# Symposium Nuclear Magnetic Resonance: from Applications in Condensed-Matter Physics to New Frontiers (SYMR)

jointly organized by
the Chemical and Polymer Physics Division (CPP),
the Biological Physics Division (BP), and
the Radiation and Medical Physics Division (ST)

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## Overview of Invited Talks and Sessions

(lecture room H1)

### Invited Talks

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|---|---|---|---|---|
| SYMR 4.1 | Tue | 9:30–10:00 | H1 | **NMR with a Magnetic Resonance Force Microscope** — •Beat H. Meier, Kai Eberhardt, Joss Rosmarie, Tomka Ivan |
| SYMR 4.2 | Tue | 10:00–10:30 | H1 | **Probing Novel Electronic States in Strongly Correlated Electron Materials Using NMR and NQR** — •Nicholas Curro |
| SYMR 4.3 | Tue | 10:30–11:00 | H1 | **Interplay of Structure and Dynamics in Macromolecular and Supramolecular Systems as Revealed by NMR Spectroscopy** — •Hans Wolfgang Spiess |
| SYMR 4.4 | Tue | 11:15–11:45 | H1 | **Big times for small NMR** — •Bernhard Blümich |
| SYMR 4.5 | Tue | 11:45–12:15 | H1 | **Traveling-Wave MRI** — •Klaas Prüssmann |
| SYMR 4.6 | Tue | 12:15–12:45 | H1 | **Life on the Edge: The Origins and Proliferation of Protein Misfolding Diseases** — •Chistopher M. Dobson |

### Symposium Session and Related Sessions

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|---|---|---|---|---|
| SYMR 1.1–1.3 | Sun | 16:00–18:30 | H3 | **Tutorial: Physics of NMR - Physics with NMR** |
| SYMR 2.1–2.11 | Mon | 16:30–18:00 | Poster C | **Poster: Nuclear Magnetic Resonance - Frontiers and Applications** |
| SYMR 3.1–3.1 | Tue | 8:30– 9:15 | H1 | **PV V** |
| SYMR 4.1–4.6 | Tue | 9:30–12:45 | H1 | **SYMR Nuclear Magnetic Resonance: From Applications in Condensed Matter Physics to New Frontiers** |
| SYMR 5.1–5.10 | Tue | 13:45–16:15 | H48 | **Nuclear Magnetic Resonance: Frontiers and Applications** |
| SYMR 6.1–6.10 | Wed | 9:30–12:45 | H48 | **Polymer Dynamics** |
| SYMR 7.1–7.11 | Wed | 14:00–17:30 | H37 | **Biopolymers and Biomaterials** |
| SYMR 8.1–8.11 | Wed | 14:00–17:30 | H48 | **Glasses and Glass Transition** |
| SYMR 9.1–9.4 | Wed | 14:00–15:20 | H41 | **Ultrasound and MRT** |

## SYMR 1: Tutorial: Physics of NMR - Physics with NMR

Time: Sunday 16:00–18:30 Location: H3

**Tutorial** SYMR 1.1 Sun 16:00 H3

**Spins as Qubits** — •Dieter Suter — Fakultät Physik, TU Dortmund

Processing of digital information has progressed at an enormous speed over the last decades and thus become an indispensable resource. Still, for some computational problems, no efficient algorithms are known for today's computers. For some of these problems, an exponential speedup is possible if the computers operate according to Schrödinger's equation, processing the information by unitary transformations. Nuclear spins were the first physical systems used to implement quantum algorithms; in the meantime, several other systems have become available for quantum information processing, all drawing directly from the techniques that NMR has developed for accurately controlling the dynamics of quantum mechanical systems. We will discuss some demonstration experiments that use magnetic resonance techniques to process quantum information stored in nuclear and electronic spins. Since today's quantum computers are based on a small number of qubits, their computational power is quite limited. To make them more powerful, it will be necessary to increase the number of qubits. Many concepts have been proposed that may eventually unlock this potential, some of them based on electronic and nuclear spins.

Literature: J. Stolze and D. Suter, *Quantum Computing: A Short Course from Theory to Experiment*, Wiley-VCH, Berlin, 2nd edition (2008).

**short session break**

**Tutorial** SYMR 1.2 Sun 17:00 H3

**Kernspin-Gitter-Relaxation: Grundlagen, Beispiele, Instrumentierung** — •Franz Fujara — Institut für Festkörperphysik, TU Darmstadt, Hochschulstraße 6, 64289 Darmstadt

Im ersten Teil des Vortrags werde ich einige grundlegende Begriffe (Ratengleichungen, Wechselwirkungs-Hamiltonian, Übergangswahrscheinlichkeiten) der elementaren semiklassischen Relaxationstheorie einführen, womit dann Phänomene wie die Relaxationsrate, die Spindiffusion, die Spintemperatur und Fragen der (Nicht)ergodizität diskutiert werden können. Sodann möchte ich instruktive Resultate der traditionellen (Festfrequenz-)Relaxometrie vorstellen, die das Potenzial und die Limitierungen des Verfahrens verdeutlichen. Der letzte Teil des Vortrages behandelt moderne Field-Cycling (FC) Relaxometrieverfahren, sowohl elektronische als auch mechanische. Anhand aktueller experimenteller Beispiele soll ausgeführt werden, dass die FC-Relaxometrie als breitbandiges dynamisches Suszeptibilitätsverfahren betrachtet werden kann, welches mit erheblichem Gewinn gemeinsam mit der Messung anderer dynamischer Suszeptibilitäten, z. B. der dielektrischen Relaxation oder der dynamischen Lichtstreuung, eingesetzt werden kann.

**Tutorial** SYMR 1.3 Sun 17:45 H3

**NMR at High Pressures and High Fields** — •Hans Robert Kalbitzer — Institute of Biophysics and Physical Biochemistry, University of Regensburg, D-93040 Regensburg, Germany

The two main methods for biomolecular structure determination are X-ray crystallography and NMR spectroscopy. The major advantage of the former is that virtually no size limit exists for the investigated macromolecules. Yet, only well crystallizeable systems can be analyzed preventing the investigation of for example transient complexes. NMR has the benefit that analysis can be performed in solution under nearly physiological conditions and dynamics can be studied in detail. High pressure NMR has developed in the last decade to a valuable tool for studying biophysical properties of proteins. Static pressure up to 400 MPa is applied to the sample located inside the high-field NMR spectrometer. The pressure is transferred to the sample cell via a pressurizing fluid and can be changed during the experiments. Besides an anisotropic compression of the protein, the most important feature of high pressure NMR spectroscopy is that conformational equilibria can be shifted reversibly, allowing the detection and structural characterization of excited states that are only weakly populated at ambient pressure. Time-dependent non-equilibrium states can be detected by pressure-jump NMR spectroscopy where the pressure is changed repeatedly by approximately 100 MPa in a time scale of 30 ms inside the NMR spectrometer. The pressure response is correlated to NMR parameters by introducing the pressure jumps in a complex pulse sequence (pressure correlation spectroscopy).

## SYMR 2: Poster: Nuclear Magnetic Resonance - Frontiers and Applications

Time: Monday 16:30–18:00 Location: Poster C

SYMR 2.1 Mon 16:30 Poster C

**A novel approach to high-pressure nuclear magnetic resonance in diamond anvil cells** — •Thomas Meissner[1], Swee Kuan Goh[2], Damian Rybicki[1], Benno Meier[1], Grant Williams[3], and Jürgen Haase[1] — [1]Faculty of Physics and Earth Science, University of Leipzig, Germany — [2]Cavendish Laboratory, University of Cambridge, United Kingdom — [3]Industrial Research, Lower Hutt, New Zealand

In addition to variation of temperature and application of external magnetic fields the electronic properties of many materials may be influenced by application of pressure. The highest pressures can be achieved in diamond anvil cells (DAC) but limited sample size and anvil cell geometry hampered their application in nuclear magnetic resonance (NMR) experiments due to a weak signal-to-noise. Recently we succeeded in improving the sensitivity of NMR measurements in DACs significantly by placing the radio-frequency coil containing the sample in the high-pressure region. Here we report on first high-sensitivity measurements at pressures up to 70 kbar.

SYMR 2.2 Mon 16:30 Poster C

**EPR and NMR of Multiferroic $Eu_xBa_{1-x}TiO_3$** — •Nataliya Georgieva[1], Andreas Pöppl[1], Rolf Böttcher[1], Marko Bertmer[1], Jürgen Haase[1], and Alex Sushkov[2] — [1]Faculty of Physics and Earth Sciences, University of Leipzig, Germany — [2]Physics Department, Yale University, New Haven, Connecticut

We are investigating multiferroic $Eu_xBa_{1-x}TiO_3$ with different $Eu^{2+}$ concentrations (x = 1, 0.75, 0.5, 0.25) using Electron Paramagnetic Resonance (EPR) and Nuclear Magnetic Resonance (NMR) spectroscopy. The ceramic samples exhibit different magnetic and electric properties, depending on their $Eu^{2+}$ concentration. The X- and Q-band EPR spectra show almost isotropic exchange-coupled $Eu^{2+}$ signals. Temperature dependent line broadening effects are observed and differ for various $Eu^{2+}$ concentrations. $^{137}Ba$ NMR spectra were recorded using frequency stepped Hahn Echo experiments and preliminary $^{47}Ti/^{49}Ti$ NMR measurements were recorded. The line width of the central $^{137}Ba$ nuclear quadrupole transition shows a striking dependence on the $Eu^{2+}$ concentration.

SYMR 2.3 Mon 16:30 Poster C

**Spatial inhomogeneities in optimally doped and underdoped high-temperature superconducting single crystals of $HgBa_2CuO_{4+d}$, a $^{63}Cu$ and $^{199}Hg$ NMR study** — •Damian Rybicki[1,2], Juergen Haase[1], Marc Lux[1], Martin Greven[3,4], Guichuan Yu[5], and Yuan Li[5] — [1]Faculty of Physics and Earth Sciences, Leipzig University, Linnéstraße 5, 04103 Leipzig, Germany — [2]Department of Solid State Physics, Faculty of Physics and Applied Computer Sciences, AGH-University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland — [3]School of Physics and Astronomy, University of Minnesota, 116 Church Street S. E. Minneapolis, MN, 55455, USA — [4]Stanford Synchrotron Radiation Laboratory, Stanford, CA 94309, USA — [5]Department of Physics, Stanford University, Stanford, CA 94305, USA

Nuclear magnetic resonance is a very important tool to study high-temperature superconducting cuprates (HTSCs). We present results of $^{63}Cu$ and $^{199}Hg$ NMR of $HgBa_2CuO_{4+d}$ single crystals with critical temperatures, $T_c$=97 K and $T_c$=74 K (optimally doped and underdoped, respectively). $HgBa_2CuO_{4+d}$ due to its very simple structure and only one Cu lattice site is a model compound for understanding the properties of HTSCs. Measurements of the central and satellite transition lines have been carried out as a function of temperature (20-300 K) and orientation of the external magnetic field, $B_0$ with respect to crystal axes. From the temperature dependence of the spin shifts, line widths and quadrupole splitting we find a very large spatial variation of the hole density even in these high quality single crystals.

SYMR 2.4 Mon 16:30 Poster C

**Modeling NMR and EPR Parameters in the Metal-Organic Framework Cu3(BTC)2** — •Nina Vankova and Thomas Heine — Jacobs University Bremen, School of Engineering and Science, Bremen, Germany

In the last decade metal-organic frameworks (MOF) have been the subject of intensive research activity due to their tunable porous structure promoting interesting properties and applications. A very powerful tool for characterization of the complex chemical and electronic structure of these nanoporous materials is magnetic resonance spectroscopy. The interpretative and analytical power of the applied NMR and EPR experimental techniques can be significantly enhanced by supplying a reliable theoretical treatment of the underlying spectroscopic parameters.

We report on the application of density functional theory (DFT) for computing the magnetic resonance properties of Cu3(BTC)2(H2O)3 (BTC = benzene 1,3,5-tricarboxylate). The ADF 2008 code with Slater basis sets incorporating relativistic corrections has been used for geometry optimization of the MOF building block. We have performed gas phase calculations modeling both the ground singlet and the excited triple state of the Cu(II) ions from the paddle-wheel unit. The nuclear shielding tensors of C and H forming the BTC linkers, as well as the ESR g- and A-tensors of the Cu(II) ions in the paddle-wheel have been calculated and compared to experimental results from the literature.

SYMR 2.5 Mon 16:30 Poster C

**NMR in pulsed magnetic fields** — •Benno Meier[1], Jürgen Haase[1], Frederik Wolff-Fabris[2], Thomas Herrmannsdörfer[2], and Joachim Wosnitza[2] — [1]University of Leipzig, Institute for Experimental Physics II, Magnetic Resonance of Complex Quantum Solids — [2]Hochfeld-Magnetlabor Dresden (HLD), Forschungszentrum Dresden-Rossendorf (FZD)

The first observation of NMR in the pulsed high magnetic field at the Hochfeldmagnetlabor Dresden (HLD), Forschungszentrum Dresden-Rossendorf (FZD) is reported. The new spectrometer that operates at up to 3.0 GHz is described, as well as its implementation in the pulsed field facility. Free induction decays and spin echo experiments on $^{1}$H and $^{63,65}$Cu in various magnets will be described and discussed in terms of sensitivity and resolution.

SYMR 2.6 Mon 16:30 Poster C

**17O and 63Cu NMR of electron-doped High-Temperature Superconductor Pr1.85Ce0.15CuO4** — •Michael Jurkutat[1], Grant Williams[2], Damian Rybicki[1], and Jürgen Haase[1] — [1]Universität Leipzig, Fakultät für Physik und Geowissenschaften, Postfach 100920, 04009 Leipzig, Germany — [2]The MacDiarmid Institute, Industrial Research, P.O.Box 31310, Lower Hutt 5040, New Zealand

We present results of a nuclear magnetic resonance (NMR) study of c-axis aligned powder samples of the electron-doped high temperature superconducting cuprate Pr1.85Ce0.15CuO4. In particular the effect of partial Ni substitution for Cu on 63Cu NMR is investigated as a function of temperature, crystal orientation and Ni substitution. We find Ni-induced broadening of the spectra and temperature-dependent effects on spin-lattice relaxation indicating spin density oscillations about the Ni site. Furthermore we analyse the temperature and field dependence of 17O NMR spectra showing unexpected resemblances to hole-doped systems.

SYMR 2.7 Mon 16:30 Poster C

**Chain Dynamics of Polymers Confined to Ordered Nanoporous Alumina Membranes** — Cornelius Franz[1], •Salim Ok[2], Fabián Vaca Chávez[1], Martin Steinhart[2,3], and Kay Saalwächter[1] — [1]Institut für Physik, Betty-Heimann-Str.7, 06120 Halle, Germany — [2]Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany — [3]Institut für Chemie, Barbarastr. 7, Universität Osnabrück, 49069 Osnabrück, Germany

Ordered anodic aluminum oxide (AAO) membranes with cylindrical 20-400nm pores are ideal inorganic model components that allow studying polymeric interphases and confinement effects in nanocomposites. Advanced NMR techniques enable characterization of polymer chain dynamics in detail. We report the study of polybutadiene (PB) melts infiltrated into AAO by means of transverse relaxometry (T2) as a qualitative indicator for changes in chain dynamics, and by multiple-quantum NMR for more detailed insights.

PB forms solid nanorods in the nanopores of the AAO. Filling kinetics experiments revealed the conditions under which the pore volume is completely filled and equilibrium is reached. At non-equilibrium stages, we observed strong deviations from the bulk-like entanglement-induced chain ordering, including much increased chain order and an inhomogeneous response, indicating possible layering effects. After the infiltration equilibrium was reached, the behavior was more homogeneous, but still significantly higher local chain order was detected. Moreover, MQ NMR data indicate a shift of Tg. All observed effects became more pronounced upon reduction of the pore diameter.

SYMR 2.8 Mon 16:30 Poster C

**Miniemulsion Polymerization Reactions Observed by Time-Resolved Xe-129 NMRR** — •Mathis Düwel, Nicolas Vogel, Clemens Weiss, Katharina Landfester, Hans W. Spiess und Kerstin Münnemann — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

In the last years, Xe-129 NMR has found many applications in material science and medicine because of two useful properties of Xenon atoms in NMR: their sensitivity to their environment due to their highly polarizable electron cloud, even without the need for covalent bonds, and the ability of being hyperpolarized. Here, Xe-129 NMR is used in the online monitoring of polymerization reactions. The method allows for the online monitoring of polymerization by reporting quantitatively the composition of the reaction mixture by the chemical shift of hyperpolarized Xe. The hyperpolarized gas is brought into contact with the reaction mixture in an NMR tube in a 7 T-NMR spectrometer by the use of hydrophobic hollow-fibre membranes, allowing for the molecular dissolution of the hyperpolarized Xe into the miniemulsion. Repeated Xe-129 NMR measurements show the time-resolved polymerization process. The depolarized Xe is continuously replaced by the gas flow from the hyperpolarizer. Kinetic data for different reaction conditions (e.g., different initiators) has been determined from the chemical shift of the dissolved Xenon, allowing for the comparison with calorimetric data.

SYMR 2.9 Mon 16:30 Poster C

**Transport and high-pressure phase equilibria in mesopores** — •Philipp Zeigermann, Muslim Dvoyashkin, Jörg Kärger, and Rustem Valiullin — Department of Interface Physics, University of Leipzig, Germany

Heterogeneous catalysis in high-pressure environments is a standard process in state-of-the-art industrial chemical synthesis. Micro- and mesoporous materials are widely used as hosts for the catalysts, while educts and products are delivered and removed under high pressure conditions. The supercritical state is here of particular interest because of its superior dynamical properties (low viscosity, no surface tension, high diffusivity).

Despite of its advantages in various applications, high-pressure phase equilibria in mesoporous host materials, and especially their interrelation with transport properties, are still poorly understood. Recently, it was shown that pulsed field gradient nuclear magnetic resonance spectroscopy (PFG NMR) is a particularly suitable tool to probe diffusion properties of sub- and near-critical fluids in mesopores.

A special NMR sample vessel has been constructed which permits to maintain pressures up to 200 bars. In this way it is possible to measure pressure-dependent self-diffusivities of organic compounds solved in supercritical solvents, e.g., in carbon dioxide in the bulk state as well as in the mesopores. Some preliminary results on molecular diffusivities at different conditions will be presented.

SYMR 2.10 Mon 16:30 Poster C

**Field-cycling-NMR: A new magnet design for reduced energy consumption** — •Dirk Plendl, Alexei F. Privalov, and Franz Fujara — Institut für Festkörperphysik, TU Darmstadt, Hochschulstraße 6, 64289 Darmstadt

Field-cycling-NMR is an establiched method for the investigation of field dependent spin phenomena, like relaxation dispersion, polarization transfer, enhanced NQR etc. In contrast to normal NMR, the magnetic field in a field-cycling experiment is switched between several distinct levels within milliseconds. This can only be achieved with specially designed, low inductive magnets.

Today, nearly all FC-spectrometers utilize air core coils made of copper or silver. Producing strong magnetic fields with normal-conducting magnets results in a large energy dissipation (tens of kW) so that the maximum field strength is limited by the amount of heat that can be extracted by the cooling system.

We present a new magnet design for fast field-cycling-NMR which uses a magnet with an iron core for field amplification, thus generating the same field with significantly reduced energy consumption and system complexity [1].

[1] D. Plendl, M. Fujara, A. F. Privalov, F. Fujara, J. Mag. Res. 198 (2009) 183-187

SYMR 2.11 Mon 16:30 Poster C

**A spatially resolved mechanical field cycling relaxometer** — •Michael Ditter[1], Holger Stork[1,3], Achim Gädke[1,4], Franz Fujara[1], Beatrice Schuster[1,2], Christina Trautmann[2], and Reinhard Neuman[2] — [1]Institut für Festkörperphysik, TU Darmstadt, Hochschulstr. 6, Darmstadt — [2]GSI Helmholtzzentrum für Schwerionenforschung, Darmstadt — [3]National des Champs Magnétiques Intenses, r. d. Martyrs, Grenoble — [4]School of Engineering and Computer Science, Victoria University, Kelburn Parade, Wellington

Recently a new method for the spatially resolved characterization of heavy ion irradiated crystals using static field gradient NMR was developed [1]. With this method it is possible to measure one-dimensional spin-lattice relaxation rate profiles with a spatial resolution in the order of 10 $\mu$m. In the meantime the spectrometer has been further improved and the method expanded to conduct frequency and temperature dependent measurements. For field cycling NMR the probe is moved inside the stray field of a superconducting magnet. Due to the strong magnetic field gradient only the nuclei within a thin excited slice are in resonance, allowing spatial resolution. It is possible to utilize fields between 6.3 and 0.008 T. The positioning system is capable of achieving switching times of less than 5 s. The accessible sample temperature ranges from RT to 500 K. The relaxometer will be used for spatially resolved spin-lattice relaxation dispersion experiments of swift heavy ion irradiated ionic crystals.

[1] Stork H, Hamburger A, Gädke A, Fujara F and Schwartz K 2008 J. Phys.: Condens. Matter 20 275236

## SYMR 3: PV V

Time: Tuesday 8:30–9:15 Location: H1

**Plenary Talk** SYMR 3.1 Tue 8:30 H1

**NMR and MRI: Basic Physics for the Sake of Society** — •Richard R. Ernst — Laboratorium für Physikalische Chemie, ETH Zürich, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland

Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI) became indispensable tools in physics, chemistry, biology, and medicine with numerous applications that are highly relevant for enhancing our understanding of nature and for diagnosing diseases. It is narrated how a fundamental physics experiment took all the way into the medical clinical practice and became useful even for exploring psychological phenomena. George E. Pake has once said: ”Magnetic resonance imaging is an irrefutable testimonial to the enormous value of basic research.”

## SYMR 4: SYMR Nuclear Magnetic Resonance: From Applications in Condensed Matter Physics to New Frontiers

Time: Tuesday 9:30–12:45 Location: H1

**Invited Talk** SYMR 4.1 Tue 9:30 H1

**NMR with a Magnetic Resonance Force Microscope** — •Beat H. Meier, Kai Eberhardt, Joss Rosmarie, and Tomka Ivan — Physical Chemistry, ETH Zurich

Magnetic Resonance Force Microscopy (MRFM) is a sensitve method to detect magnetic resonance in small volume elements and has the potential to be used for magnetic resonance imaging (MRI) on the nanoscale. As with MRI, MRFM is not limited to the three spatial dimensions. Spectroscopic dimensions can be added, providing detailed chemical and structural information at the atomic level. The talk will introduce the basic principles of imaging with the microscope and discuss the available spectral information, e.g. from dipolar and quadrupolar interactions and - most demanding but most usefull - from chemical shift.

**Invited Talk** SYMR 4.2 Tue 10:00 H1

**Probing Novel Electronic States in Strongly Correlated Electron Materials Using NMR and NQR** — •Nicholas Curro — Department of Physics, University of California, Davis CA 95616, USA

In the last two decades several new materials have been discovered which exhibit strong electron-electron interactions that lead to novel ground states such as superconductivity, coexisting antiferromagnetism and superconductivity, and ”hidden” order. NMR/NQR are ideal probe of these new states, several of which only emerge under extreme conditions in high magnetic fields, low temperatures and high pressures. By taking advantage of the hyperfine interaction, NMR/NQR can provide detailed information about order parameters and their dynamics throughout the phase diagram of these systems. Furthermore, NMR provides a local spectroscopy of the response of these systems to impurity doping. Several heavy fermion and iron pnictide materials will be discussed.

**Invited Talk** SYMR 4.3 Tue 10:30 H1

**Interplay of Structure and Dynamics in Macromolecular and Supramolecular Systems as Revealed by NMR Spectroscopy** — •Hans Wolfgang Spiess — Max-Planck-Institute for Polymer Research, Mainz, Germany

Traditionally, the determination of structure and the elucidation of dynamics of matter are considered separately. With the advancement of characterization techniques, however, this separation becomes more and more artificial. For instance, advanced solid state NMR spectroscopy provides information on the geometry and the time scale of molecular motions independently. This site selective and specific information is highly valuable, as in soft matter function of complex synthetic as well as natural systems is often achieved by separating regions of order and disorder. Incompatibility of building blocks, e.g., backbone and side groups in macromolecules, or non-covalent interactions, such as hydrogen bonds, ionic forces or pi-pi interactions lead to self organization, in which the different units are spatially separated and may display different dynamics. Solid state NMR techniques combining fast magic angle spinning (MAS) and double quantum (DQ) NMR spectroscopy provide site-specific information about these aspects and their relation to processing and function of the materials, e.g., proton- and photoconductivity.

**15 min. break**

**Invited Talk** SYMR 4.4 Tue 11:15 H1

**Big times for small NMR** — •Bernhard Blümich — RWTH Aachen University, ITMC, Worringerweg 1, D-52056 Aachen, Germany

NMR is most widely known for diagnostic imaging in medicine and molecular analysis in chemistry. The measurement procedure requires magnetic fields and radio-frequency waves. The largest component of an NMR machine is the magnet. While the electronics are shrinking noticeably over the years, the magnets become bigger as higher field strength is realized. Small magnets can be built from permanent magnet material at field strengths common four decades ago. Recent advances in magnet design have led to desktop magnets and miniature magnets that surround the sample in the conventional way and in magnets that accommodate the object in the stray field for relaxation analysis, imaging, and high-resolution spectroscopy. Such magnets are inexpensive and portable. Their availability makes a diversity of studies possible, which are out of question for high-field super-conducting magets. These are high-throughput analysis by parallel operation of many spectrometers, in-line monitoring with long-time use of an NMR machine in one application, NMR analysis at the site of the object, and NMR analysis in dangerous environments. The advances in building small NMR magnets are summarized, and the use of small-scale NMR devices is demonstrated with applications to chemical engineering, medicine, and materials testing.

**Invited Talk** SYMR 4.5 Tue 11:45 H1

**Traveling-Wave MRI** — •Klaas Prüssmann — Insitute for Biomedical Engineering, ETH and University of Zurich, Switzerland

High-field magnets of sufficient inner diameter permit the formation of axially traveling RF waves at NMR frequencies. Such traveling waves can be exploited to excite and detect NMR across large distances. This principle has been demonstrated in a wide-bore 7T magnet with an inner RF screen of 58 cm in diameter, using a patch antenna for RF transmission and reception. Proton NMR spectra of an ethanol solution have been obtained at antenna distances up to more than 3 m. In high-field MRI of humans the traveling-wave approach has the potential to improve RF uniformity, as illustrated by initial in-vivo results. The presentation will also include brief discussions of the reciprocity and efficiency of traveling-wave probes, wave impedance matching, and propagation-related phase delays. Finally it will address the feasibility of using multiple waveguide modes for establishing spatial diversity of RF fields, which underlies the practically important concepts of RF shimming and parallel MRI.

**Invited Talk** SYMR 4.6 Tue 12:15 H1

**Life on the Edge: The Origins and Proliferation of Protein Misfolding Diseases** — •Chistopher M. Dobson — University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK

The failure of proteins to fold, or to remain correctly folded, can give rise to serious cellular malfunctions that frequently lead to disease. One particularly important group of such diseases is associated with the aggregation of misfolded proteins into thread-like structures known as amyloid fibrils, and includes disorders ranging from Alzheimer's disease to late-onset diabetes. The manner in which the normal soluble forms of peptides and proteins can convert into these pathogenic amyloid structures is being uncovered by a wide variety of in vitro experimental studies along with theoretical simulations and bioinformatics studies [Dobson and Chiti, Annu. Rev. Biochem. 75, 333-366 (2006)]. As with folding, these studies are increasingly being linked to events occurring in vivo using a variety of strategies. Of particular interest are experiments designed to link the principles of misfolding and aggregation to the effects of such processes in model organisms such as Drosophila (the fruit fly). This talk will try to draw together some of the ideas that are emerging from recent in our laboratory based on NMR spectroscopy, including evidence for the extremely narrow boundary between normal and aberrant behaviour [Tartaglia et al., Trends Biochem. Soc. 32, 204-206 (2007)], and how this concept sheds light on the origin, current proliferation and potential means of prevention of the associated diseases.

## SYMR 5: Nuclear Magnetic Resonance: Frontiers and Applications

Time: Tuesday 13:45–16:15 Location: H48

SYMR 5.1 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 apromising 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 examinine two perylene tetracarboxydiimides (PDIs) with different side chains attached and a larger triangular-shaped PAH. Specifically, we measure 1H chemical shifts using fast MAS and their spatial connectivities through 2D 1H-1H DQ-SQ correlation spectra and probe the molecular dynamics via 1H-13C heteronuclear dipolar couplings. To support the experimental findings we have performed CPMD-NMR calculations to reveal the effects of packing on the 1H 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.

SYMR 5.2 Tue 14:00 H48

**NMR studies of benzene mobility in microporous metal-organic framework MOF-5** — •Stefan Hertel[1], Saeed Amirjalayer[2], Markus Wehring[1], Rochus Schmid[2], and Frank Stallmach[1] — [1]Universität Leipzig, Fakultät für Physik und Geowissenschaften, Deutschland — [2]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.

SYMR 5.3 Tue 14:15 H48

**Exploring the limits to spatially resolved NMR** — Achim Gädke[1,2] and •Nikolaus Nestle[1,3] — [1]TU Darmstadt, Institute of condensed matter physics, Germany — [2]Present adress: Victoria University of Wellington, New Zealand — [3]Present adress: BASF SE, GKC/R, Ludwigshafen, Germany

Recent advances in MRI have demonstrated resolutions down to 1 $\mu$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 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.

SYMR 5.4 Tue 14:30 H48

**Polymers under mechanical stress- an NMR investigation**

— •Ute Böhme[1], Bo Xu[2], Johannes Leisen[2], Haskell W. Beckham[2], and Ulrich Scheler[1] — [1]Leibniz Institute of Polymer Research Dresden — [2]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.

SYMR 5.5 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 observation 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)

SYMR 5.6 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.

SYMR 5.7 Tue 15:15 H48

**Structural characterization of lyotropic lamellar phases by NMR spectroscopy** — Bruno Medronho[1,2], Maria G. Miguel[1], Ulf Olsson[2], and •Claudia Schmidt[3] — [1]Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal — [2]Physical Chemistry, Center of Chemistry and Chemical Engineering, Lund University, Box 124, 221 00 Lund, Sweden — [3]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.

SYMR 5.8 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 alumino-silicate 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 27Al NMR and 1H CRAMPS (combined rotation and multipulse spectroscopy) data. On the basis of DFT calculations, the 1H 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 27Al 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 particiating 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.

SYMR 5.9 Tue 15:45 H48

**Heparin-polynitroxide derivatives: biocompatible polarizing agents for dynamic nuclear polarization (DNP)** — •Björn C. Dollmann[1], Andrei L. Kleschyov[2], Vasily Sen[3], Valery Golubev[3], Laura Schreiber[4], Kerstin Münnemann[1], and Dariush Hinderberger[1] — [1]Max Planck Institute for Polymer Research, Mainz, Germany — [2]Second Department of Medicine, Johannes Gutenberg University, Mainz, Germany — [3]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia — [4]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 $^1H$ 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 $^1H$-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.

SYMR 5.10 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[1], Sophie Lhuillier[2], Bernard Gilquin[1], Sandrine Brasilès[2], Elena Orlova[3], Joël Couprie[1], Paulo Tavares[2], and •Sophie Zinn-Justin[1] — [1]Laboratoire de Biologie Structurale et Radiobiologie, iBiTec-S, CEA Saclay, Gif-sur-Yvette, France — [2]Unité de Virologie Moléculaire et Structurale, UMR CNRS 2472, UMR INRA 1157 and IFR 115, Gif-sur-Yvette, France — [3]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.

# SYMR 6: Polymer Dynamics

Time: Wednesday 9:30–12:45 Location: H48

**Invited Talk** SYMR 6.1 Wed 9:30 H48

**On the dynamics of polymers in nanocomposites and under confinement** — •Dieter Richter — Jülich Centre for Neutron Science and Institute for Solid State Research, Research Center Jülich, D-52425 Jülich, Germany

Confinement effects in polymer melts may lead to unusual properties. This concerns both, the chain conformation as well as chain dynamics that may be altered due to the surface interactions and changes of topology. In my presentation I will display neutron scattering data, addressing length and time scales from the single monomer to the entanglement network and beyond. These experiments reveal the basic relaxation rates related to monomeric friction, the intermediate scale Rouse dynamics as well as the entanglement controlled dynamics. Polymer nanocomposites have been investigated at various compositions using filler particles smaller and larger than the polymer size. I will discuss the effects of the filler size and concentration on the polymer conformation as well as on the dynamics on the various important length scales. The effect of confinement was also studied on well defined porous alumina samples which were filled with polyethylene oxide (PEO). Thereby the chain dimensions were much larger or smaller than the lateral pore size D. While for the long chains an expanded entanglement network is observed, the confinement seems to have a weaker effect on the short chains. In particular we do not observe any corset effect as proposed by NMR relaxometry.

**Topical Talk** SYMR 6.2 Wed 10:00 H48

**From simple liquids to polymers: Dynamics revealed by field cycling $^1$H NMR** — Axel Herrmann, Azza Abou Elfadl, Roman Meier, Danuta Kruk, Vladimir N. Novikov, and •Ernst A. Rössler — Experimentalphysik II, Universität Bayreuth, 95440 Bayreuth, Germany

We apply field cycling NMR to study the crossover from glassy through Rouse to reptation dynamics in series of different linear polymers (PB, PDMS, PPO, PI) with molecular weight $M$ ranging from the low-$M$ limit (simple liquid) to the high-$M$ limit. Dispersion data of the spin-lattice relaxation time $T_1(\omega)$ are transformed to the susceptibility representation $\chi''(\omega\tau_s) = \omega/T_1$, and using frequency-temperature superposition master curves $\chi''(\omega\tau_s)$ ($\tau_s$:= segmental correlation time) are constructed which reflect spectral contributions from glassy as well as polymer specific dynamics. We are able to cover six decades at $\omega\tau_s < 1$ allowing to monitor in detail the emergence of polymer specific relaxation contributions. Transforming the master curves into the time domain yields the segmental reorientational correlation function which we follow over six decades in amplitude. From this the order parameter as well as bond-vector correlation function are derived. Comparison with theoretical predictions by the tube-reptation model as well as renormalized Rouse theory reveals significant discrepancies whereas good agreement is found with Monte Carlo simulations. We conclude that the crossover to entanglement dynamics appears to be highly protracted. This is confirmed by accompanying measurements of dielectric normal mode spectra.

SYMR 6.3 Wed 10:30 H48

**Bond-correlation functions determined in MD simulations of entangled polymer melts** — •Hendrik Meyer — Institut Charles Sadron, CNRS UPR22, 67034 Strasbourg, France

The polymer dynamics of entangled bead-spring chains is analysed based on large scale molecular dynamics simulations. As found in previous studies, the predicted power law regimes of mean-square displacements attributed to Rouse-motion in the tube (cross-over from $t^{0.5}$ to $t^{0.25}$) are only well developed beyond $Z \geq 10$ entanglements per chain. Similar power law regimes are present for bond time-autocorrelation functions ($P_1 \propto t^{-0.5}$ and $t^{-0.25}$). NMR experiments measure a correlation function proportional to the second Legendre polynomial $P_2$ of the bond correlations, which is found to be proportional to the square of $P_1$ only for flexible chains, whereas a slower time decrease is found for chains with a small angular potential. Clear evidence is found that the terminal relaxation time increases stronger than predicted by reptation theory for $Z > 5$. We critically compare this finding with theories of contour length fluctuations, often invoked as the main explanation of this slowing down.

**15 min. break**

SYMR 6.4 Wed 11:00 H48

**The role of the intermolecular magnetic dipole-dipole interaction in low frequency proton NMR in polymer melts.** — •Nail Fatkullin[1], Anvar Gubaidullin[1], Siegfried Stapf[2], and Rainer Kimmich[3] — [1]Kazan State University, Kazan 420008, Tatarstan, Russia — [2]Technische Universität Ilmenau, Dept. Technical Physics II, 98684 Ilmenau, Germany — [3]University of Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany

The different contributions to the dynamic magnetic dipole-dipole correlation function, which is responsible for proton NMR phenomena like the spin-lattice relaxation, the free induction decay, the solid echo, etc.„ are analyzed. For the anisotropic tube-reptation model the relative weight of the intra-molecular contribution in the time dependent magnetic dipole-dipole correlation function should progressively increase with time, corresponding to lower resonance frequency, compared to the intermolecular contribution. For the isotropic n-Renormalized Rouse model the situation is opposite: with increasing of time/decreasing frequency the relative weight of the intermolecular contribution progressively increases and may eventually dominate. Theoretical estimations and analyses of published experimental results, connected with proton NMR spin-lattice relaxations in polymer melts, directly show that at times longer than and at frequencies below the regime, neglecting the intermolecular contributions to proton NMR phenomena in polymer melts, as had been done in the majority of scientific papers, is incorrect.

SYMR 6.5 Wed 11:15 H48

**Multiple quantum NMR observation of reptation and constraint release in polymer melts** — •Fabian Vaca Chavez and Kay Saalwaechter — Institute of Physics, Martin-Luther-University Halle-Wittenberg, Halle (Saale), Germany

In his seminal paper, de Gennes [1] propose a qualitative explanation of the polymer melts dynamics, far above the entanglement molecular weight Me, in terms of a reptative, snake-like motion of the chain through a mesh of fixed topological constraints (entanglements) set by the other chains. Here we show results from 1H multiple quantum (MQ) NMR on a benchtop spectrometer [2], probing the validity of the tube model of polymer dynamics, which combines the reptation concept with the Rouse theory for unentangled chains. This fixed-tube model is insuficient for the quantitative description of actual mechanical data, and ongoing discussions focus on including dynamics of the tube itself, caused by contour-length fluctuations (CLF), arising from chain-end motions of the test chain, or constraint release (CR), arising from matrix chain motions. We also observe characteristic deviations from the tube model predictions up to high molecular weights, and show that CR processes are responsible for modified chain modes faster than actual reptation. Our results extend previous observations by neutron spin-echo spectroscopy (NSE), whose limited dynamic range poses limitations to the study of well-entangled systems.

[1] P. G. de Gennes, J. Chem. Phys., 55, 572 (1971). [2] K. Saalwaechter, Progr. NMR Spectrosc., 51, 1 (2007).

SYMR 6.6 Wed 11:30 H48

**Atomistic molecular dynamics simulations of polybutadiene at graphite: slowing down of orientation relaxations in confinement vs. bulk system** — •Leonid Yelash[1], Peter Virnau[1], Wolfgang Paul[2], and Kurt Binder[1] — [1]Institut für Physik, Johannes-Gutenberg Universität Mainz — [2]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg

A nanoscopic thin polybutadiene film confined between two graphite surfaces is studied using molecular dynamics simulations. Polymer is described with an united atom model incl. Lennard-Jones, bending and torsion interactions[1]. The crystalline surface is modeled by several layers of graphite atoms placed at their crystallographic positions[2]. Our previous study has shown that the confinement affects the statics as well as the dynamics. E.g., gyration radius calculated perpendicular to the surface decreases strongly near the surface showing that the whole molecules prefer to orient parallel to the surface. The mean square displacement shows a preferred lateral diffusion of polymer; the diffusion perpendicular to the surface is significantly slowed down.

Here we report results of our recent analysis of the MD data for the orientation relaxations of specific chemical bonds ($\alpha$-, $\beta$-, and double-bonds) present in polybutadiene as well as dielectric relaxation in bulk and confined systems. Such relaxation functions can be obtained experimentally, e.g., from NMR measurements[3].

[1] Smith, G.D., and Paul, W., *J. Phys. Chem. A*, *102*, 1200 (1998); Krushev, S., *Diss.* Mainz 2002. [2] Steele, W.A., *Surf. Sci.*, *36*, 317 (1973). [3] Saalwächter, K., *Prog. NMR Spec.*, *51*, 1 (2007)

SYMR 6.7 Wed 11:45 H48

**Understanding the Origin of Dynamical Heterogeneities in Polymer Blends** — •Diddo Diddens[1,2], Andreas Heuer[1,2], and Martin Brodeck[3] — [1]Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 30, 48149 Münster, Germany — [2]NRW Graduate School of Chemistry, Corrensstraße 36, 48149 Münster, Germany — [3]Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Polymer blends composed of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) have been the focus of many investigations such as neutron scattering or NMR experiments. Within this polymer blend both components have greatly different glass transition temperatures, so that the low-$T_\mathrm{g}$ compound (PEO) moves in a random, nearly frozen environment imposed by the high-$T_\mathrm{g}$ compound (PMMA), leading to strong dynamical heterogeneities within the PEO dynamics. One common approach to model the dynamics of the PEO chains is the phenomenological Random-Rouse Model, in which the random environment imposed by the slow PMMA component is modelled by a Rouse chain with different friction coefficients on each bead.

Here we discuss the merits and limitations of the Random-Rouse Model for a simulated PEO/PMMA blend. By using a recently developed method to determine local mobilities in polymeric systems, we can check the different assumptions of this model. Moreover, the length-scale dependence of the retardation of the PEO dynamics in the blend compared to the homopolymer was studied.

SYMR 6.8 Wed 12:00 H48

**Investigation of structural heterogeneities of porous diblock copolymer membranes by single particle tracking** — •Chandrashekara R. Haramagatti[1], Dominique Ernst[1], Felix Schacher[2], Mathias Ulbricht[3], Axel H. E. Müller[2], and Jürgen Köhler[1] — [1]Experimental Physics IV, University of Bayreuth, 95440, Bayreuth, Germany — [2]Macromolecular Chemistry II, University of Bayreuth, 95440, Bayreuth, Germany — [3]Technical Chemistry II, University of Duisburg-Essen, 45117, Essen, Germany

We study the structural heterogeneity of porous diblock copolymer membranes employing single particle tracking. The membranes were prepared by non solvent induced phase separation (NIPS) methods. Information on the thickness and pore sizes of the membranes is known from scanning electron microscopy. Fluorescent polystyrene beads were used as fluorescent particles and the spatial position of which was monitored with sub-diffraction limited accuracy. The diffusion behavior of these particles provides information of the structural properties of the membranes.

SYMR 6.9 Wed 12:15 H48

**Dynamics in thin polymer films probed by single molecule fluorescence microscopy at high temperatures** — •Bente Flier, Moritz Baier, Johannes Huber, Dominik Wöll, Stefan Mecking, and Andreas Zumbusch — Fachbereich Chemie, Universität Konstanz, Universitätsstraße 10, 78457 Konstanz, Germany

Wide-field fluorescence microscopy is a versatile technique for the investigation of single molecule dynamics. We use this technique for the analysis of dynamical properties of thin polymer films in the vicinity of the glass transition temperature. In this contribution we present first results of high temperature single molecule studies above 400 K of polystyrene and poly butyl methacrylate films with thicknesses between 10 nm and 100 nm. For single molecule measurements fluorescent dyes are either covalently bound to the polymer chains or used as probes of free volume. The measurements yield the temperature dependence of the diffusion coefficients which can be explained by free-volume theory. Compared to bulk techniques, however, the single molecule approach allows for an investigation of diffusional heterogeneities.

SYMR 6.10 Wed 12:30 H48

**Dynamics of semiflexible treelike polymeric networks** — •Maxim Dolgushev and Alexander Blumen — Theoretische Polymerphysik, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Deutschland

Extending the generalized Gaussian structure model[1] we study the dynamics of treelike networks, in which we include stiffness using mean-field restrictions on the bonds' orientations. We proceed by using the Bixon-Zwanzig-model[2] and also the maximum entropy principle[3]. For semiflexible treelike networks both approaches turn out to be equivalent[4]. The dynamics of semiflexible treelike polymers obeys Langevin equations, which we succeeded in deriving analytically[4]. This allows us to determine straightforwardly the dynamical characteristics relevant to mechanical and dielectric relaxation[4,5].

[1] A. A. Gurtovenko and A. Blumen, Adv. Polym. Sci., 182, 171 (2005).

[2] M. Bixon and R. Zwanzig, J. Chem. Phys., 68, 1896 (1978).

[3] R. G. Winkler, L. Harnau, P. Reineker, J. Chem. Phys., 101, 8119 (1994).

[4] M. Dolgushev and A. Blumen, J. Chem. Phys., 131, 044905 (2009).

[5] M. Dolgushev and A. Blumen, Macromolecules, 42, 5378 (2009).

## SYMR 7: Biopolymers and Biomaterials

Time: Wednesday 14:00–17:30 Location: H37

**Topical Talk** SYMR 7.1 Wed 14:00 H37

**Atomic Layer Deposition (ALD) as a Versatile Tool for Nanoscience** — •Mato Knez[1], Seung-Mo Lee[1], Adriana Szeghalmi[1], Yong Qin[1], Eckhard Pippel[1], Christian Dresbach[2], and Gerd Hause[3] — [1]Max-Planck-Institute of Microstructure Physics, Halle, Germany — [2]Fraunhofer Institute IWM, Halle, Germany — [3]Martin-Luther-University, Halle-Wittenberg, Germany

Atomic layer deposition (ALD) is a thin film deposition technique which was developed in the 1970s to meet the needs for processing thin film electroluminescent displays (TFEL). Being a non-line-of-sight deposition technique, ALD allows for good coating conformality even with 3D nanostructured substrates or structures with a high aspect ratio together with a good capability for upscaling. An increasing number of researchers make use of the precision of ALD for fabrication or functionalization of nanostructures, optical coatings, catalytically active coatings, encapsulation, corrosion protection or even infiltration of soft materials with metals.

The most recently evolving application of ALD deals with the modification of mechanical properties of soft materials after infiltration of metals by ALD. Although the detailed chemistry behind the approach is not yet understood, biological materials, such as spider silk or collagen, can positively change their mechanical properties after being treated with pulsed vapors of metal precursors. The toughness of such materials increased by up to 10-fold, outperforming most manmade materials.

### SYMR 7.2 Wed 14:30 H37

**Interplay between nanostructure and mechanical properties in natural and artificial polymer fibers** — •Periklis Papadopoulos, Roxana Ene, and Friedrich Kremer — Universität Leipzig, Institut für Experimentelle Physik I

The comparison of mechanical with infrared spectroscopy can be used to explore the multi-level nanostructure of semi-crystalline polymers. In this study we attempt to determine the interconnection of the nanocrystal and amorphous phases in two states of spider dragline silk, native and supercontracted with water, and compare it with artificial systems, such as polyamide 6. Crystal stress can be measured with a high time resolution through the analysis of frequency shifts of absorption bands, while varying mechanical fields are applied. The results show that in both states of silk a serial arrangement between the crystalline and amorphous phase dominates the nanostructure. Polyamide 6 films and electrospun fibers have a similar morphology. In silk, however, water can break the hydrogen bonds of the amorphous chains, and, in combination with hydrophobic effects, it induces the formation of a physical network in the amorphous phase. This network increases in stiffness, until a stress limit is reached. At higher stress, the nanostructure of supercontracted silk is irreversibly transformed to one similar to native silk. This enables one to make a complete description of the mechanical properties of silk in both states, by taking into account the energy required to break these bonds in the previous structural model that assumed a pre-strain distribution of worm-like amorphous chains.

### SYMR 7.3 Wed 14:45 H37

**Interplay between morphology and mechanical properties of silk investigated by X-ray microdiffraction on single fibers combined with *in situ* tensile tests** — Florian Kunze$^1$, Igor Krasnov$^1$, •Christina Krywka$^1$, Martin Müller$^2$, Malte Ogurreck$^2$, Manfred Burghammer$^3$, and Christian Riekel$^3$ — $^1$IEAP der CAU, Kiel, Germany — $^2$GKSS Forschungszentrum, Geesthacht, Germany — $^3$ESRF, Grenoble, France

Silk is a natural composite material known to have special mechanical properties. Produced by the silkworm (*Bombyx mori*) it provides high tensile strength and elasticity combined with low weight. It is extremely stretchable with a high degree of toughness and great elongation before breaking. It would be highly desirable to produce artificial fibers with such mechanical properties. Silk fibers have a semicrystalline morphology, which means they are composed of a crystalline and a disordered phase. To determine the characteristics of the mechanical properties and the composition of the silk fibers we are using a combination of *in situ* tensile tests and X-ray microdiffraction. Utilizing the Microfocus Beamline ID13 at the European Synchrotron Radiation Facility (ESRF) it was possible to execute first Wide Angle X-Ray Scattering (WAXS) measurements combined with *in situ* stretching experiments on single silk fibers. The detected effects are similar to those of measurements on small bundles of silk fibers. Overall we have observed a strong interplay between the morphology of silk and the fibers‘ mechanical properties.

### SYMR 7.4 Wed 15:00 H37

**SANS on Silkworm Silk under Tensile Stress** — •Malte Blankenburg, Martin Müller, and Melissa Sharp — GKSS Research Centre Geesthacht, Germany

Natural silks exhibit extraordinary mechanical properties, combining high tensile strength with a high elongation at failure. Due to their remarkable mechanical properties and potential medical applications the ability to synthesize silk is still a matter of debate. Silkworm silk fibroin is a semicrystalline nanocomposite, with ordered regions ($\beta$-sheet protein nanocrystals) embedded in a softer, amorphous matrix of disordered material [1]. Therefore the contrast between matrix and crystallites could be improved for neutron experiments by deuterating the silk. SANS experiments performed *in situ* during tensile stretching experiments at the SANS-2 instrument at the GKSS showed a peak in the meridional direction of the scattering pattern of deuterated silkworm silk. Since this peak moves to lower q-values by stretching the fibres, an enlargement of the scattering structure could be observed. It was shown before in X-ray experiments [2], that the crystals in the matrix are stretched proportionally to the applied external tensile stress but by a factor of 4 to 18 less than the macroscopic strain. As the percentage elongation is nearly the same for fibre and scattering structure, the scattering objects are not the crystals but rather the ensemble of crystals and disordered material in a periodic arrangement, reflecting the mean distance between crystals in fibre direction.

[1] Y. Shen *et al.*; Macromolecules **31** (1998), 8857

[2] I. Krasnov *et al.*; Phys. Rev. Lett. **100** (2008), 048104

### SYMR 7.5 Wed 15:15 H37

**Rheological properties of wheat dough and corresponding model systems** — •Birgitta Schiedt and Thomas Vilgis — Max-Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz,

Wheat dough is a complex material exhibiting non-linear rheological properties, whose underlying molecular origin is still not fully understood. To dumb it down, the macropolymer gluten (protein) present in wheat flour, forms upon hydration and energy input (kneading) an elastic network, into which starch granules are embedded as filler particles. In order to gain more information about the dough formation process as well as the influence of network (protein) - filler (starch) interactions on the overall behaviour of the dough, rheological measurements and microscopy studies are conducted.

The systems investigated include natural wheat dough made from flour and water at different water contents as well as artificial model dough. The latter consists of gluten and various amounts of starch or other filler particles such as glass beads or silica with different chemical surface modifications. The resulting different types of interactions between the starch and filler particles provide deeper insight about the physics of the temporary network.

## 15 min. break

### SYMR 7.6 Wed 15:45 H37

**Influence of humidity on casein films - an in situ investigation with a combination of $\mu$GISAXS and imaging ellipsometry** — •Volker Körstgens$^1$, Robert Meier$^1$, Johannes Wiedersich$^1$, Jan Perlich$^2$, Stephan Volkher Roth$^2$, and Peter Müller-Buschbaum$^1$ — $^1$TU München Physikdepartment LS E13, James-Franck-Str. 1, D-85747 Garching — $^2$HASYLAB at DESY, Notkestr. 85, D-22607 Hamburg

Glues based on casein are known since ancient Egypt. Nowadays casein-based adhesives are being used in versatile labeling applications. Already pure casein shows adhesive properties depending on humidity as shown with tack experiments in this work. The structural changes of thin casein films are investigated in situ with a combination of $\mu$GISAXS (grazing incidence small angle x-ray scattering with a $\mu$m-sized beam) and imaging ellipsometry. With this new instrument [1] built up at HASYLAB, DESY, Hamburg, a comprehensive sample characterization is possible including local film thickness and optical properties combined with structural information with a spatial resolution depending on the size of the x-ray beam. Swelling and drying cycles with casein thin films are performed in situ and the relation between structure and adhesive properties is discussed.

[1] V. Körstgens et al., Anal. Bioanal. Chem., DOI 10.1007/s00216-009-3008-1

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### SYMR 7.7 Wed 16:00 H37

**Biofunctionalization of Diamond Microelectrodes** — •Andreas Adam Reitinger$^1$, Naima Aurelia Hutter$^2$, Simon Quartus Lud$^1$, Gerhard Richter$^2$, Rainer Jordan$^2$, Martin Stutzmann$^1$, and Jose Antonio Garrido$^1$ — $^1$Walter Schottky Institut, TU München, Germany — $^2$WACKER-Chair of Macromolecular Chemistry, TU München, Germany

In this work we present two main routes for the biofunctionalization of nanocrystalline diamond films, aiming at the application of diamond microelectrodes as amperometric biosensors. We report on direct covalent grafting of biomolecules on nanocrystalline diamond films via diazonium monophenyls and biphenlys as well as other linker molecules, forming self-assembled monolayers on the diamond surface. Monolayers with different functional head groups have been characterized. Patterning of the available functional groups using electron beam-induced chemical lithography allows the selective preparation of well-localized docking sites for the immobilization of biomolecules. Furthermore, polymer brushes are expected to enable novel paths for designing more advanced biosensing schemes, incorporating multifunctional groups and a higher loading capacity for biomolecules. Here, we will focus on the preparation of polymer grafts by self-initiated photografting and photopolymerization. Further chemical modification of the grafted polymer brushes results in the introduction of additional functional molecules, paving the way for the incorporation of more complex molecular structures such as proteins. In a comparative study we investigate the advantages and disadvantages of both approaches.

SYMR 7.8 Wed 16:15 H37

**Real-time in-situ study of oligo(ethylene glycol) reordering dynamics and immersion effects using PMIRRAS** — •Stefan Zorn, Alexander Gerlach, and Frank Schreiber — Institut für Angewandte Physik, Universität Tübingen, Germany

Owing to their high importance in biological and medical applications, e.g. as tethering group for specific binding or, importantly, for passivation of surfaces against unspecific protein absorption, oligo(ethylene glycols) have been the subject of extensive studies. SFG and IR studies revealed strong interactions of water and SAM and strong conformational changes [1]. However, the exact mechanism of protein repulsion is still not fully understood. Here we present a real-time in-situ study of the reordering of the SAM structure during its growth in solution. Using a home build liquid cell with a very thin solution layer (ca. 1 um) we were able to monitor changes in conformation in real time in aqueous environment. With increasing surface coverage there is a change from an amorphous structure with mixed all-trans und helical conformation to a high ordered structure with predominantly helical conformation. A comparison with spectra measured in air shows differences in conformation due to the interaction with water which are more pronounced for lower surface coverage. We also monitored the stability of the SAM over long periods of time and the change in conformation with increasing temperature in solution. Our results shed new light onto the role of water on the structure and protein resistance of OEG SAMs and help to explain the conflicting results in various recent studies.

[1] M.W.A. Skoda et al., Langmuir 23 (2007) 970.

SYMR 7.9 Wed 16:30 H37

**Protein-resistant polymer coatings based on surface-adsorbed poly(aminoethyl methacrylate)/poly(ethylene glycol) copolymers** — •Leonid Ionov[1], Alla Synytska[1], Elisabeth Kaul[1], Stefan Diez[2], and Manfred Stamm[1] — [1]Leibniz-Institut fuer Polymerforschung Dresden e.V., Dresden, Germany — [2]Max-Planck-Institute of Molecular Cell Biology and Genetics, Dresden, Germany

We report on the protein-resistant properties of glass substrates coated with novel copolymers of 2-aminoethyl methacrylate hydrochloride and poly(ethylene glycol) methyl ether methacrylate (AEM-PEG). In comparison to currently available protein-blocking polymer systems, such as poly-L-lysine - poly(ethylene glycol), silane-based poly(ethylene glycol) and poly(ethylene glycol) brushes prepared by surface-initiated polymerization, the proposed AEM-PEG offers the combined advantages of low cost, simplicity of use and applicability in aqueous solutions. We demonstrate the capability of AEM-PEG to block the surface binding of globular proteins (tubulin), their assemblies (microtubules) and functional motor proteins (kinesin-1). Moreover, we demonstrate the applicability of AEM-PEG for surface patterning of proteins in microfluidic devices.

SYMR 7.10 Wed 16:45 H37

**Protein folding monitored at six different magnetic field strengths** — •Michael Kovermann and Jochen Balbach — Institut für Physik/Fachgruppe Biopyhsik, Martin-Luther-Universität Halle-Wittenberg, Betty-Heimann-Straße 7, D-06120 Halle/Saale, Germany

The folding mechanism of an elongated polypeptide chain into its native three dimensional structure is still of high common interest. Using NMR spectroscopy we are able to follow the permanently occuring folding and unfolding of the cold shock protein B from Bacillus subtilis, *Bs*CspB, in equilibrium and kinetically on a ms timescale.

So-called NMR relaxation dispersion experiments are able to monitor these dynamic events on a ms - to - $\mu$s timescale at atomic resolution. We performed these kind of experiments at six different magnetic field strengths to get reliable results. As the folding (and the unfolding) rate of a protein should be independent of the external magnetic field strength we fitted this kinetic parameter in a global procedure to the NMR relaxation data. In addition to these folding rates we get out structural and thermodynamic information by these dynamic NMR experiments.

**Topical Talk** SYMR 7.11 Wed 17:00 H37

**Recognition dynamics and kinetics for ubiquitin** — •Christian Griesinger — MPI for Biophysical Chemistry, Goettingen, Germany

We measured residual dipolar couplings in a large number of alignment media for ubiquitin and derived an ensemble with the EROS method that reflects motion up to the microsecond time scale. The ensemble fits very well the NMR parameters used for the refinement and cross validates other unused NMR parameters such as J-couplings and other dipolar couplings. The ensemble has an rmsd of approximately 1Åand shows large fluctuations in loops as well as in secondary structure elements. The ensemble reflects mainly motion on the previously inaccessible time scale between ns and microseconds. Its implications for molecular recognition will be discussed. We have further measured the time scale of the recognition dynamics and find a previously unobservable sub-$\beta$-peak in dielectric relaxation spectroscopy in solution that can be explained by a modulation of the ion conductance by the conformational ensemble. From the temperature dependence of this effect, on can expect to slow down the dynamics in supercooled solution to approximately 50 $\mu$s. Indeed, relaxation dispersion measurements in supercooled solution reveal that the time scale of major conformational interconversions is 50 to 100 $\mu$s and that the above mentioned ensembles predict correctly the relaxation dispersion data. Furthermore, correlated motion in the ensemble has been quantified experimentally with cross correlated relaxation. We find that the above mentioned rdc derived ensembles agree much better with the cross correlated relaxation data than ensembles that reflect only individual motion.

## SYMR 8: Glasses and Glass Transition

Time: Wednesday 14:00–17:30 Location: H48

**Invited Talk** SYMR 8.1 Wed 14:00 H48

**New Approach to the Old Problem: Cooperativity in Dynamics of Glass Forming Systems** — •Alexei Sokolov — Oak Ridge National Lab and UT Knoxville, USA

The mechanism behind the steep slowing down of molecular motions upon approaching the glass transition remains a great puzzle. Most of the theories relate this mechanism to the cooperativity in molecular motion. In this talk we present estimates and analysis of the molecular cooperativity in many glass-forming systems. We demonstrate that the cooperativity length scale directly correlates to the dependence of the structural relaxation on volume. This dependence presents only one part of the mechanism of slowing down the structural relaxation. Our analysis reveals that another part, the purely thermal variation of the structural relaxation, does not have a direct correlation with molecular cooperativity. These results call for a conceptually new approach to the analysis of the mechanism of the glass transition and to the role of molecular coopertaivity in slowing down of structural relaxation.

SYMR 8.2 Wed 14:30 H48

**THz Signatures of the Glass Transitions in Polymers** — •Marco Reuter[1], Steffen Wietzke[2,3], Christian Jansen[2,3], Tilmann Jung[1], Sangam Chatterjee[1], Wiebke Dempwolf[4], Henning Menzel[4], and Koch Martin[1,3] — [1]Fachbereich Physik, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany — [2]Institut für Hochfrequenztechnik, TU Braunschweig, Schleinitzstr. 22, 38106 Braunschweig, Germany — [3]Joint Optical Metrology Center, c/o TU Braunschweig, Fakultät für Elektrotechnik und Informationstechnik, Hans-Sommer-Str. 66, 38106 Braunschweig, Germany — [4]Institut für Technische Chemie, TU Braunschweig, Hans-Sommer-Str. 10, 38106 Braunschweig, Germany

The glass transition temperature of polymers is found with terahertz time-domain spectroscopy. In the region of the glass transition the thermo-quasi-optic coefficient changes noticeably. THz time-domain spectroscopy is a non-destructive and non-contact technique to analyse polymers.

SYMR 8.3 Wed 14:45 H48

**The elusive nature of the Debye process in monohydroxy alcohols: A new approach with $^2$H-NMR techniques** — •Sebastian Schildmann, Catalin Gainaru, and Roland Böhmer — Experimentelle Physik III, Fakultät für Physik, Technische Universität Dortmund

Viscous monohydroxy alcohols, also water, exhibit a so called Debye process in their dielectric spectra. This relaxational feature corresponds to degrees of freedom which are about 100 times slower than those giving rise to the structural rearrangements ($\alpha$-process). In spite of numerous experimental investigations [1], the nature of these slow "superstructure" relaxation modes is not agreed upon, although it is clear that they are to be related with the presence of hydrogen bonds. The Debye process separates from the structural process if the network is interrupted chemically by diluting or topologically by confining the system in pores. Here butanol diluted with bromobutane was studied with several $^2$H-NMR techniques. Correlation times measured with stimulated-echo experiments are compared with data obtained from dielectric spectroscopy [2]. Spin-lattice relaxation times were measured for O-D deuterated samples to check how the hydrogen bonds affect the dynamics.

[1] M. Poeschl & H.G. Hertz, J. Phys. Chem. 98, 8195 (1994).

[2] T. El Goresy & R. Böhmer, J. Chem. Phys. 128, 154520 (2008).

SYMR 8.4 Wed 15:00 H48

**Relaxation Kinetics of Nanoscale Indents in a Polymer Glass** — •Armin Knoll, Dorothea Wiesmann, Bernd Gotsmann, and Urs Duerig — IBM Research - Zurich, 8803 Rueschlikon, Switzerland

Nanometer scale indents have been written in a cross-linked polystyrene sample, and their relaxation has been studied at annealing temperatures well below the glass transition of the polymer. The indents represent a highly nonequilibrium state of the polymer which is subjected to mechanical stress of up to 0.4 GPa and thermal quench rates on the order of $10^8$ K/s during writing. It is shown that the relaxation towards equilibrium evolves logarithmically over more than 10 orders of magnitude in time. The relaxation kinetics are accurately described in terms of a thermally activated process with an energy barrier whose magnitude decreases linearly with the distance from equilibrium [1].

[1] A. Knoll, D. Wiesmann, B. Gotsmann, and U. Duerig, *Phys. Rev. Lett.*, **102**, 117801 (2009)

SYMR 8.5 Wed 15:15 H48

**Studying the dynamics of water molecules on a complex lattice: KOH doped tetrahydrofuran clathrate hydrate** — •Helge Nelson[1], Catalin Gainaru[1], Andre Nowaczyk[1], Sebastian Schildmann[1], Burkhard Geil[2], and Roland Böhmer[1] — [1]Experimentelle Physik III, Fakultät für Physik, TU Dortmund — [2]Institut für Physikalische Chemie, Universität Göttingen

Because of kinetic hindrance during the freeze-out of the protons in clathrate hydrates an orientational glass transition is observed. By adding minute amounts of ionic dopants, e.g., KOH, the timescale of ordering can be accelerated significantly and an ordered phase is reached [1]. We applied a combination of dielectric and $^2$H-NMR techniques to study the lattice dynamics of the water molecules in a temperature range from 30 K to 260 K. The $^2$H-NMR techniques include temperature dependent lineshape analysis, measurement of relaxation times, and the stimulated-echo technique. This combination allows the observation of dynamics in a broad frequency and temperature window. We found several reorientational processes on the lattice, which are absent in the undoped sample. In addition we were able to detect the phase transition into the proton ordered phase with both dielectric and NMR measurements close to 62 K.

[1] see O. Yamamuro, et al., Physica B 213, 405 (1995) and references cited therein.

**15 min. break**

**Invited Talk** SYMR 8.6 Wed 15:45 H48

**Slow domains percolation in polymer melts and blends close to the glass transition: a unifying concept regarding bulk dynamics, dynamics in the vicinity of interfaces, and the physical properties of nanocomposites** — •Didier R. Long — Laboratoire Polymères et Matériaux Avancés; CNRS/Rhodia; F-69192 Saint Fons, France.

Experiments have demonstrated over past 15 years that the dynamics in liquids close to and below the glass transition temperature is strongly heterogeneous, on the scale of a few nanometers and, independantly, that the glass transition temperature in the vicinity of interfaces can be very different from that in the bulk, with shifts either positive or negative depending on the interaction between the polymer and the interface. By considering thermally induced density fluctuations in the bulk, we proposed that the 3-D glass transition is controlled by the percolation of small domains of slow dynamics, which allows to explain the heterogeneous dynamics close to Tg. This model allowed then for interpreting a priori unrelated features of polymer dynamics: 1) the main feature of confinement effects on the dynamics; 2) Unique reinforcement, plastic and recovery behaviour of nano-filled elastomers; 3) ageing and rejuvenating dynamics polymeric liquids; 4)case II diffusion, which is how a solvent penetrates and finally melts a glassy polymer matrix.

Regarding these various issues, I will put the emphasis on how percolation of slow domains is key for explaining their main features.

SYMR 8.7 Wed 16:15 H48

**Glass Transition of Molecules Sorbed in Zeolites** — Özlen F. Erdem[1], •Dieter Michel[2], Pavel Sedykh[2], and Jürgen Haase[2] — [1]Max-Planck-Institute of Bioinorganic Chemistry, Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany — [2]University of Leipzig, Faculty of Physics and Earth Sciences, Linnéstraße 5, 04103 Leipzig, Germany

Proton MAS NMR, nuclear spin relaxation, and deuteron NMR spectroscopy are combined to study the mobility of ethylene glycol molecules sorbed in various zeolites over a wide temperature range. The results obtained will be also compared with broad-band dielectric measurements and with previous extensive dielectric studies by Kremer *et al.* [1]. The main question is whether the adsorbed species show a so called single-molecule behavior characterized by an Arrhenius type temperature dependence of the correlation times or the respective dielectric relaxation times. In contrast, a Vogel-Fulcher-Tammann (VFT) type temperature dependence of the dielectric relaxation rate would point out collective motions and is typical for the appearance of a glass-transition. An important question is the competition between molecule-to-molecule and molecule-to-surface interactions.

[1] F. Kremer, A. Huwe, M. Arndt, P. Behrens, W. Schwieger, J. Phys. Cond. Mat. **11**, A175-A188 (1999); A. Huwe, F. Kremer, J. Kärger, P. Behrens, W. Schwieger, G. Ihlein, O. Weiss, F. Schuth, J. Mol. Liquids **86**, 173-182 (2000).

SYMR 8.8 Wed 16:30 H48

**Molecular glass formers in hard and soft confinement probed by $^{31}$P and $^2$H NMR** — •Daniel Bock, Sabine Gradmann, and Ernst Rössler — Experimentalphysik II, Universität Bayreuth

Low molecular glass formers confined in nanoporous silica matrices (hard confinement) are investigated by different $^{31}$P and $^2$H NMR methods such as spin-lattice-, spin-spin relaxation, line-shape and stimulated echo decay.

Decreasing the radius of the pores pronounced dynamic heterogeneities are observed. For example, the correlation function revealed by the stimulated echo exhibits a quasi-logarithmic decay in contrast to Kohlrausch decay in the bulk. As shown by 2D spectra the dynamic heterogeneities are transient in time, i.e., we observe exchange between slow and fast molecules. The effects are explained by assuming dynamics being inhomogeneous in space; that is the dynamics given by a correlation time $\tau(r)$ depend on the distance $r$ from the confining wall.

Similar NMR features are found for low molecular additives dissolved in polymer matrices (soft confinement). The additive dynamics are decoupled from those of the polymer, and liquid-like additive dynamics are revealed below $T_g$, i.e., in a solid polymer matrix. Again, strongly stretched correlation functions are observed.

SYMR 8.9 Wed 16:45 H48

**Quantitative Lineshape Analysis for 1D- and 2D-Spectra of Amorphous Materials** — •Jörn Schmedt auf der Günne, Sabarinathan Venkatachalam, Johannes Weber, and Yamini Avadhut — Department of Chemistry, Munich University (LMU), Germany

NMR is quantitative, is an often stated feature in magnetic resonance. In $^1$H solid-state NMR the results from simple MAS experiments can be disappointing though. We present a model study [1] which identifies and quantifies different sources of errors and a new strategy which gives reliable results even under low resolution conditions.

A second aspect will be 2D deconvolution of the lineshapes of amorphous/glassy materials. We analyze the unexpected splittings in the 2D lineshape of many typical glasses with a new analytical fitting function. Based on these findings we suggest a structural model based on different subunits, which should also find their imprint in bulk properties.

[1] Y.S.Avadhut, D.Schneider, J.Schmedt auf der Günne, J. Magn. Reson. 201 (2009) 1-6.

SYMR 8.10 Wed 17:00 H48

**Low-Frequency Excess Contribution in Simple Liquids Revealed by Fast Field Cycling NMR** — •Roman Meier, Axel Herrmann, Robert Kahlau, Danuta Kruk, and Ernst Rössler — Experimentalphysik II, Universität Bayreuth, Germany

The main relaxation ($\alpha$-relaxation) of simple liquids studied by dielectric spectroscopy is well described by a Cole-Davidson (CD) susceptibility. In particular the low-frequency limit follows a Debye behavior $\chi''_{DS} \propto \omega^1$. Applying fast field cycling (FFC) $^1$H NMR and transforming the spin-lattice dispersion data $T_1$ into the susceptibility representation $\chi''_{NMR} \propto \nu/T_1$ we have discovered a low-frequency excess contribution for systems like glycerol and its homologues as well as fluoroaniline. The CD function fails to describe the data due to a retarded transition to the limit $\omega^1$, i.e., a "shoulder" is observed on the low frequency side of the a-relaxation peak ($\omega\tau_\alpha < 1$) possibly reflecting a slower relaxation process. Actually only a few liquids like o-terphenyl and tristyrene studied by FFC NMR do not show this phenomenon. Collecting dispersion data over a large temperature range, the relaxation strength of the excess contribution is specified quantitatively. Measurements of dilution series of propylene glycol in deuterated chloroform proved an intermolecular origin of the excess contribution. Dilution experiments of deuterated in protonated glycerol suggest this additional contribution being also fully reflected by sole intramolecular spin-spin vectors. A possible explanation of this effect are transient molecular clusters due to chemical interactions (e.g. H-bonds).

SYMR 8.11 Wed 17:15 H48

**Glass transition of colloidal particles with long-ranged interactions in two dimensions** — •David Hajnal, Martin Oettel, and Rolf Schilling — Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, D-55099 Mainz, Germany

We study the glass transition behavior of binary mixtures of colloidal particles with long-ranged dipolar interactions in two dimensions in the framework of mode-coupling theory (MCT). We first present a minimal model for the theoretical description of the thermodynamic properties of the experimental system studied by König et al. [1]. By applying MCT to this model, we determine its glass transition diagram, i.e. we calculate the variation of the critical interaction strength upon composition changes. Finally, we compare the mixing effects predicted by MCT for this model to both experiments [1] and MCT results for binary mixtures of hard disks [2].

[1] H. König, R. Hund, K. Zahn, and G. Maret, Eur. Phys. J. E **18**, 287 (2005).

[2] D. Hajnal, J. M. Brader, and R. Schilling, Phys. Rev. E **80**, 021503 (2009).

## SYMR 9: Ultrasound and MRT

Time: Wednesday 14:00–15:20 Location: H41

SYMR 9.1 Wed 14:00 H41

**Ultraschallinduzierte Kontraste in der Magnetresonanztomographie** — •Peter Wolf, Christian Höhl, Fahime Jahanbakhsh, Felix Repp und Karl Maier — Helmholtz-Institut für Strahlen- und Kernphysik, Rheinische Freidrich Wilhelms-Universität, Bonn

Magnetische Nanopartikel (NMPs) sind in der NMR Relaxationszentren und werden deshalb in der Magnetresonanztomographie (MRT) als Kontrastmittel eingesetzt. Sie bestehen aus einem oder mehreren magnetischen Kernen und einer nichtmagnetischen Hülle die nahezu beliebig chemisch funktionalisiert und mit Makromolekülen beschichtet werden kann. In MMR-Experimenten konnte gezeigt werden, dass durch resonanten Ultraschall (US) mit NMR Lamorfrequenz zwischen einseitig beschichteten und nicht beschichteten NMPs unterschieden werden kann. Dies birgt interessant Eigenschaften für ortsaufgelöste Messungen an einem MRT. Allerdings ist resonanter Ultraschall dort schwerlich anwendbar, da elektromagnetische Übersprecher der US-Apparatur mit Lamorfrequenz den MRT-Empfangskreis empfindlich stören. Außerdem beträgt bei üblichen Lamorfrequenzen die Eindringtiefe in Gewebe nur Zentimeter. Deshalb schlagen wir das Konzept der Frequenzverdopplung vor. Der Energietransfer ins Gewebe erfolgt mit einem Ultraschallemitter mit einer niedrigen Grundfrequenz. Im Fokus eines Ultraschallemitters erzeugt man aufgrund von Nichtlinearitäten des Gewebes höhere Harmonische der Schallwelle. Erste Messungen und Experimente werden vorgestellt.

SYMR 9.2 Wed 14:20 H41

**Ultraschall (US) als MR-Kontrastgeber (ARC-MRI) für elastische Eigenschaften** — •Deniz Ulucay[1], Anna-Lisa Kofahl[1], Jessica Mende[1], Marcus Radicke[1], Judith Schindler[1], Bernd Habenstein[1], Peter Trautner[2], Bernd Weber[2], Christoph Bourauel[3] und Karl Maier[1] — [1]HISKP, Universität Bonn — [2]Life&Brain GmbH, Bonn — [3]Poliklinik für Kieferorthopädie, Bonn

Während einer bewegungssensitiven Spin-Echo-Sequenz eingestrahlter US kann zur Sichtbarmachung von elastischen Eigenschaften genutzt werden. Dazu wurde eine Spin-Echo-Sequenz durch 2 zusätzliche, symmetrisch um den 180°-Puls angeordnete Gradienten erweitert. Der US wird während des 2. Gradienten eingestrahlt und führt zu einer von der Verschiebung proportionalen Phasenänderung. Die vom US erzeugte Schallstrahlungskraft wird in homogenem Gewebe/Material exponentiell abgeschwächt, entsprechend der US-Absorption. Eine sich im Strahlverlauf befindende Verhärtung kann durch gleiche Kraft nur weniger bewegt werden, daher kommt es zu einem Dip im exponentiellen Verlauf. US wird mittels eines MR-tauglichen US-Emitters in ein Brust-Phantom eingekoppelt, dessen elastische Eigenschaften denen menschlichen Gewebes entsprechen. In dieses Phantom sind Läsionen eingelassen, welche 3x härter als das umgebende Material sind. Die Verhärtung ist im Phasenbild sichtbar und im exponentiellen Verlauf zeigt sich der erwartete Dip. Aus der Simulation des Schallstrahlungskrafteinflusses mit Finiten Elementen lässt sich quantitativ der Härteunterschied bestimmen.

SYMR 9.3 Wed 14:40 H41

**Ultraschall induzierte Relaxation in MRT** — •Fahimeh Jahanbakhsh, Christian Höhl, Felix Repp, Peter Wolf und Karl Maier — Helmholtz-Institut für Strahlen- und Kernphysik, Rheinische Friedrichs-Wilhelm Universitat, Bonn

Der Einsatz von Kontrastmittel erlaubt der Magnetresonanztomographie (MRT) bestimmte Stoffwechselprozesse abzubilden. Vorraussetzung dafür ist stets, dass die Stoffwechselprozesse zu einer lokalen Anreicherung des Kontrastmittels führen. Eine wichtige Klasse von Kontrastmitteln sind magnetische Nanopartikel (MNP), deren Oberfläche praktische beliebig funktionalisiert werden kann.

Die Reaktion von Makromolekülen mit der Oberfläche der MNPs kann unabhängig von deren lokaler Anreicherung in H-NMR Experimenten beobachtet werden, wenn die Probe während der Messung resonantem Ultraschall ausgesetzt ist. Dieser Effekt wurde in Wasser entdeckt, die Anwendbarkeit der Methode in Gewebephantomen wird diskutiert. Dabei wird auch der Einfluss auf die Querrelaxationszeit $T_2$ betrachtet.

SYMR 9.4 Wed 15:00 H41

**Schallstrahlungskraft in Magnetresonanzaufnahmen: Detektion von Mikrokalk** — •Judith Schindler[1], Anna-Lisa Kofahl[1], Jessica Mende[1], Marcus Radicke[1], Deniz Ulucay[1], Bernd Habenstein[1], Jürgen Finsterbusch[2], Michael Deimling[3] und Karl Maier[1] — [1]HISKP, Uni Bonn — [2]Universitätsklinikum Hamburg-Eppendorf — [3]Siemens Healthcare, Erlangen

Die Kontrasterzeugung durch die Schallstrahlungskraft in Magnetresonanzaufnahmen ist eine neuartige und nicht invasive Methode die elastischen Eigenschaften von Gewebe darzustellen. Eine Anwendungsmöglichkeit ist die Detektion von Mikrokalk. Es wurde ein für das Problem optimierter MR-kompatibler piezoelektrischer Emitter mit einer Resonanzfrequenz von 2,5 MHz benutzt, um ein Brustphantom der Schallstrahlungskraft auszusetzen. Die so erzeugte Bewegung in Richtung der Schallausbreitung wurde in Phasenbildern einer bewegungssensitiven Spin-Echo Sequenz an einem 1,5 T Tomographen und mit einer 4-kanaligen Brustspule sichtbar gemacht. Um Mikrokalk zu simulieren, wurden Eierschalenstücke (von 0,8 x 0,8 mm bis 1,5 x 1,5 mm) in das gelartige Phantom eingefügt. Das Phantom wurde durch das Verschieben des Ultraschalls abgerastert. Bei ausgeschaltetem Ultraschall war die Eierschale nicht sichtbar. Bei eingeschaltetem Ultraschall wird die Eierschale aufgrund des großen Unterschieds in der Schallkennimpedanz zwischen umgebendem Gewebe und Eierschale innerhalb des Schallstrahls sichtbar. Aus Vergleichen mit einer Simulation und durch Variation der Richtung der Bewegungsempfindlichkeit wird auch eine quantitative Charakterisierung möglich.