

## CPP 16: Nuclear Magnetic Resonance: Frontiers and Applications

Time: Tuesday 13:45–16:15

Location: H48

CPP 16.1 Tue 13:45 H48

**Probing the Assembly and Dynamics of Graphene-Inspired Molecular Wires by Solid-State NMR Spectroscopy** — ●MICHAEL RYAN HANSEN, ROBERT GRAF, DANIEL SEBASTIANI, and HANS-WOLFGANG SPIESS — Max Planck Institute for Polymer Research

Molecular wires based on polycyclic aromatic hydrocarbons (PAHs) are a promising class of materials for future applications in nano-scale electronic devices. Critical for the performance of such wires are their molecular assembly, which on the NMR length and time scales translates into the local packing arrangement, molecular dynamics, and pitch angle(s) between successive molecules. Here, we show that solid-state NMR in combination with MD and ab-initio calculations can provide unique information with respect to these structural features. To illustrate this we examine two perylene tetracarboxydiimides (PDIs) with different side chains attached and a larger triangular-shaped PAH. Specifically, we measure  $^1\text{H}$  chemical shifts using fast MAS and their spatial connectivities through 2D  $^1\text{H}$ - $^1\text{H}$  DQ-SQ correlation spectra and probe the molecular dynamics via  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear dipolar couplings. To support the experimental findings we have performed CPMD-NMR calculations to reveal the effects of packing on the  $^1\text{H}$  chemical shifts for the PDIs, including an estimate of the line broadening due to local disorder. This provides a series of finger prints for different pitch angles between neighboring molecules, that are closely related to the electronic conduction properties of the supramolecular stacks.

CPP 16.2 Tue 14:00 H48

**NMR studies of benzene mobility in microporous metal-organic framework MOF-5** — ●STEFAN HERTEL<sup>1</sup>, SAEED AMIRJALAYER<sup>2</sup>, MARKUS WEHRING<sup>1</sup>, ROCHUS SCHMID<sup>2</sup>, and FRANK STALLMACH<sup>1</sup> — <sup>1</sup>Universität Leipzig, Fakultät für Physik und Geowissenschaften, Deutschland — <sup>2</sup>Ruhr-Universität Bochum, Fakultät für Chemie und Biochemie, Deutschland

Microporous metal-organic frameworks (MOF) are crystalline coordination polymers with regular three dimensional pore networks. These pore networks enable adsorption and diffusion of guest molecules. Molecular Dynamics (MD) simulations show that benzene has a liquid-like mobility inside the pores of MOF-5. Nuclear Magnetic Resonance (NMR) methods allow experimental access to guest mobilities inside such pore networks. This report presents the results of pulsed field gradient NMR (PFG NMR) self-diffusion measurements of benzene adsorbed in MOF-5. In these experiments multi-exponential spin echo decays were observed, which are usually caused by different phases of self-diffusion. These different phases of benzene mobility were unexpected for diffusion of molecules inside an isotropic framework and have to originate in the host-guest and guest-guest interaction. By modern diffusion-relaxation correlation spectroscopy (DRCOSY) translational self-diffusion and microscopic relaxation behavior were correlated. Together with magic angle spinning (MAS) NMR spectroscopy these investigations reveal that the faster component of the diffusion coefficients can be assigned to diffusion inside the porous crystal structure of MOF-5.

CPP 16.3 Tue 14:15 H48

**Exploring the limits to spatially resolved NMR** — ACHIM GÄDKE<sup>1,2</sup> and ●NIKOLAUS NESTLE<sup>1,3</sup> — <sup>1</sup>TU Darmstadt, Institute of condensed matter physics, Germany — <sup>2</sup>Present address: Victoria University of Wellington, New Zealand — <sup>3</sup>Present address: BASF SE, GKC/R, Ludwigshafen, Germany

Recent advances in MRI have demonstrated resolutions down to  $1\ \mu\text{m}$ . Magnetic resonance force microscopy has the potential to reach sensitivity for single nuclear spins. Given these numbers, in vivo imaging of single cells or even biomacromolecules may seem possible. However, for in vivo applications, there are fundamental differences in the contrast mechanisms compared to MRI at macroscopic scales as the length scale of molecular self-diffusion exceeds that of the spatial resolution on the NMR time scale. Those effects - which are fundamentally different from the echo attenuation in field gradient NMR - even may lead to general limitations on the spatial resolution achievable in aqueous systems with high water content. In our contribution, we explore those effects on a model system in a high-resolution stray-field imaging

setup. In addition to experimental results, simulations based on the Bloch-Torrey equation will be presented.

CPP 16.4 Tue 14:30 H48

**Polymers under mechanical stress- an NMR investigation** — ●UTE BÖHME<sup>1</sup>, BO XU<sup>2</sup>, JOHANNES LEISEN<sup>2</sup>, HASKELL W. BECKHAM<sup>2</sup>, and ULRICH SCHELER<sup>1</sup> — <sup>1</sup>Leibniz Institute of Polymer Research Dresden — <sup>2</sup>Georgia Institute of Technology, Atlanta, Georgia

Low-field NMR using permanent magnets in Halbach arrangements permit NMR investigation without the limits present in high-field NMR. The lower field in conjunction with confined stray field permit the application of NMR, in particular relaxation NMR in a stretching apparatus and a rheometer [1,2]. Crystalline and amorphous fraction of semi-crystalline polymers are distinguished by their transverse relaxation times. Upon mechanical load the relaxation times of the amorphous fraction changes as seen in in-situ measurements on polypropylene rods. During the formation of a neck the crystalline fraction becomes more prominent.

[1] S. Kahle et.al., KGK- Kautschuk Gummi Kunststoffe 61 (2008), 92.

[2] G. Mazzanti et.al., J. Am. Oil Chem. Soc. 85 (2008), 405.

CPP 16.5 Tue 14:45 H48

**Segmental Order in Polymer Networks** — ●JENS-UWE SOMMER — Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, 01069 Dresden, Germany

Polymer networks are structurally and topologically disordered soft solids. We consider orientation order of chain segments in polymer networks to relate NMR-experiments with molecular models of polymer networks [1,2]. We derive a general relation between segmental order and local forces acting on a chain under external constraints. Using this result, we consider good solvent conditions and we show that the solvent plays a crucial role for the tensor order parameter. In particular, we show that the tensor order parameter decreases due to excluded volume interactions. Using analytical results and scaling arguments we derive a universal behavior for the order parameter with respect to the equilibrium degree of swelling which can be experimentally verified [2]. In the light of these observations we discuss several microscopic models of network swelling. Using the general relation between local forces on chain bonds and the tensor order parameter we further discuss possible observations on structurally regular networks such as obtained recently in experiments based on force-balance arguments, as well as the role of entanglements.

[1] J.-U. Sommer and K. Saalwächter, European Phys. J. E 18 (2005) 167-182

[2] J.-U. Sommer, Walter Chassé, Juan López Valentín, and Kay Saalwächter, Phys. Rev. E 78, 051803 (2008)

CPP 16.6 Tue 15:00 H48

**Ultrafast velocity-mapping in microfluidic setups** — ●EVA PACIOK, ANDREA AMAR, FEDERICO CASANOVA, and BERNHARD BLÜMICH — ITMC, RWTH Aachen University, Germany

NMR in combination with designated rf coils has proven to be a powerful tool for the investigation of microfluidic setups, e.g. microreactors, micromixers and fluid drops, since it has the potential to reveal both spectroscopic, spatial and velocity information non-invasively. Despite the high spatial resolution NMR offers, the temporal resolution of NMR imaging and velocity mapping experiments in microfluidics has been low so far, because the application of ultrafast NMR velocity mapping methods to microfluidics has failed. These methods are based on multi-echo generation give rise to problems concerning magnetic field inhomogeneities (EPI), rf field inhomogeneities (PGSE-RARE) and velocity/acceleration limitations (EPI and PGSE-RARE).

In this work, we exploit the advantages of the FLIESSEN (Flow Imaging Employing a Single Shot ENcoding) pulse sequence, a new ultrafast RARE-based imaging and velocity mapping method. An adjusted phase encoding strategy and a frequent update of velocity encoding during the multi-echo train makes FLIESSEN highly resilient to field inhomogeneities and velocity/acceleration effects. The performance of this technique is demonstrated on acetone flow in a microstructured phantom. Using FLIESSEN and a surface rf coil, high-

fidelity 2D velocity maps were acquired within seconds.

CPP 16.7 Tue 15:15 H48

**Structural characterization of lyotropic lamellar phases by NMR spectroscopy** — BRUNO MEDRONHO<sup>1,2</sup>, MARIA G. MIGUEL<sup>1</sup>, ULF OLSSON<sup>2</sup>, and •CLAUDIA SCHMIDT<sup>3</sup> — <sup>1</sup>Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal — <sup>2</sup>Physical Chemistry, Center of Chemistry and Chemical Engineering, Lund University, Box 124, 221 00 Lund, Sweden — <sup>3</sup>Department of Chemistry, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany

The lyotropic lamellar  $L_\alpha$  phase is usually considered to consist of stacks of extended parallel layers. However, the application of shear may lead to defect structures consisting of close-packed multilamellar vesicles, also known as onions. Furthermore, it has been suggested that an intermediate structure of multilamellar cylinders occurs during the transformation from layers to vesicles. In this contribution we will give an overview on what kind of structural information can be obtained by deuterium NMR spectroscopy applied in situ under shear. It will be shown how different structures can be distinguished, how onions can be formed and destroyed by the application of shear and how the onion size can be measured on the basis of an NMR line shape analysis.

CPP 16.8 Tue 15:30 H48

**Complete NMR spectral assignment in gibbsite by first-principle calculations** — •ANASTASIA VYALIKH and ULRICH SCHELER — IPF Dresden, Hohe Str. 6, D-01069 Dresden, Germany

The structure of the mineral gibbsite is often considered as a representative of many aluminosilicate clay minerals, and therefore we use it in the present study as a model compound to establish the suitability of the computational method. Here we apply a gradient-corrected DFT method with a plane-wave basis set to assign the crystallographically distinct Al sites in gibbsite and to relate them to the hydroxide network. The experimental observation is based on high-resolution solid-state <sup>27</sup>Al NMR and <sup>1</sup>H CRAMPS (combined rotation and multiple spectroscopy) data. On the basis of DFT calculations, the <sup>1</sup>H CRAMPS signals have been attributed to six symmetry independent hydrogen atoms and ascribed to two distinct types associated with intralayer and interlayer hydrogen bonds. The <sup>27</sup>Al NMR spectrum shows signals for octahedral aluminium only, however with two distinguished signals. The correlation between experimental and theoretical NMR parameters demonstrates that the character of the hydrogen bonds formed by the hydroxide ions is responsible for the structural differentiation of Al sites. That is, the Al-I site (CQ=4.2 MHz) is surrounded by the OH-groups participating in 4 intralayer and 2 interlayer hydrogen bonds, while the Al-II site (CQ=2.4 MHz) is coordinated by the hydroxides, 2 of which point towards the intralayer cavities and 4 OH-bonds are aligned towards the interlayer gallery.

CPP 16.9 Tue 15:45 H48

**Heparin-polynitroxide derivatives: biocompatible polarizing**

**agents for dynamic nuclear polarization (DNP)** — •BJÖRN C. DOLLMANN<sup>1</sup>, ANDREI L. KLESCHYOV<sup>2</sup>, VASILY SEN<sup>3</sup>, VALERY GOLUBEV<sup>3</sup>, LAURA SCHREIBER<sup>4</sup>, KERSTIN MÜNNEMANN<sup>1</sup>, and DARIUSH HINDERBERGER<sup>1</sup> — <sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany — <sup>2</sup>Second Department of Medicine, Johannes Gutenberg University, Mainz, Germany — <sup>3</sup>Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia — <sup>4</sup>Johannes Gutenberg University Medical Center, Mainz, Germany

A versatile and biocompatible class of spin-labeled macromolecules was investigated by electron spin echo-detected (ESE) electron paramagnetic resonance (EPR), continuous-wave (CW) EPR, double electron-electron resonance (DEER) and dynamic nuclear polarization (DNP). These heparin macromolecules could be utilized for *in vivo* magnetic resonance imaging (MRI DNP enhanced) and EPR imaging (EPRI). The distance distributions of the spin labels were measured and compared with the crystallographic structure of heparin. All presented heparin-polynitroxides show reasonably high <sup>1</sup>H DNP enhancement factors up to  $E = -108$ . The heparin-polynitroxides intrinsically feature high dipolar electron spin-electron spin coupling frequencies  $\nu_{dd}$ . Together with the finding that the best <sup>1</sup>H-signal enhancements are found in the low concentration region, this proves the influence of the anisotropic electron spin distribution on DNP in liquids at room temperature.

CPP 16.10 Tue 16:00 H48

**Structure of Phage SPP1 Head-to-Tail Connector Reveals Gating Mechanism for DNA Ejection: an EM and NMR study** — MATTHIEU GALLOPIN<sup>1</sup>, SOPHIE LHUILLIER<sup>2</sup>, BERNARD GILQUIN<sup>1</sup>, SANDRINE BRASILÈS<sup>2</sup>, ELENA ORLOVA<sup>3</sup>, JOËL COUPRIE<sup>1</sup>, PAULO TAVARES<sup>2</sup>, and •SOPHIE ZINN-JUSTIN<sup>1</sup> — <sup>1</sup>Laboratoire de Biologie Structurale et Radiobiologie, iBiTec-S, CEA Saclay, Gif-sur-Yvette, France — <sup>2</sup>Unité de Virologie Moléculaire et Structurale, UMR CNRS 2472, UMR INRA 1157 and IFR 115, Gif-sur-Yvette, France — <sup>3</sup>Department of Crystallography, Birkbeck College, University of London, London, UK

Understanding the principles that govern macromolecular assembly is a current challenge for biochemists, molecular biologists, and structural biologists. Assembly of bacterial virus (bacteriophages) particles is a highly suitable system to investigate the molecular mechanisms that support efficient formation of a complex macromolecular machine and its function. A large number of phages and eukaryotic viruses use a portal system to control genome entry and exit from their capsids. The portal and head completion proteins form the viral head-to-tail connector. The pseudo-atomic structure of the complete closed connector of tailed bacteriophage SPP1 was determined (Lhuillier et al., PNAS 2009). Opening of the connector and DNA ejection from virions was reproduced in vitro by adding the host purified receptor YueB. These achievements recommend SPP1 as an excellent system to investigate the structural organization and dynamics of the viral DNA gatekeeper.