Cover picture: At the cover page the logo of the conferences of the "International Dielectric Society (IDS)" is shown. The meeting in 2012 took place in Leipzig.
6. Graduations

Doctoral degree:
M. Sc. Ciprian Iacob “Rotational and Translational Diffusion of Glass-Forming Ionic Liquids Confin ed in Nanoporous Silica”

Bachelor of Science:
Benjamin Schott “Untersuchung photophysikalischer Eigenschaften des Photosensibilisators THPTS”

Master of Science:
Markus Fuchs “Moleculare Dynamik in sub-Mikrometer dünnen Block-Copolymer Schichten”

7. Industry collaborations

Novocontrol
Hundsangen, Germany

BOREALIS Polyolefine GmbH
Linz, Austria

IST METZ GmbH
Nürtingen, Germany

Süd-Chemie AG
München, Germany

8. Patent applications

Titel: “Detektorvorrichtung zur Funktionsprüfung von Dichtungssystemen”
Erfinder: Prof. Dr. F. Kremer

The year 2012

In 2012 we organized the “7th International Conference on Broadband Dielectric Spectroscopy and its Applications”, in short BDS 2012. There were many things to celebrate: (i) one hundred years ago P. Debye published (Phys. Zeitschrift 13, 97 (1912)) for the first time his famous formula, which is still the basis for analysing dielectric relaxation processes; (ii) the International Dielectric Society (IDS) has developed since its foundation in 2002 in a splendid manner. International conferences were organized in 2001 (Jerusalem), 2002 (Leipzig), 2004 (Delft), 2006 (Poznan), 2008 (Lyon) and 2010 (Madrid) with increasing attendance; (iii) the “Peter Debye Prize for Young Investigators for Excellence in Dielectric Research” has been recognized as an extraordinary distinction in the field with Anatoli Serghei as prize winner in 2006, Periklis Papadopoulos and Daniele Prevosto in 2008, Catalin Gainaru in 2010 and Simone Napolitano in 2012; (iv) the equipment has developed strongly, covering typically 8-10 decades (or more) in frequency or time; (v) temperature- and pressure-dependent measurements can be carried out readily with commercially available systems; (vi) the amount of sample material required for dielectric measurements can be reduced down to the limit of monomolecular layers and of isolated polymer coils. The scope of the conferences has widened enormously covering nowadays hot topics like “Scaling of relaxation frequencies”, “Terahertzspectroscopy”, “Charge transport and glassy dynamics”, “The interrelationship between Impedance Spectroscopy, Electrochemical measurements and Broadband Dielectric Spectroscopy”, “Biological systems” to mention a few. Dielectric methods have gained increasing interest in modern technology. It was for me, as chairman of IDS, a pleasure to have had the chance to outline and organize this conference again in Leipzig. I am deeply obliged to my coworkers, without their extraordinary engagement the conference would have not been possible.

January 2013

Friedrich Kremer
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2.4. Dynamics of poly(cis-1,4-isoprene) in 1- and 2D geometrical confinement (E.U. Mapesa, W.K. Kipnusu, M. Treß and F. Kremer)

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2.8 Enhanced charge transport in nano-confined ionic liquids (C. Iacob, J. R. Sangoro, W. K. Kipnusu, J. Kärger and F. Kremer)

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2.11 Molecular dynamics and morphology in confined 4-heptan-4'-isothiocyanatobiphenyl liquid crystals (M. Jasiurkowska, W. Kossack, R. Ene, C. Iacob, W. Kipnusu, P. Papadopoulou, J. R. Sangoro and F. Kremer)

2.12 Intra- and inter-molecular dynamics in glass forming low molecular polymeric systems (M. Jasiurkowska, W. Kossack, W. Kipnusu, J. R. Sangoro, C. Iacob and F. Kremer)

5. Financial support

Prof. Dr. F. Kremer

FOR 877 "From local constraints to macroscopic transport" TP 7 "Electric field driven motion of single polyelectrolyte grafted colloids"

Prof. Dr. F. Kremer

SPP 1191 "Ionic Liquids" TP "Charge transport and glassy dynamics in ionic liquids"

Prof. Dr. F. Kremer


Prof. Dr. F. Kremer

Graduate School "Leipzig School of Natural Sciences –Building with Molecules and Nano-objects” BuildMoNa, TP 15 "Dynamics of DNA under tension and in confinement” GSC 185/1 (2008-2013)

Prof. Dr. F. Kremer is Principal Investigator in the "Leipzig School of Natural Sciences – Building with Molecules and Nano-Objects” in the framework of a Graduate School funded by the “Federal Excellence Initiative”. This supports several Ph.D. projects.

Prof. Dr. F. Kremer

IRTG "Diffusion in Porous Materials” TP "Molecular Dynamics in Intentionally Tailored Nanopores” GRK 1056/02 (2009-2013)

Prof. Dr. F. Kremer is Principal Investigator and Lecturer in the International Research Training Group "Diffusion in Porous Materials” headed by Prof. Dr. R. Gläser and Prof. Dr. F. Kapteijn.

Prof. Dr. F. Kremer

SFB/TRR 102 "Polymers under multiple constraints: restricted and controlled molecular order and mobility” TP B05 "Structural levels of organisation in spider-silk - a combined mechanical and IR-spectroscopic study” (2011-2015)

TP B08 "Broadband Dielectric Spectroscopy to study the molecular dynamics in nanometer thin layers of block copolymers” (2011-2015)

Prof. Dr. F. Kremer is deputy chairman of the SFB-TRR 102 on “Polymers under multiple constraints: restricted and controlled molecular order and mobility” of the Universities of Halle and Leipzig.
3. Publications

1. Iacob, C., J. R. Sangoro, W. K. Kipnusu, J. Kärger, F. Kremer
   "Enhanced charge transport in nano-confined ionic liquids"

2. Ueberschär, O., C. Wagner, T. Stangner, C. Gutsche, F. Kremer
   "A novel video-based microsphere localization algorithm for low contrast silica particles under white light illumination"

3. Sangoro, J. R., F. Kremer
   "Charge transport and glassy dynamics in ionic liquids"

   "Molecular dynamics and morphology in confined 4-heptyl-4-isothiocyanatoctylphenyl liquid crystals"

5. Sangoro, J. R., M. Mierzwa, C. Iacob, M. Paluch, F. Kremer
   "Brownian dynamics determine the universality of charge transport in ionic liquids"

   "Molecular Order and Dynamics of Tris(2-ethylhexyl)phosphate Confined in Uni-Directional Nanopores"

   "Structure changes in Nephila dragline: The influence of pressure"

8. A. Schönhals, F. Kremer
   "Amorphous Polymers" in:
   Polymer Science: A Comprehensive Reference Vol. 1, pp. 201-226, Matyjaszewski K. and Möller M. (Eds)

   "Molecular Dynamics of Polymers at Nanometric Length Scales: From Thin Layers to Isolated Coils" in:
   Recent Advances in Broadband Dielectric Spectroscopy, Y. P. Kalmykov (Eds.)
   NATO Science for Peace and Security Series B: Physics and Biophysics, Chapter 12,

10. Serghel A., J. R. Sangoro, F. Kremer
    "Broadband Dielectric Spectroscopy on electrode polarization and its scaling" in:
    Electrical Phenomena at Interfaces and Biointerfaces: Fundamentals in Nano- Bio- and Environmental Sciences,
    Chapter 15, Hiroyuki Oshima (Eds.)

11. Semenov, I., S. Raafatnia, M. Sega, V. Lobaskin, C. Holm, F. Kremer
    "Electrophoretic mobility and change inversion of a colloidal particle studied by single-colloid electrophoresis and molecular dynamics simulations"

    "Microfluidic mobility of single (DNA-grafted) colloids in dilute DNA suspensions"

13. Papadopoulos P., W. Kossack, F. Kremer
    "Intra- and inter-molecular dynamics in glass-forming liquids"

4. Books


2. Physical Aging in glassy systems as reflected in inter- and intramolecular dynamics
   (W. Kossack, K. Kaminski and F. Kremer)

3. Pressure-dependent FTIR-spectroscopy on the counterbalance between external and internal constraints in spider silk of Nephila pilipes
   (M. Anton, W. Kossack, R. Figuli (Ene), P. Papadopoulos, C. Gutsche and F. Kremer)

4. Time-dependent FTIR-spectroscopy on fibrillization of Amyloid-β (1-40) protein
   (M. Anton, J. Adler, D. Huster and F. Kremer)

5. The interaction between HPT-101 and tau-peptides with different phosphorylation patterns investigated by optical tweezers
   (C. Wagner, D. Singer, T. Stangner, C. Gutsche, R. Hoffmann and F. Kremer)

6. Investigating the interactions between GPCRs and ligands on a single-contact level

7. FACS-sorted particles reduce the data variance in Optical Tweezers assisted Dynamic Force Spectroscopy measurements
   (T. Stangner, D. Singer, C. Wagner, O. Ueberschär, C. Gutsche, R. Hoffmann and F. Kremer)

8. Amino acid sequence dependent interactions between receptors and ligands studied with Optical Tweezers
   (T. Stangner, D. Singer, C. Wagner, C. Gutsche, O. Ueberschär, R. Hoffmann and F. Kremer)

9. Electrophoretic mobility and charge inversion of a colloidal particle studied by SCE and MD simulations
   (I. Semenov, S. Raafatnia, M. Sega, V. Lobaskin, C. Holm and F. Kremer)

10. Microfluidic mobility of single (DNA-grafted) colloids in dilute DNA suspensions
    (O. Ueberschär, M. Krüger, C. Gutsche, T. Stangner, C. Wagner, K. Kühne and F. Kremer)

11. Publications

12. Books

13. Financial Support

14. Graduations

15. Industry collaborations

16. Patent applications
By employing single particle tracking on the basis of fast video microscopy, we directly measure the equilibrium short and long time diffusion coefficients of blank and DNA-grafted (molecular weight of 250, 1000 and 4000 base pairs (bp)) tracer colloids in dilute λ-DNA solutions. We compare these results to recently reported microfluidic mobilities under non-equilibrium steady state flow and to the predictions of quantitative theoretical models. A pronounced discrepancy between the measured equilibrium and non-equilibrium mobilities is observed for colloids grafted with 4000 bp DNA molecules, revealing the inapplicability of the Stokes-Einstein relation under these conditions. We demonstrate that this deviation may be interpreted as a strong micro-shear-thinning effect that is caused by the formation of entanglements between the grafted DNA brush and λ-DNA coils from the suspension.

Fig. 1. Left: Short and long time diffusion coefficients of grafted microspheres. (a) Comparison of the directly measured diffusion coefficients $D_0^c$ and $D_0^s$ to the corresponding $D_0^{\text{theo}}$ values derived from drag measurements as function of the molecular weight $\text{MW}$ . For $\text{MW} = 4000$ bp , a clear discrepancy of $D_0^c = 0.4D_0^{\text{theo}}$ is observed. The predictions of the hydrodynamic brush (H. B.) model are depicted as thin solid lines whereas the agglomeration (Aggl.) model results are plotted as thick solid lines. The agglomeration model yields a correct prediction for $D_0^c$ and $D_0^s$ . Right: Schematic of agglomerate formation. Entanglements between grafted DNA molecules (4000 bp , orange) on the tracer microsphere core (grey) with λ-DNA coils (purple) from the suspension lead to the formation of a diffusing agglomerate. The effective hydrodynamic radii of the bare core ($R_c$ ), of the grafted microsphere ($R_{\text{c,eff}} = R_c + H_4$ , black circle) and the agglomerate ($R^{\text{Aggl.}} = R_{\text{c,eff}} + 2R_c$ , blue circle) are depicted schematically.

References:

Funding:
Financial support by the Graduate School BuildMoNa, the DFG priority program SPP1164 and the Deutsche Forschungsgemeinschaft under grant number KR 3844/1-1 is gratefully acknowledged.

2.21 Microfluidic mobility of single (DNA-grafted) colloids in dilute DNA suspensions

O. Ueberschär, M. Krüger, C. Gutsche, T. Stangner, C. Wagner, K. Kühne and F. Kremer
2.20 Electrophoretic mobility and charge inversion of a colloidal particle studied by SCE and MD simulations

I. Semenov, S. Raafatnia, M. Sega, V. Lobaskin, C. Holm and F. Kremer

A novel experimental method and computer simulations are used to examine the ion-surface interactions and the structure of the ionic double layer as a function of added KCl, CaCl₂, and LaCl₃ salt [1, 2]. Mobility reversal of a negatively charged latex colloid is observed in the presence of trivalent La³⁺ ions (Fig. 1(top left)). Moreover, these observations are corroborated by the results of molecular dynamics (MD) simulations of the restricted primitive model [3], which are used to calculate the electric double layer structure and the ζ potential (Fig. 1(top right)), and then, augmented by the standard electrokinetic model [4], the colloid mobility. It is shown that the experimental mobilities in mono- and divalent salts can be well reproduced with the electrostatic mechanism alone, whereas for the trivalent La³⁺ ions an additional attractive term between ions and colloid surface is essential to reproduce the observed mobilities. The importance of electrostatic correlations in the observed electrophoretic mobility reversal is confirmed with the measurements in the presence of trivalent salt (LaCl₃) aqueous solutions of varying valency (KCl, CaCl₂, and LaCl₃). Since the monovalent salt screens the Coulomb interactions, a shift of the isoelectric point to higher ionic strengths is observed as expected (Fig. 1(bottom)). [5]

References:

Funding: SFG FOR 877 and SFB1716, DFG

2.1 Glassy dynamics of condensed isolated polymer coils

M. Treß, E. U. Mapesa, M. Reiche and F. Kremer

The glassy dynamics of randomly distributed, condensed isolated and semi-isolated poly(2-vinylpyridine) (P2VP) polymer chains is studied by means of Broadband Dielectric Spectroscopy (BDS). For this purpose, a recently developed nano-structured electrode arrangement is refined to achieve an electrode-to-electrode distance of only 40 nm (see section 2.2). The P2VP polymer coils are deposited from solution on one of the ultra-flat, highly conductive silicon electrodes and a thorough annealing procedure applied to remove the solvent. Atomic Force Microscopy scans of the identical samples studied in the BDS measurements reveal that the mean volume of the coils resembles 1 to 2 times the volume expected for a single chain (Fig. 1). Accordingly, the measurement averages over single (or sometimes two) polymer chains; for two molecular weights also the semi-isolated case, where coil volumes correspond to 5 to 15 times the estimated single chain volume, is investigated.

The experiments show, that even isolated condensed polymer chains exhibit glassy dynamics. Further, in the case of P2VP on silicon, the mean relaxation time corresponds to the bulk (Fig. 2). An extensive analysis of the relaxation time distribution function reveals a broadening due to the occurrence of new relaxation modes mostly at longer times. This is attributed to interfacial interactions of chain segments with the substrate in their direct vicinity (Fig. 1).

References:

Collaborations: (1) Max-Planck-Institute of Microstructure Physics, Halle, and (2) MicroFAB Bremen

Funding: BuildMoNa, DFG priority program SPP1369 (polymer-solid contacts: interfaces and interphases).
2.2 Nanometric sample capacitors

M. Treß, E. U. Mapesa, M. Reiche and F. Kremer

Recently, a novel method has been introduced to study thin polymer layers with a free upper interface by means of BDS [1]. With the aid of highly conductive ultra-flat silicon electrodes which are covered with strongly insulating silica nano-structures as spacers glassy dynamics in different polymers were investigated [2,3,4]. Due to a low filling fraction of the capacitor (and the resulting small signal to noise ratio) this technique was limited to layers thicker than ~5 nm [5].

To push this limitation, we refined this technique in several ways. First of all, the cleaning procedure has been improved significantly; the previous sonication in solvent (which possibly breaks conductive silicon particles from the edges and transfers these contaminants to the flat surface) is replaced by a plasma treatment followed by a particle removal with a snow-jet gun. Second, the height of the spacers was reduced from previously 100 nm [4,5] to only 35 nm. A third modification concerns the fabrication of the electrodes itself; to counterbalance the increasing capacity due to reduced electrode distance we decreased the area of the counter electrode from initially 3 x 8 mm² to 1 x 1 mm². Besides the geometric adjustment of the capacity, this step improves the realization of electrode separations in the range of the spacer height (which previously has been off by factors of 2 or mostly much more).

Finally, sample capacitors of a thickness of only 40 nm were realized and enabled the investigation of the glassy dynamics of condensed isolated polymer chains (section 2.1).

References:

Collaborations: (1) Max-Planck-Institute of Microstructure Physics, Halle, and (2) MicroFab Bremen

Funding: DFG priority program SPP1369 (polymer-solid contacts: interfaces and interphases)

2.19 Amino acid sequence dependent interactions between receptors and ligands studied with Optical Tweezers

T. Stangner, D. Singer, C. Wagner, C. Gutsche, R. Hoffmann and F. Kremer

For diagnostic procedures that rely on monoclonal antibodies (mAb), it is imperative to know whether the antibody (e.g. HPT-101) recognize the epitope of its target peptide/protein (e.g. tau-protein) specific or whether possible cross-reactivity may occur with other forms of the protein. In Wagner et al. [1] non-specific interactions of two antibodies with the tau-peptide were detected. Based on this result, an epitope mapping was generated. By means of the so called alanine scan, it is possible to identify essential as well as secondary amino acids for the interaction between the tau-peptide and four different monoclonal antibodies (Table 1, performed by Dr. D. Singer with ELISA, BBZ Leipzig). It is apparent that the specificity of the antibody refers not only to a specific isolated phosphorylation site, but to the surrounding amino acid sequence in the tau-peptide. First Optical Tweezers assisted measurements show that the dynamic force spectroscopy approach can make qualitative statements about the existence of essential amino acids and secondary amino acids and identify them, respectively.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>V</th>
<th>A</th>
<th>V</th>
<th>V</th>
<th>R</th>
<th>pT</th>
<th>P</th>
<th>P</th>
<th>K</th>
<th>pS</th>
<th>P</th>
<th>S</th>
<th>A</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPT-104</td>
<td>pT</td>
<td>V</td>
<td>A</td>
<td>V</td>
<td>V</td>
<td>R</td>
<td>pT</td>
<td>P</td>
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<td>K</td>
<td>pS</td>
<td>P</td>
<td>S</td>
<td>A</td>
</tr>
</tbody>
</table>

Table 1: Epitop mapping of monoclonal antibody HPT-101, HPT-104 and HPT-110. The antibody specific phosphorylation sites are underlined (abbreviation: p = phosphorylation) and essential amino acids are shown in red. Secondary amino acids, which contribute to binding, are highlighted in orange. White fields are not significant for the specific interaction between antigen and antibody.

References:

Collaborations: Biotechnologisch-Biomedizinisches Zentrum Leipzig

Funding: ESF, BuildMoNa
2.18 FACS-sorted particles reduce the data variance in Optical Tweezers assisted Dynamic Force Spectroscopy measurements

T. Stangner, D. Singer, C. Wagner, O. Ueberschär, C. Gutsche, R. Hoffmann and F. Kremer

By Optical Tweezers assisted dynamic force spectroscopy experiments combined with fluorescence activated cell sorting (FACS), we demonstrate a new approach to reduce the data variance in measuring receptor-ligand-interactions on a single molecule level by ensuring similar coating densities. Therefore, the carboxyfluorescein-labeled monophosphorylated peptide tau226-240[Thr231] is anchored on melamine resin beads and these beads are sorted by FACS to achieve a homogeneous surface coverage (Fig. 1). To quantify the impact of the fluorescence dye on the bond parameters between the phosphorylated peptide and the corresponding phosphorylation specific anti-human tau monoclonal antibody HPT-104, we perform dynamic force spectroscopy and compare the results to data using unsorted beads covered with the non-fluorescence peptide analogue. Finally, we demonstrate that the data variance of the relative binding frequency is significantly decreased by a factor of 3.4 using presorted colloids with a homogeneous ligand coating compared to unsorted ones.

Fig. 1: 2D-density plot of tau-peptide labeled MF-particles (diameter: 2.3 μm) in dependence on intensity signal of channel FL2-H vs. FL1-H. a) FACS data before the selection process. Two populations are visible: A1 contains uncoated colloids and A2 contains the fluorescence tagged tau-particles. It is apparent that both populations can be distinguished. b) Same batch of colloids as in a), but after sorting. Population A1 is sorted out, only the target population A2 remains with a significant reduction in width and a pronounced increase in density (blue color).

References:

Collaborations: Biotechnologisch-Biomedizinisches Zentrum Leipzig

Funding: ESF, BuildMoNa

2.3 Segmental and chain dynamics in thin layers of poly(cis-1,4-isoprene)

E.U. Mapesa, M. Treß and F. Kremer

Broadband Dielectric Spectroscopy (BDS) – in combination with a nanostructured electrode arrangement – is used to study thin layers of poly(cis-1,4-isoprene) (PIP). Being a Type A polymer, PIP enables the investigation of two distinct relaxation modes taking place at two different length scales: the segmental motion which involves structures of about one nanometer in size and the normal mode which represents the global dynamics of the chain [1]. For molecular weights (24.5, 44.5, 53 and 75 kg/mol) much greater than M_c (the critical molecular weight, M_c = 10^4 g/mol), down to thicknesses comparable to the respective radii of gyration, it is observed (see Fig.1) that: (i) the segmental mode as a local relaxation process is unaffected by the confinement in thin layers – consistent with our previous results [2]; (ii) the normal mode becomes faster with decreasing layer thickness, and (iii) this change in the normal mode is molecular-weight dependent. For M~M_c, it is shown that both the segmental and normal modes remain unaffected by changes in layer thickness.

Fig. 1: Temperature dependence of the dielectric loss ε'' at 80 Hz for (a) PIP-11.6, (b) PIP-24.5, (c) PIP-44.5, (d) PIP-53, and (e) PIP-75 kg/mol. For graphical reasons, Havriliak-Negami fits (assuming Vogel-Fulcher-Tammann (VFT) temperature-dependence) for some data are shown by lines. In (f), (g), (h) and (i) respectively, the same dielectric data is shown normalized w.r.t. the maximum loss value of the segmental mode. (k), (l), (m), (n) and (o) show the respective relaxation time distribution functions as obtained from the HN fit parameters at 312 K.

References:

Collaborations: (1) Max-Planck-Institute of Microstructure Physics, Halle and (2) MicroFAB, Bremen

Funding: DFG SPP 1369 (Polymer-Solid Contacts: Interfaces and Interphases

- 22 –

- 7 –
2.4 Dynamics of poly(cis-1,4-isoprene) in 1- and 2D geometrical confinement


A current study addresses the question: How does the dimensionality of geometric confinement affect the dynamics of the constrained material? For the same material, 1- and 2-D confinements are attained by preparing thin films and by infilling unidirectional nanopores, respectively. Poly(cis-1,4-isoprene) (PIP), being a Type A [1] polymer, is the apt candidate for this study because both the local and global dynamics of the chain can be accessed by Broadband Dielectric Spectroscopy (BDS). BDS measurements on thin films are carried out using a state-of-the-art nano-structured silicon electrode arrangement where highly insulating silica structures are employed as spacers. For the polymer in anodized aluminium oxide (AAO) pores, a fractionated filling procedure (from solution) has been developed achieving filling factors better than 70% in seven days. First results (Fig.1) show that, compared to bulk, the mean relaxation rate of the segmental mode is independent of the dimensionality of confinement. Further, it is clearly evident that both 1- and 2-D confinement affect the normal mode, that is, the conformation of the chains; this effect is more pronounced in the latter case. This study is being extended to different molecular weights of PIP.

Fig. 1: (a) Typical spectra showing dielectric loss (both heating and cooling cycles) as a function of temperature for PI (M_w = 53 000 g/mol) in AAO pores of mean diameter 55 nm. In (b), comparison is made at 120 Hz, between PI in bulk and the confined cases; the temperature position of the normal mode is shifted by about 25 K for the case of PIP in pores relative to PIP in thin layers of comparable size.

References

Collaborations: (1) MPI for Microstructures, Halle; and (2) MicroFAB, Bremen

Funding: DFG SPP 1369 (Polymer-Solid Contacts: Interfaces and Interphases)

2.17 Investigating the interactions between GPCRs and ligands on a single-contact level


Optical tweezers provide an extraordinary technique for the investigation of the interactions between biological macromolecules on a single-molecule level as they allow for positioning a micron-sized particle with nanometer resolution and measuring the forces acting on it with an accuracy of ~50 fN. In this project, the system of interest is the interaction between G-protein coupled receptors (GPCRs) and ligands. GPCRs are receptors, which transduce signals through the cell membrane. They consist of extracellular, transmembrane and intracellular loops (Fig. 1 a). The binding of a ligand causes a structural change of the receptor. To measure the binding between the Y2 receptor and its ligand neuropeptide Y by means of optical tweezers, the colloid held in the optical trap is covered with phospholipid bilayers mimicking the cell membrane. The GPCRs will then be inserted into this membrane. Also, the ligand will be immobilized on the surface of a microparticle, which is attached to the tip of a micropipette (Fig. 1 b). In a first step, control experiments have to be carried out to investigate the interaction between membrane-covered particles as well as between a membrane covered particle and a blank one.

References:
2.16 The interaction between HPT-101 and tau-peptides with different phosphorylation patterns investigated by optical tweezers

C. Wagner, D. Singer, T. Stangner, C. Gutsche, R. Hoffmann and F. Kremer

Optical tweezers-assisted dynamic force spectroscopy is employed to investigate specific receptor/ligand bindings on the level of single binding events [1]. Here, the specific binding of the anti-human tau monoclonal antibody (mAb) HPT-101 to synthetic tau-peptides with 2 potential phosphorylation (Thr231 and Ser235) sites is analyzed (Fig. a). The binding parameters bond lifetime \( \tau_b \), the characteristic length \( x_0 \) and the free energy of activation \( \Delta G \) are determined for the interactions to the biphosphorylated as well as to the two monophosphorylated peptides. It is shown that the specific binding to the biphosphorylated peptide is much stronger than expected from the summation of the interactions to each monophosphorylated peptide (Fig. b). Calculating the relative affinity from the single-molecule data reveals a significantly higher value for the binding to the biphosphorylated peptide (Fig. c).

References:

2.5 Dynamics of poly(styrene-block-isoprene-1.4) diblock copolymers in nanometer thin layers using novel nano-structured electrodes

M.M. Elmahdy, M. Fuchs, M. Treß, E. Mapesa and F. Kremer

Broadband Dielectric Spectroscopy (BDS) using the novel nano-structured electrodes arrangement is employed to investigate the molecular dynamics of poly(styrene-block-isoprene-1.4) (PS-b-PI) diblock copolymers in nanometer thin layers with different PI volume fraction (\( f_b \)) and identical molecular weight of the PS blocks [1]. Three relaxation processes are observed, which can be assigned to the two segmental modes of the styrene and isoprene blocks and to a relaxation process related to the normal mode of the PI chain (Fig. 2). The dynamic glass transition related to the segmental mode of the styrene and isoprene blocks is independent of the layer thickness, while the normal mode of the PI chains becomes slightly faster with decreasing the layer thickness. The ordered state morphology, studied by Tapping mode AFM, revealed the formation lamellar structure (Fig. 1) in good agreement with the literature [2].

Fig. 1: Optical microscope image showing representative regions of the surface topography of the spin-coated PS-b-PI films with \( f_b=0.53 \) and film thickness of ~200 nm. The films are annealed under oil-free high vacuum (10⁻⁶ mbar) at 423 K for 48 h. (b) Tapping mode AFM-height image (scan size 40×40 \( \mu \)m²) (c) Height profile extracted from the AFM-height image shown in (b). This profile is plotted from a single scan line across the film (The red-dotted arrow) and shows terraces of well-defined thickness ranges between ~30-40 nm.

Fig. 2: (a, b and c) are the dielectric loss ('\( \varepsilon'' \)) spectra under 'isochronal' conditions of the PS-b-PI with \( f_b=0.53 \) and film thicknesses of 200, 40 nm and 20 nm obtained at frequency of 304.32 Hz. The dashed and dotted lines in are the fitted curves corresponding to the PI segmental and normal modes, respectively. The solid lines represent theoretical fit with two HN function (assuming Vogel-Fulcher-Tammann (VFT) temperature-dependence). The dashed-dotted line is the HN fit to the PI segmental mode. (d and e) temperature dependence of the relaxation times corresponding to the PI segmental mode (filled symbols), PI-normal mode (open symbols) and PS-segmental mode (hatched-filled symbols) of PS-b-PI diblock copolymer with \( f_b=0.53 \) and 0.66 (a). (d) Relaxation map of PS-b-PI with \( f_b=0.53 \) and film thicknesses of 200 nm (squares), 40 nm (circles) and 20 nm (triangles). The bulk PI and PS-homopolymers with \( M_L=44500 \) and 58800 gram/mol, respectively, are included for comparison (pentagons). (e) Corresponding Arrhenius plot of PS-b-PI diblock copolymer with \( f_b=0.66 \) and film thicknesses of 430 nm (squares), 247 nm (circles), 103 nm (up triangles), 21 nm (diamond) and 12 nm (pentagon). For comparison, the bulk PI and PS-homopolymers with \( M_L=44500 \) and 58800 gram/mol, respectively, are included (stars). The solid lines are Vogel-Fulcher-Tammann (VFT) fits to the experimental data.

References:

Collaborations: C.M. Papadakis (Technische Universität München)

Funding: The project B08 of the SFB/TRR 102 (polymers under multiple constraints)
2.6 The interplay between inter- and intra-molecular dynamics in a series of alkylcitrates

W. K. Kipnusu, W. Kossack, C. Iacob, P. Zeigermann, J. R. Sangoro, R. Valiullin and F. Kremer

The inter- and intramolecular dynamics in a series of glass-forming alkylcitrates is studied by a combination of Broadband Dielectric (BDS), Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR), Fourier-Transform Infrared (FTIR) Spectroscopy and Differential Scanning Calorimetry (DSC). Analyzing the temperature dependencies of specific IR absorption bands in terms of their spectral position and the corresponding oscillator strengths enables one to unravel the intermolecular dynamics of specific molecular moieties and to compare it with the (primarily dielectrically) determined intramolecular dynamics. With decreasing temperature, the IR band positions of carbonyls (part of the core units) and H-bonded moieties of citrates, show a red shift with a kink at the calorimetric glass transition temperature \( T_g \) while other moieties whose dynamics are decoupled from those of the core units, exhibit a blue shift with nominal changes at \( T_g \). The oscillator strength of all units in citrates depict stronger temperature dependencies above \( T_g \) and in some, the ester linkage and H-bonded units show a change of slope at a temperature where structural and faster secondary relaxations merge. By that, a wealth of novel information is obtained proving the fundamental importance of intramolecular mobility in the process of glass formation, beyond coarse-grained descriptions.

Fig. 1: Comparison of dynamics (from BDS) and IR vibrational properties of the alkylcitrates as a function of scaled T. (a) \( \alpha \), \( \beta \) and \( \gamma \) relaxation rates are compared with IR bandshifts for different moieties shown in (b-d). (e) dielectric relaxation strengths for \( \alpha \), \( \beta \) and \( \gamma \) processes compared with the oscillator strength for (f): \( v(C=O) \) (open symbols, left-Y axis), \( v(\delta(C-O)) \) (crossed symbols, right-Y axis), (g): \( \delta(CH_3) \) (crossed symbols, right-Y axis) and \( \delta(CH_2) \) (open symbols, left-Y axis), (h): \( v(\alpha) \) (OH) and \( v(\beta) \) (OH) vibrations of H-bonds

References:

Funding: IRTG diffusion in porous materials (Leipzig)

2.15 Time-dependent FTIR-spectroscopy on fibrillization of Amyloid-\( \beta \) (1-40) protein

M. Anton, J. Adler, D. Huster, F. Kremer

The fibrillation of peptides is a subject of great current interest. On the one hand, the formation of fibrils is symptomatic of many diseases, Alzheimer’s, Parkinson’s, or Creutzfeld-Jacob disease for instance, on the other hand these structures are of interest for novel applications in terms of nanotechnology [1].

Amyloid-\( \beta \)-[1-40] protein is a naturally occurring peptide in human brains and is believed to play a crucial role in Alzheimer’s disease. It forms a cross-\( \beta \) structure resulting in a rigid fibril. It is known that toxic forms of this and other proteins share the identical chemical structure as non-toxic forms, which led to the hypothesis that the physical state determines the possible toxicity of the protein [2]. It is believed that amyloid formation is not a matter of amino acid sequence; instead it is an aspect of polymer dynamics. Interestingly not only the protein parts incorporated in \( \beta \)-sheets exhibit a high order parameter, also the motion of the N-terminus of a peptide chain integrated into a fibril is somewhat suppressed [3].

FTIR-spectroscopy combines the specificity of vibration spectroscopy with fast data acquisition. Therefore it is suitable to investigate the dynamics during fibrillation in situ. Infrared studies are commonly focused on the amide I band, which is associated with C=O stretching vibration and, hence, the \( \beta \)-sheet content of a structure. Unfortunately, this band results from a superposition of up to 12 different single peaks [4]. Consequently, the extraction of unambiguously spectral information is difficult. To extract reliable information, we concentrate our study on the fingerprint region. In preliminary measurements we found a drastic change in vibrational spectra from non-fibrillized to the fibrillized state. Additionally, the spectra of \( ^{13} \)C and \( ^{15} \)N labeled wildtype A\( \beta \)-[1-40] peptide and labeled mutants of it show differences due to isotopic effects and varied amino acid sequence.

Fig. 1: The left hand panel shows the fingerprint region of non-fibrillized and fibrillized A\( \beta \)-[1-40] and the drastic changes coming from fibrilization. The right hand panel depicts an enlargement of the fingerprint region. Effects due to exchange of isotopes and amino acids are visible.

References:
[4] F. Kremer

Funding: by DFG (projects A6 and B5 within SFB/TRR 102)
2.14 Pressure-dependent FTIR-spectroscopy on the counterbalance between external and internal constrains in spider silk of Nephila pilipes

M. Anton, W. Kossack, R. Figuli (Ene), P. Papadopoulos, C. Gutsche, F. Kremer

Spider silk exhibits outstanding mechanical properties elevating it to a promising new material for mechanically highly loaded applications, e.g. bullet-proof vests [1]. The reason for that lies in spider silk's unique structure of a glycine-rich amorphous, glassy matrix reinforced by nanocrystals mainly composed of β-sheet polyalanine, which are, additionally, in serial connection by pre-strained chains. FTIR-spectroscopy in combination with external mechanical fields (uniaxial stress and hydrostatic pressure) is a suitable tool to gain insight into this structural organization. Since both stretching and pressing experiments are performed on the same material, the way the nanocrystals are connected with the amorphous phase can be better understood. Unidirectional stress was produced while stretching the sample controlled by micrometer screws and monitored with a force sensor, while hydrostatic pressure was applied by means of a diamond anvil cell (DAC) and determined through the pressure-dependent ruby fluorescence [2].

The non-overlapping N-Cα polyalanine stretching vibration at $\overline{\nu} = 965$ cm$^{-1}$ can be used as molecular sensor of relative force changes within the β-sheet nanocrystals [16]. Hence, one is able to study the microscopic response to external mechanical fields through the observation of shifts of this vibration. In the case of applied unidirectional stress a linear red shift and for applied hydrostatic pressure a blue shift with a preceding plateau of the vibration is observed. The linear dependence of the blue shift bends off for hydrostatic pressure greater than 1.4 GPa and is fully reversible up to 7 GPa. The seamless connection of negative and positive pressure regimes corroborate quantitatively our structural model of spider silk as composed of pre-stressed alanine-rich nanocrystals embedded in a glycine-rich amorphous matrix. It is also confirmed that nanocrystals withstand high pressures without undergoing structural transition or deteriorating their mechanical properties.

Preliminary measurements in collaboration with Jihaan Allah and Prof. Dr. Christine Kuntscher from the University of Augsburg are highly acknowledged.

References:


Funding: by DFG (project B5 within SFB/TRR 102) and Leipzig School of Natural Science (BuildMoNa)

2.7 Decoupling of ionic conduction from structural dynamics in polymerized ionic liquids

C. Iacob, J. R. Sangoro, S. Berdzinski, V. Strehmel, A. P. Sokolov, and F. Kremer

Ionic conduction and structural dynamics in neat and polymerized bis(trifluoromethyl-sulfonyl)imide-based ionic liquids (IL) are investigated by a combination of Broadband Dielectric Spectroscopy, dynamic mechanical spectroscopy and differential scanning calorimetry. While in the low-molecular weight IL rotational and translational diffusion follow Einstein and Einstein-Smoluchowski equations, for the polymerized system a decoupling between charge transport and structural dynamics by up to two orders of magnitude at low temperatures is found. If rescaled to the calorimetric glass transition temperature $T_g$ charge transport is more efficient for the polymeric IL [1-4].

Fig 1: The dc conductivity, $\sigma_0$ (black symbols), as well as the inverse shear viscosity $1/\eta_0$ (blue symbols) versus $T_g/T$ for the polymerized ionic liquid (poly (PVIM) NTf$_2$ – full symbols) and the low molecular weight ionic liquid PVIM NTf$_2$ (open symbols). The constant X with values 1 and $10^{-4}$ is employed for a low molecular weight and polymerized ionic liquid, respectively, for direct comparison of the temperature dependence of $\eta_0$. The disparity in the values of X presumably stems from the differences in the molecular weights of the two materials. Inset: (a) BNN plot; dc conductivity, $\sigma_0$, versus the characteristic frequency, $\omega_c$, for the materials under study as indicated, and, (b) product of the dc conductivity and the zero shear viscosity normalized with respect to the high temperature values for the materials investigated versus $T_g/T$. This quantifies the degree of decoupling of ion transport from structural dynamics in the two classes of ionic liquids probed.

References:

Funding: Financial support from DFG (Germany) and NOW (The Netherlands) within IRTG "Diffusion in Porous Materials" and DFG Priority Program SPP1191 on Ionic Liquids is gratefully acknowledged.
2.6 Enhanced charge transport in nano-confined ionic liquids

C. Iacob, J. R. Sangoro, W. K. Kiprusu, J. Kärger and F. Kremer

Charge transport and glassy dynamics of several classes of ionic liquids confined in unidirectional nanoporous silica membranes are investigated in a wide frequency and temperature range by a combination of Broadband Dielectric Spectroscopy (BDS), Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) and Fourier Transform Infrared spectroscopy (FTIR). Two opposite effects are observed: (i) surface effects and (ii) confinement effects. More than 10-fold systematic decrease in the effective diffusion coefficient (for HMIM+ based ionic liquids with PF6−, Br anions) from the bulk value is observed in the silica nanopores. For a second category of ILs including BF4− and NTf2− based ionic liquids, it is experimentally demonstrated that the ionic mobility at lower temperatures is enhanced by more than two decades under nanoconfinement in comparison to the bulk value. In summary, the resultant macroscopic transport properties of glass-forming ionic liquids in silica nanopores are controlled by a subtle balance between surface- and confinement-effects [1-4].

References:

Funding: Financial support from DFG (Germany) and NOW (The Netherlands) within IRTG “Diffusion in Porous Materials” and DFG Priority Program SPP1191 on Ionic Liquids is gratefully acknowledged.

Fig 1: (A) Diffusion coefficient determined by applying the Einstein-Smoluchowski equation to the dielectric spectra of HMIM PF6 in bulk (red squares), untreated nanopores (blue circles) and silanized nanopores (black triangles) versus inverse temperature. The respective values obtained by PFG-NMR are shown by crossed symbols. (B) Diffusion coefficients versus inverse temperature as obtained by PFG-NMR (crossed open symbols) and BDS measurements (filled symbols) for bulk and confined BMIM BF4 as indicated. Inset: (a) enlargement of the spectra at lower temperatures.

2.13 Physical Aging in glassy systems as reflected in inter- and intramolecular dynamics

W. Kossack, K. Kaminski and F. Kremer

Physical aging of fucose was studied by measuring the time dependence of Fourier-transform infrared (FTIR) and Broadband Dielectric (BDS) spectra in between 30 K to 4 K below the calorimetric glass transition temperature (Tg=305K). Relaxation times τ were determined by fitting the spectral position (FTIR) and the dielectric loss (BDS) with respect to time by a stretched exponential function [1, 2]. Comparing the results to frequency and temperature dependent BDS measurements above Tg, it turns out that τ of the OH stretching band interlinks segmental (T > Tg) and isostructural (T < Tg) relaxation times from BDS. This indicates the fundamental role of the hydrogen bonding network in structure formation below Tg. Furthermore, subtle changes of spectral shape and position appear for a CH deformation vibration with a characteristic time being approximately 1/3 of τ(OH). Hereby, the different behavior of the different molecular moieties is emphasized linking up to molecular flexibility and individualism.

References:

Funding: Financial Support of the Leipzig School of Natural Sciences, Building with Molecules and Nano-objects BuildMoNa, and the Sächsische Forschungsgemeinschaft SFB77: “From local constraints to macroscopic transport” (DFG-Projekt KR 1138/21-2) is highly acknowledged.

The shift of spectral position of the OH stretching (a) and CH deformation band (b) are shown depending on time for different temperatures. Red lines depict exemplary fits according to a stretched exponential function. The different dependencies are shifted vertically for graphical reasons. In (c) the BDS results of the segmental (c, black circles) and secondary (b, black squares) relaxation times are depicted together with the isostructural (aging) relaxation times from infrared (magenta) and BDS (black). Stars refer to the relaxation rate of oscillator strength and circles to spectral position, whereas filled symbols depict data from D and hollow ones data from L-fucose.
2.12 Intra and inter-molecular dynamics in glass forming low molecular polymeric systems

M. Jasiurkowska, W. Kossack, W. Kipnusu, J. R. Sangoro, C. Iacob and F. Kremer

Broadband Dielectric Spectroscopy (BDS) and Fourier-Transform Infrared Spectroscopy (FTIR) are employed to study the inter- and intra-molecular interaction of two low molecular systems: poly(ethylene glycol) phenyl ether acrylate (PEGEA) and poly(ethylene glycol) dibenzoate (PEGD), confined in non-intersecting nano-pores. The temperature dependencies of various IR absorption bands are analyzed in term of their spectral position and corresponding oscillator strength and compared with intramolecular dynamic properties obtained by BDS. The conformational changes of the OCC group accompanying the glass transition become less pronounced with the decreasing pore size. The results for PEGEA are presented in Fig. 1.

Funding: Financial support by the Alexander von Humboldt Foundation is gratefully acknowledged.

Fig. 1: Comparison of intra- and inter-molecular dynamic of PEGEA in bulk and confined in nanopores of mean diameters of 4 nm, and 8 nm: Relaxation rates of the segmental (α) and the local (β) processes a) and the shift of the absorption bands of PEGEA with respect to the spectral position at 323 K b).

2.9 Electrode polarisation at the interface between a metal and an ionic liquid

L. Popp, W. K. Kipnusu, C. G. Iacob, M. Treß and F. Kremer

Charge transport and electrode polarization phenomena are investigated in a homologous series of imidazolium-based ionic liquids by Broadband Dielectric Spectroscopy (BDS) [4] in a large temperature (190 - 300 K) and frequency range (10^{-3} - 10^5 Hz). The dielectric spectra are dominated – on the low frequency side – by electrode polarization, while, for higher frequencies, charge transport (in a disordered matrix) is the underlying physical mechanism [2]. The absolute values of the dc conductivity vary over 5 decades upon systematic variation of ILs structure and electrode material [3].

A microscopic model is applied to quantitatively describe the electrode polarization [1]. The applicability of the model to the experimental data in a broad frequency range is discussed in more detail.

Fig. 1: Comparison of the experimental data curves to the curves calculated by the model for the ionic liquid [HMIM][I] measured with platinum electrodes at 276 K.

Fig. 2: „dc“ conductivity σ_0: Comparison of (i) the data measured directly with BDS (Exp.) and (ii) the values calculated by the model for the indicated ILs and platinum electrodes.

References:
[3]. J. R. Sangoro, Ph.D. Thesis (2010), University of Leipzig
2.10. Comparative study on the molecular dynamics of a series of polypropylene glycols


Broadband Dielectric Spectroscopy (BDS) is employed to study the molecular dynamics of hydroxyl (OH)- and amino (NH2)-terminated polypropylene glycols (PPG) of varying molecular weight. Besides the dynamic glass transition (α relaxation), a normal mode process and a secondary γ-relaxation is observed, the latter being assigned to librational fluctuations of the polar COC moiety. Additionally a further process is found and proven in two independent experiments (annealing PPGs at high temperatures and physical aging) to originate from residual H2O impurities in the sample and not being related to the dynamics of PPG. It is occasionally discussed in the literature incorrectly as Johari-Goldstein (JG) relaxation. Furthermore aging in the systems under study is analyzed and found to follow the Nagel- Leheny equation.

Fig. 1: (a) Relaxation times versus inverse temperature for the PPG samples studied in the current work. Some data from literature (L) [1] is also included in this relaxation map. Inset: dielectric loss spectra of PPG NH2 showing water relaxation which is removed after annealing (b) Scheme 3 PPG hydroxyl terminated with degree of polymerization n=6 with the assignments of the normal modes, α, β and γ relaxations.

References:

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Funding: Polish National Science Centre within the program Sonata 2 and the SFB-TRR 102. DFG (Germany) and NOW (The Netherlands) within IRTG “Diffusion in Porous Materials” and DFG SPP1369 Priority Program

2.11 Molecular dynamics and morphology in confined 4-heptan-4'-isothiocyanatobiphenyl liquid crystals

M. Jasiurkowska, W. Kossack, R. Ene, C. Iacob, W. Kipnusu, P. Papadopoulos J. R. Sangoro and F. Kremer

Broadband Dielectric and Fourier Transform Infrared Spectroscopy are combined to study the mobility and orientation of 4-heptyl-4'-isothiocyanatobiphenyl (7BT) mesogen confined in nanochannels of mean diameters from 4 nm to 10.5 nm [1]. The smectic E phase observed in bulk 7BT is replaced by short-range molecular order imposed by the surface potential within the pores. Transition Moment Orientational Analysis is employed to explore the orientational order of molecules in pores. The highest degree of molecular order of the mesogenic cores is found for 7BT confined in 6 nm pores.

Fig. 1: (A) Infrared absorption spectra of 7BT obtained on cooling for the bulk (solid lines) and in 6 nm pores (dotted lines) at the indicated temperatures. In the bulk one has the following phases: isotropic at 353 K, SmE at 301 K and the crystalline phase at 230 K. The spectra are normalized with respect to the band at 1400 cm⁻¹. The roman numerals denote the following vibrations: I: CH₂ twisting mode and deformation of CH aromatic, II: CH₂ deformation and CH₃ wagging, III: CH₃ deformation modes, IV: CH₃ scissoring, CH₂ deformation modes, C–C aromatic stretching, CH aromatic deformation, V: C–C aromatic stretching C1–C2, stretching CH aromatic deformation, VI: C–C aromatic stretching, CH aromatic, VII: NCS stretching. ( B ) Dielectric loss ε'' measured at 1.218 kHz as a function of temperature on cooling (empty symbols) and subsequent heating (solid symbols) of the sample in the bulk and in pores.

References:

Funding: Financial support by the Alexander von Humboldt Foundation is gratefully acknowledged.