Review of neutron spectroscopy for studies of the dynamics in confinement

Reiner Zorn

JCNS-1, Forschungszentrum Jülich, 52425 Jülich, Germany
r.zorn@fz-juelich.de
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The dynamics of liquids and polymers confined in nanoscopically small (1...10 nm) pores, tubes or lamellae has become a field of increasing interest in experimental physics. In this introductory talk three exemplary studies using inelastic/quasielastic neutron scattering [1] will be presented.

1. Quasielastic neutron scattering is used to study the $\alpha$ relaxation in glassforming liquids in confinement [2]. Neutron scattering is a suitable method to study such composite materials because the scattering of the liquid component can be emphasized by proper choice of isotopes. These studies may contribute to the understanding of the glass transition which is still one of the unsolved problems in solid state physics. Especially, the question of a cooperativity length scale may be addressed. These experiments usually require a large dynamical range which can be accessed by combination of backscattering and time-of-flight spectroscopy in the time domain.

2. Incoherent inelastic neutron scattering gives direct access to the vibrational density of states. In amorphous materials the VDOS shows a characteristic enhancement over the value expected from sound waves. The reason for the deviation from the crystalline spectrum is still heavily discussed. Studies of this phenomenon, the so-called boson peak, in confinement provide information on its origin [3].

3. Neutron spin-echo spectroscopy is a standard tool to investigate the chain dynamics in polymers (Rouse, reptation) and can also be applied for polymers in confinement. In the ideal case contrast matching should be able to suppress residual small-angle scattering from the confining pore structure. Although for subtle statistical reasons contrast matching does not work as well for polymers as it does for low-molecular materials [4], valuable information can be obtained.

References:
Dynamics of Liquids in Nanoporous Silicon and Carbon as Studied by Quasi-Elastic Neutron Scattering

Mark Busch, Tommy Hofmann, Patrick Huber

1 Institute of Materials Physics and Technology, Hamburg University of Technology, D-21073 Hamburg, Germany
2 Helmholtz-Zentrum Berlin for Materials and Energy, Hahn-Meitner-Platz 1, D-14109 Berlin

quasi-elastic neutron scattering, ionic liquids, hydrocarbons, mesoporous silicon, mesoporous carbon.

Spatial confinement in nanoporous media affects the structure, thermodynamics and mobility of molecular soft matter often markedly. Here, we present incoherent quasi-elastic neutron scattering measurements in a wave vector transfer range from 0.4 Å⁻¹ to 1.6 Å⁻¹ on liquid n-hexane confined in cylindrical, parallel-aligned nanochannels of 6 nm mean diameter and 260 µm length in monolithic, mesoporous silicon. They are complemented with, and compared to, measurements on the bulk system in a temperature range from 50 K to 250 K. The time-of-flight spectra of the bulk liquid (BL) can be modeled by microscopic translational as well as fast localized rotational, thermally excited, stochastic motions of the molecules. In the nano-confined state of the liquid, which was prepared by vapor condensation, we find two molecular populations with distinct dynamics, a fraction which is immobile on the time scale of 1 ps to 100 ps probed in our experiments and a second component with a self-diffusion dynamics slightly slower than observed for the bulk liquid. No hints of an anisotropy of the translational diffusion with regard to the orientation of the channels’ long axes have been found. The immobile fraction amounts to about 5% at 250 K, gradually increases upon cooling and exhibits an abrupt increase at 160 K (20 K below bulk crystallization), which indicates pore freezing.

Moreover, we present quasi-elastic neutron backscattering experiments on an ionic liquid (1-N-butylpyridinium bis-((trifluoromethyl)sulfonyl)imide [BuPy] [Tf2N]) imbibed in carbide-derived mesoporous carbon samples. The analysis of quasi-elastic spectra enables us to study the thermally-activated molecular mobility of the spatially nanoconfined ions as a function of temperature and pore diameter. Foregone elastic and inelastic fixed window scans while the temperature is varied between 2 K and 350 K were particularly helpful to select the temperature for the measurement of the quasi-elastic spectra and provide global insights into the activation of molecular motions in the confined state.

References:
Neutron- and dielectric spectroscopy - taking advantage of the strengths of each technique in confinement studies: Vibrational and Molecular Dynamics of Nanoconfined Liquid Crystals

A. Schönhals¹, W. Lohstroh², M. Zamponi³, B. Frick⁴, R. Zorn³

¹Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany
²Technische Universität München, Physik Department, Garching, Germany
³Forschungszentrum Jülich, Jülich, Germany
⁴Institut Laue-Langevin, Grenoble, France

Andreas.Schoenhals@bam.de

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The effect of a nanometre confinement on the molecular dynamics of liquid crystals was studied by broadband dielectric and neutron spectroscopy. As confining host the molecular sieve Al-MCM-41 (Si/Al=60) with a mean pore diameter of 3 nm was selected. As guest the liquid crystals 8CB and E7 were chosen where the latter does not crystallize but undergoes a glass transition forming a nematic glass.

Dielectric spectroscopy shows that for the confined systems one relaxation process is observed. Its characteristic relaxation time is much lower compared to that of the bulk. No signature of the phase transition characteristics of the bulk liquid crystal is detected. The temperature dependence of the relaxation time of this relaxation process has to be described by the Vogel-Fulcher-Tammann equation and thus shows similarities to glassy dynamics.

The vibrational density of states measured by neutron spectroscopy (IN6, ILL; TOFTOF, MLZ) shows excess contributions with respect to the Debye density of states (boson peak). For the confined systems the low frequency contributions of the boson peak are suppressed, an effect which is also found for conventional glass forming systems.

In addition elastic scans were carried out at the backscattering spectrometer (BS) IN10 at ILL. Such measurements provide an overview about the temperature dependence of the microscopic dynamics. Assuming a Gaussian form for the elastically scattered intensities the effective mean square displacement was calculated. For the nanoconfined samples the mean square displacement is strongly reduced in comparison to the bulk. Also these measurements show the signature of a glass transition indicated by a change in the temperature dependence of the mean square displacement. For confined E7 the extracted glass transition temperature is shifted by more than 20 K to higher temperatures.

Broadband inelastic neutron scattering was carried out by combining time-of-flight (IN6, ILL; TOFTOF, MLZ) and backscattering (IN10, ILL; SPHERES, MLZ) experiments in the time domain. The time dependence of the incoherent intermediate scattering function $S_{inc}(q,t)$ shows two relaxation processes which were quantitatively analyzed by fitting the KWW function to the data. The process at shorter times shows a close similarity the methyl group rotation found for polymeric systems. The process at longer times was assigned to glassy dynamics. The obtained data are compared in detail in their temperature dependence to the dielectric results.
Dynamics of polymer melt in nanoconfinement

Margarita Krutyeva, Michael Monkenbusch, Stefano Pasini, Jon Maiz, Carmen Mijangos, Andreas Wischnewski, Dieter Richter

1Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science (JCNS-1), Jülich, Germany
2Instituto de Ciencia y Tecnología de Polímeros, CSIC, Madrid, Spain

m.krutyeva@fz-juelich.de

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Polymer dynamics is very rich and shows different phenomena depending on the temperature and length scale of observation. Close and above the glass transition temperature $T_g$, the dynamics is dominated by the $\alpha$-relaxation at inter-molecular level. Increasing the temperature, chain mobility is enhanced and, at length scales larger than those corresponding to the statistical segment, the chain dynamics can be well described by the well-established model.

Confinement of polymers by a solid surface on the nanometer scale leads to variety of the structural and dynamical effects that are crucial for nanotechnology. In particular, functional polymeric nanomaterials typically consist of nano-sized particles, which are homogeneously dispersed in a polymeric matrix (nanocomposites). Alternatively, the polymer chains are confined in porous media, e.g. in long cylindrical nanopores (nanoconfinement). In both cases, presence of a large amount of solid surface reduces the number of possible conformations of a polymer chain and influences the dynamics, in particular for those macromolecules, which are close to the surface [1].

In a neutron study we have shown that the attractive polymer-surface interaction influences polymer dynamics. In particular, adsorption of polymer to the Alumina pore surface led to the formation of a surface layer with the dynamics slowed down as compared to the dynamics of pure polymer [2]; anchoring of polymer segments on the Alumina surface creates an interphase between the polymer in close vicinity to the solid surface and pure polymer [3]. In addition, at strong confinement conditions the dilution of the entanglement network is observed [4]. Here we also focus on influence of the confinement on the polymer dynamics in absence of specific adsorption of the polymer segment on the Alumina surface, i.e. repulsive or neutral polymer-surface interaction will be considered.

[1] Polymer Interfaces and Interphases, Soft Materials: Special Issue. 12 (2014); DOI: 10.1080/1539445X.2014.964803
Lipid Bilayer Dynamics Confined by Single-Sided Hard Wall

Sebastian Jaksch¹, Olaf Holderer¹, Michael Ohl², Michael Monkenbusch³, Henrich Frielinghaus¹

¹Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH, Outstation at MLZ, D-85747 Garching, Germany
²Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH, Outstation at SNS, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
³Jülich Centre for Neutron Science JCNS-1 and ICS-1, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

h.frielinghaus@fz-juelich.de

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Lipid bilayers serve as model membranes that appear manifold in living organisms at various places. The observation of membrane-stack relaxations at solid-liquid interfaces is highly interesting because such stacks support the low friction movements of cartilage in joints. The results from grazing incidence neutron spin echo spectroscopy measurements on such membrane stacks explain how point-like excitations are dissipated over wider distances and so local membrane destruction is minimized.

We studied soyPC lipid bilayers that were swollen by heavy water in the vicinity to a solid interface. The newly developed resonator is a neutron wave guide at a large silicon slab, consisting of three double layers. Through constructive interference at small incidence angles, well below the critical angle of total reflection, the neutron intensity is dramatically enhanced and so the evanescent wave highlights the near-surface dynamics of the membrane stack. Using a neutron spin echo spectrometer, the nanosecond dynamics are perfectly resolved. The asymmetric incidence and exit angles serve for a small in-plane scattering vector that highlights long-wavelength membrane modes. Astonishingly, we found propagating wave modes along the surface besides the otherwise dominating over-damped membrane undulations. This viscoelastic twofold behavior on the nanosecond time scale is for the first time observed in neutron spin echo spectroscopy for a Soft Matter system: Oscillating relaxation curves are obtained.

Apart from the bare lipid system we were interested on the influence of the additive ibuprofen. While high ibuprofen contents destroy the lamellar stack structure (that explains stomach bleeding for long application times), the dynamics show fewer wave modes at intermediate concentrations and again more wave modes at highest concentrations.