calculations and computer simulations. In their work, single pore models of fractally rough pores are used to model the pore geometry. A significant decrease in the Knudsen diffusivity has been predicted with increased surface roughness. For the experimental validation of these results, an Ultra-High Vacuum Diffusion Setup was built as a scale-up of the pore [4] . Such a setup uses ultra-high vacuum conditions with the same Knudsen number (ratio of mean free path to local channel diameter) as in the mesopore and a 3D-printed channel. The channel contains random Koch fractal segments to create the internal channel surface, which simulates the fractal surface roughness of the mesopore walls.

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Poster session / Tuesday, 11 October 2022, 17h00

Protein short-time diffusion in a naturally crowded environment

Tilo Seydel; Marco Grimaldo; Hender Lopez; Christian Beck; Felix Roosen-Runge; Jean-Louis Barrat; Martin Oettel; Frank Schreiber

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Knowledge of the protein tracer diffusion constitutes a key element to describe intracellular transport, which can be modeled by the self-diffusion in colloid systems. However, it is necessary to test the underlying assumption that neither the protein shape and size nor the polydisperse nature of the cytosol matter. We present a combined experimental and simulation study of the protein tracer diffusion in deuterated E.coli cellular lysate. Quasi-elastic neutron scattering accesses the short-time diffusion of immunoglubulin (IgG) in this lysate. Varying the mixing ratio and volume fraction of IgG and lysate, we observe that this diffusion only depends on the total volume fraction of macromolecules. Stokesian dynamics simulations confirm that when the tracer size agrees with the average size of the polydisperse lysate, these proteins are indeed slowed down similar to a monodisperse solution of same volume fraction. In contrast, larger/smaller proteins diffuse slower/faster, respectively. IgG being close to this average size, we obtain a consistent picture on the diffusion from simulations and experiments. Ongoing investigations with different tracer proteins in lysate as well as binary mixtures of proteins support this colloid picture of the self-diffusion even in such complex polydisperse cell-like environments, which is promising for a future quantitative understanding of reaction pathways in biology.

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Acknowledgement:
This project was funded by jointly by the DFG and ANR (ANR-16-CE92-0009).

Poster session / Tuesday, 11 October 2022, 17h00

Using polarisation analysis to compare the dynamics of protonated and per-deuterated samples of proteins.

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Neutron scattering data collected from biological systems are mostly analysed with classical approaches; however, it has already been proven for instance that purely quantum-based effects such as tunnel effects can explain the enhancement of information rates in enzyme catalysis. Our approach is to study both a per-deuterated sample of the green fluorescent protein (dGFP) and a fully protonated sample (pGFP) hydrated in D_2 O, in order to evidence signature of quantum effects thanks to the difference of mass of the two isotopes of hydrogen nuclei combined to supposedly equivalent dynamics. However, it quickly raised more fundamental questions about how careful one has to be when analyzing per-deuterated samples.

We performed QENS experiments on the TOF spectrometer IN5 at ILL. We describe the subdiffusive motion of hydrogen atoms in the protein with fractional Brownian dynamics, using a Mittag-Leffler function as relaxation function. It yields a 3-parameter model for dGFP dynamics that catches the importance of the dynamics of water through a heterogeneity parameter (α), the impact of water within the time window with the relaxation time parameter (τ) and the impact of coherent scattering from both water and the protein through the shape of the Elastic Coherent Scattering Factor obtained with the pseudo-EISF parameter (EISF). This corroborates with static studies combined with polarized neutrons carried out on the diffuse diffractometer D7 at ILL. Therefore, in order to correctly compare the dynamics of deuterium to the dynamics of hydrogen it is paramount to access only the incoherent contribution of scattering for our dynamic studies using QENS combined to polarization analysis.

Polarization analysis applied to QENS at 310K and 220K are planned for October on LET spectrometer at ISIS. To our knowledge this is the first time that this type of studies is applied to biological macromolecules, although the interest for polarized neutrons has already emerged.

Poster session / Tuesday, 11 October 2022, 17h00

Model lignin monomer dynamics in zeolite catalysts with varying structures and compositions

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Reducing our dependence on crude oil for producing fuels and commodity chemicals is a major challenge of our time. Lignin is an abundant component of lignocellulosic biomass and has significant potential as a renewable feedstock. Zeolite catalysts will be of great importance for lignin upgrading, not least due to their commercial use in the petrochemical industry, where mixed feeds of biomass and crude oil have already been employed. Probing the fundamental behaviour of model lignin monomers, such as the cresol isomers, within microporous zeolite frameworks is crucial for designing and optimizing the catalytic conversion of lignin into products such as gasoline and other precursors for drugs, dyes and polymers.
To probe the rotational and translational diffusion mechanisms of cresols loaded into zeolites, quasielastic neutron scattering (QENS) was applied.
Initially, the diffusion of bulk liquid cresol from 340-390 K was probed, to aid the parameterization of molecular dynamics (MD) simulations. The linear para-isomer exhibited faster rates of both isotropic rotation and translational jump diffusion, in comparison to meta-cresol. Modelled translational self-diffusion coefficients indicated the same trend.
Upon dosing cresols into zeolites, models of isotropic rotation fit closely to the experimental elastic incoherent scattering function (EISF). A greater population of mobile cresol was observed in the larger pores of zeolite HY (7.4 Å in diameter) compared to the pores of HBEA (6.7 Å in diameter).
Inelastic neutron scattering (INS) has also been employed to probe the zeolite acid site to cresol interaction strengths by analysing changes in the vibrational frequencies of the cresol molecules. The diminishing of peaks relating to the hydroxyl bending of the cresol when inside the zeolite indicates its adsorption to acid sites, which is also essential for catalysis.

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Dynamics and conductivity of nanoconfined amino acid based ionic liquid crystals: Influence of the side chain length

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Ionic Liquid Crystals (ILCs) are emerging class of materials that combine the properties of liquid crystals with ionic conduction similar to ionic liquids. It's known that liquid crystals exhibit intriguing properties when confined, and are of importance from both fundamental and technological perspectives. Here, we study the molecular dynamics and electrical conductivity of a homologous series of Dopamine (DOPA) based ILCs, ILCn (n = 12,14,16) confined in self-ordered nanoporous alumina oxide membrane of 180 nm pore size using Broadband Dielectric Spectroscopy (BDS). We aim to understand how the alkyl chain length and confinement influence the dynamics in this system.
In bulk, for all ILCs, we observe two relaxation modes in the crystalline phase, the □ and α1 relaxation respectively, and one relaxation mode in the columnar phase, the α2 relaxation, but for ILC16, where two relaxation modes (α2 and α3) are detected in the columnar phase.
For the confined case, all relaxation processes slowdown compared to the bulk. For ILC16, the α1 relaxation is completely suppressed. For all ILCs, the absolute values of DC conductivity are reduced by three orders of magnitude. We discuss in detail the possible molecular origin of the relaxation processes and the charge transport in this system.

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Anisotropy of water dynamics confined in model silica material

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The study of aqueous solution transport in nanoporous media such as clays, mineral and biomineral phases, cement, glass alteration layer …, is of interest in the fields of construction, environment, geochemistry, effluent treatment, catalysis, energy storage, and nuclear wastes. Indeed, the strong interactions between water molecules and pore surfaces in these restricted nanomedia, modify the water structure and slow down its dynamics from nanoscale to macro-scale. Today, tortuosity, large pore size distribution and pore orientation make it difficult to link between these various scales. To reach this goal, highly oriented nanopores have to be used.

In this study, for the first time, we have used silica model systems made of highly oriented mesopores (4.8 nm) having a micrometric length [1] in order to characterize the water dynamics anisotropy at a picosecond timescale using Quasi-Elastic Neutron Scattering (IN5 time-of-flight spectrometer at ILL). The scattering intensity was collected in 2 orientations to obtain the mean dynamics of water molecules in both, parallel and perpendicular orientations. The sum over Q spectra show a slight broadening when rotating the sample from 45 to 135°. The data were fitted using a diffusive model with two translational diffusion coefficients, perpendicular and parallel, as fitting parameters [2]. The results show that the water molecules are slower in the axial pore direction than in the direction perpendicular to the surface (D =0.61$10^{-9}$ m^2/s *vs. D =0.35*10^{-9} m^2/s). This finding shows that the confinement promotes the radial water dynamics, i.e. perpendicular, rather than the axial one.

These model systems open new perspectives to study the fluids dynamics at various timescales and to extend the solution transport in these model systems to the solution transport in nanoporous materials.

[1] G. Kickelbick, *Small* **1**, 168-170 (2005)

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