Cover picture: Scheme of the sample capacitor built by crossed silicon wafer dice (top left); optical microscope and AFM pictures of the silica nano-structures with a heights of 100 nm (top and right) and a sub-layer of poly(2-vinyl pyridine) (bottom and left).
The year 2010

*Tempora mutantur nos et mutamur in illis* – times are changing and we are changing in it.

While 5 – 10 years ago our group was the first to measure the molecular dynamics in polymer layers as thin as 10 – 20 nm, the focus has changed in the meantime to study molecular assemblies as thin as 1-2 nm and even isolated polymer coils. This could be achieved only due to the development of novel nanostructured electrode arrangements (s. cover page) which are now routinely used to determine by Broadband Dielectric Spectroscopy the molecular dynamics in extraordinary wide frequency and temperature ranges. As first result it was shown that the molecular mobility in the 1-dimensional confinement of thin polymer layers is bulk-like down to thicknesses smaller than 5 nm – a finding confirmed as well by Ellipsometry and Calorimetry. Many further highly promising experiments are on course, for instance to unravel the impact of the dimensionality of the geometrical constraints on the dynamics of glass-forming systems.

- In our other main fields of activity, polarized time-resolved Fourier-Transform Infrared Spectroscopy and experiments with Optical Tweezers substantial progress was made. The structural levels of organization of spider silk are in the mean time quantitatively understood and the phenomenon of super-contraction in spider silk is well analyzed by deuteration experiments. Furthermore the novel technique of IR Transition Moment Orientational Analysis was developed and proven to be very versatile to analyze the mean orientation and the molecular order parameter of the different moieties in liquid crystalline polymers. In the experiments with Optical Tweezers great progress was made in various fields for instance in determination of the interaction potential between polymer brushes, in measurements on the electrophoretic mobility of single (polymer-grafted) colloids and refined studies on single receptor/ligand contacts. Recently an (HBFG)-application for the first commercially available Optical Tweezers set-up was positively approved.

January 2011

Friedrich Kremer
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preface</td>
<td>1</td>
</tr>
<tr>
<td>1. Organization of the group</td>
<td>4</td>
</tr>
<tr>
<td>2. Projects</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Glassy dynamics and glass transition in nanometric thin layers of polystyrene (E. U. Mapesa, M. Tress, A. Serghei and F. Kremer)</td>
<td>6</td>
</tr>
<tr>
<td>2.3 Glassy dynamics in thin layers of <em>cis</em>-polyisoprene (E. U. Mapesa, M. Tress and F. Kremer)</td>
<td>7</td>
</tr>
<tr>
<td>2.4 Molecular dynamics of <em>cis</em>-polyisoprene under geometrical confinement (W. K. Kipnusu, E. U. Mapesa, C. Iacob, J. R. Sangoro and F. Kremer)</td>
<td>8</td>
</tr>
<tr>
<td>2.5 Rotational and translational diffusion in hyperbranched polyglycerols (T. Schubert, J. R. Sangoro, C. Iacob, and F. Kremer)</td>
<td>9</td>
</tr>
<tr>
<td>2.6 Dielectric properties of ionic liquids: the effect of temperature and pressure (J. R. Sangoro and F. Kremer)</td>
<td>10</td>
</tr>
<tr>
<td>2.7 Diffusion in ionic liquids: the interplay between molecular structure and dynamics (J. R. Sangoro, C. Iacob, and F. Kremer)</td>
<td>11</td>
</tr>
<tr>
<td>2.8 Charge transport and dipolar relaxations in alkali metal-based ionic liquids (J. R. Sangoro, C. Iacob and F. Kremer)</td>
<td>12</td>
</tr>
<tr>
<td>2.9 Charge transport in confined ionic liquids (C. Iacob, J. R. Sangoro, and F. Kremer)</td>
<td>13</td>
</tr>
<tr>
<td>2.10 Liquid crystals in confining geometry (M. Jasiurkowska, C. Iacob, P. Papadopoulos, F. Kremer, and M. Massalska-Arodz and F. Kremer)</td>
<td>14</td>
</tr>
<tr>
<td>2.11 Infra-Red Transition Moment Orientational Analysis (IR-TMOA) (W. Kossack, P. Papadopoulos and F. Kremer)</td>
<td>15</td>
</tr>
<tr>
<td>2.12 Hierarchies in the structural organization of spider silk – a quantitative model (R. Ene, P. Papadopoulos and F. Kremer)</td>
<td>16</td>
</tr>
<tr>
<td>2.13 Receptor/Ligand-interaction as studied on a single molecule level (C. Wagner, D. Singer, R. Hoffmann and F. Kremer)</td>
<td>17</td>
</tr>
</tbody>
</table>
5. Graduations

Doctoral degree:
M. Sc. J. R. Sangoro "Rotational and translational diffusion in ionic liquids"
Dipl.-phys. C. Gutsche "Rheologische Untersuchungen an einzelnen Kolloiden mit Optischen Pinzetten"
Dipl.-phys. K. Kegler "Kraftmessungen zwischen DNS-beschichteten Kolloiden mittels Optischer Pinzetten"

Diploma

cand. phys. C. Krause "Charge transport and dipolar relaxations in imidazolium-based ionic liquids"
cand. phys. T. Stangner "Wechselwirkungskräfte zwischen Polymer-gepapften Kolloiden"

6. Industry collaborations

Novocontrol
Hundsangen, Germany

Clariant Produkte (Deutschland) GmbH
Frankfurt am Main, Germany

Comtech GmbH
München, Germany

inotec FEG mbH
Markkleeberg, Germany

7. Patent applications

Deutsche Patentanmeldung Nr. 10 2005 045 065,2-54
Titel: "Detektorvorrichtung zur Funktionsprüfung von Dichtungssystemen"
Erfinder: Prof. Dr. F. Kremer

8. Awards

Prof. Dr. Friedrich Kremer was elected to give the Whitehead Memorial Lecture
1. Organization of the group

**Leader:** Prof. Dr. Friedrich Kremer

**Academic Staff and Postdocs**

<table>
<thead>
<tr>
<th>Academic Staff and Postdocs</th>
<th>Students</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. Mahdy Elmahdy</td>
<td>Dipl. Phys. Tim Stangner</td>
</tr>
<tr>
<td>Dr. Periklis Papadopoulos</td>
<td>Dipl.-Phys. Olaf Ueberschär</td>
</tr>
<tr>
<td>Dr. Joshua Sangore</td>
<td>Dipl.-Phys. Carolin Wagner</td>
</tr>
<tr>
<td>Dr. Christof Gutsche</td>
<td>M. Sc. Ciprian Ghiorghita iacob</td>
</tr>
<tr>
<td></td>
<td>Dipl.-Phys. Kati Kegler</td>
</tr>
<tr>
<td></td>
<td>Dipl.-Phys. Wilhelm Kossack</td>
</tr>
<tr>
<td></td>
<td>M. Sc. Wycliffe Kiprop Kipnusu</td>
</tr>
<tr>
<td></td>
<td>Dipl.-Phys. Christina Krause</td>
</tr>
<tr>
<td></td>
<td>M. Sc. Ilya Semenov</td>
</tr>
<tr>
<td></td>
<td>Dipl. Phys. Martin Tress</td>
</tr>
<tr>
<td></td>
<td>M. Sc. Emmanuel Mapesa</td>
</tr>
<tr>
<td></td>
<td>cand. phys. Tilman Schubert</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Technical staff</th>
<th>Guests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hartmut Domröse</td>
<td>Dr. Malgorzata Jasiurkowska</td>
</tr>
<tr>
<td>Karin Girke</td>
<td></td>
</tr>
<tr>
<td>Ines Grünwald</td>
<td></td>
</tr>
<tr>
<td>Dipl.-Ing.(FH) Jörg Reinmuth</td>
<td></td>
</tr>
<tr>
<td>Dipl.-Phys. Wiktor Skokow</td>
<td></td>
</tr>
<tr>
<td>Dipl.-Phys. Cordula Babara Krause</td>
<td></td>
</tr>
</tbody>
</table>

**Alumni**

Prof. Dr. Siegbert Grande

4. Financial support

**Prof. Dr. F. Kremer**


**Prof. Dr. F. Kremer**


**Prof. Dr. F. Kremer**


**Prof. Dr. F. Kremer**

DFG-Projekt "In-Situ Untersuchung der Wechselwirkungskräfte an Polyelektrolytbürsten", KR 1138/20-2 (2009–2011)

**Prof. Dr. F. Kremer and Prof. Dr. K. Kroy**


**Prof. Dr. F. Kremer**


**Prof. Dr. F. Kremer**


**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** 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.
2. Projects

2.1 Glassy dynamics of mono-molecular layers of poly(2-vinyl pyridine)

M. Tress, E. U. Mapesa, A. Serghei and F. Kremer*

Recently, a preparation method using ultra-flat, highly doped silicon wafers as electrodes which are covered with strongly insulating silica nano-structures as spacers was developed in our group. This enables us to apply Broadband Dielectric Spectroscopy (BDS) to samples which do not exhibit a full surface coverage; in particular, the investigation of the glassy dynamics of ultra-thin layers of polymers down to and below the mono-molecular limit (where the polymer chains form sub-layers) is feasible [1]. In the case of poly(2-vinyl pyridine) (P2VP), it will be possible to study the dynamics of isolated coils which do not interact with each other and hence, can be treated as a statistical average over a single polymer chain in different conformations. First results reveal that in sub-layers with an average thickness of 3 nm neither the mean relaxation rate nor the shape of the relaxation time distribution function is changed compared to the bulk.

Fig. 1: a) Dielectric loss ε'' versus Temperature of two P2VP samples with thicknesses as indicated recorded at a frequency of 1.2 kHz. The α-relaxation peak coincides with the corresponding bulk value. b) and c) AFM picture (20 x 20 µm) and histogram of a scratch on the 3-nm-thick sample; the broad distribution of the heights of the polymeric surface indicates the characteristic of a sub-layer. d) and e) AFM pictures (5 x 5 µm²) of the surface topology of the same sample taken before and after the measurement show the stability of the sample and especially the absence of dewetting; the corresponding values of the root mean square (RMS) roughness are 0.64 nm and 0.96 nm, respectively.

References:

Collaborators:
#Present address: Université Lyon 1, CNRS, Ingénierie des Matériaux Polymères, France

Funding: Financial support by the BuildMoNa Graduate School is gratefully acknowledged.

* Underlining indicates the author who initiated the project.
2.2 Glassy dynamics and glass transition in nanometric thin layers of polystyrene

E. U. Mapesa, M. Tress, A. Serghei and F. Kremer

In 2009, our group initiated an investigation on the glassy dynamics of ultra-thin (≥ 5 nm) layers of polystyrene (PS) by means of Broadband Dielectric Spectroscopy (BDS) and vis-Ellipsometry under identical and well controlled conditions for a wide range of molecular weights (58.9 kg/mol - 8090 kg/mol). First results examined no shift of \( T_g \) and no broadening in the glassy dynamics for PS layers as thin as 5 nm [1]. Recently, we extended this study by applying AC-calorimetry and X-ray reflectometry and confirmed our previous findings [2]. The characteristic temperature of the \( \alpha \)-relaxation \( T_\alpha \) as well as \( T_g \) of all molecular weights under study lies within a range of 4 K while the experimental error is as big as ± 2 K. Knowing about the strong impact of the sample preparation the present investigation emphasizes the identical preparation procedures in all applied methods and the resulting coincidence of the findings. [Fig. 1: Logarithm of the inverse relaxation time \( \tau^{-1} \) plotted versus inverse temperature for several PS samples (of diverse thicknesses and molecular weights) measured by different experimental methods as indicated. The dashed and solid lines are fits of the Vogel- Fulcher-Tammann equation to the BDS data of the 37 nm and 169 nm sample (58.9 kg/mol). The inset shows the molecular weight dependence of \( T_g \) and \( T_\alpha \) (recorded at a frequency of 1 kHz) for bulk samples measured with different techniques.]

References:

Collaborators:
Ellipsometry, DSC: M. Erber, K.-J. Eichhorn, B. Voit, Institut für Polymerforschung Dresden (IPF)
X-ray reflectometry: J. Müller, H. Huth, C. Schick, Universität Rostock
Support for AC-Calorimetry: H. Huth, C. Schick, Universität Rostock

#Present address: Université Lyon 1, CNRS, Ingénierie des Matériaux Polymères, France
MicroFAB Bremen

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

3. Publications

2.18 Single colloid electrophoresis on DNA-grafted colloids.
I. Semenov, P. Papadopoulos and F. Kremer

The novel method of Single Colloid Electrophoresis (SCE) [1,2] is applied to determine the electrophoretic mobility of single blank and DNA-grafted colloids. For that Optical tweezers are employed to measure separately the complex electrophoretic mobility of a single colloid and the complex electroosmotic response of the surrounding medium. For the bare particles pronounced effects are observed in dependence on concentration and valency of the ions in the surrounding medium and on its pH. For monovalent KCl solutions for instance a peak of the electrophoretic mobility at low concentrations is found (Fig. 1) which agrees well with the predictions of the standard electrokinetic model [3]. For trivalent LaCl₃ solutions at high concentrations charge inversion of the colloid as a whole takes place.

SCE is extended to polyelectrolyte-grafted colloids. This enables one to determine (Fig. 1) for the first time the electrophoretic mobility of soft (DNA-grafted) particles under conditions of varying concentration and valency of the ions in the surrounding medium and to compare with the predictions of an approach suggested by Hill and Saville [4].

Fig. 1: Electrophoretic mobility vs. ionic strength of KCl and CaCl₂ aqueous solutions for a single DNA grafted (4000 bps, 1250 molecules per colloid) and similar blank negatively charged PS colloid (diameter: 2.0 μm). Laser power 0.2 W. Electric AC field frequency 12.5 kHz. For comparison the electrophoretic mobility in KCl solutions predicted by the Hill and Saville approach is displayed (solid line).

References:

Funding: Sächsische Forschergruppe FOR 877, DFG.

2.3 Glassy dynamics in thin layers of cis-polyisoprene
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 cis-1,4-polyisoprene. From the viewpoint of BDS, polyisoprene belongs to a special type of polymers because a part of its molecular dipole moment attached to each monomer unit is aligned along the main chain. This 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 (2 to 3 monomer units) and the normal mode which represents the dynamics of the whole macromolecule. Previous studies [1-3] involved the evaporation of a metal counter-electrode onto the spin-cast layer. As a result of this (sandwich) geometry, a confinement-induced mode shows up between the normal and segmental modes, and gains dielectric strength with reducing film thickness at the expense of that of the normal mode. In the current study – where highly insulating silica nanostructures are used as spacers – one interface is free. The spin-cast samples are checked before and after dielectric measurement so that any dewetted layers are excluded from this study (Fig. 1). Down to 7 nm, it is observed (Fig. 2) that: (i) the segmental mode as a local relaxation process is unaffected by the 1-D confinement; (ii) the normal mode becomes faster with decreasing layer thickness; (iii) the normal mode gains dielectric strength with reducing layer thickness; and (iv) the so-called confinement-induced mode does not show up. For a quantitative analysis of these intriguing observations, simulations are planned to be carried out where the chain is treated as an ideal random walk in 3-D taking place between one penetrable and one impenetrable wall. Furthermore, a variation of the molecular weight is envisioned.

References:

Funding: Funding by DFG priority program SPP1369 (polymer-solid contacts: interfaces and interphases) is highly appreciated.

- 22 -
2.4 Molecular dynamics of cis-polyisoprene under geometrical confinement

W. K. Kipnusu, E.U. Mapesa, C. Iacob, J.R. Sangoro and F. Kremer

Broad-band dielectric spectroscopy is employed to study cis 1,4 polyisoprene. In the bulk state two distinct molecular processes are observed. The normal mode process due to dipole component parallel to the chain contour appears at higher temperatures (lower frequencies) and is proportional to the correction function of the fluctuations of the end-to-end vector of the whole polymer chain. Segmental mode which appears at lower temperatures (higher frequencies) as shown in Fig. 1, is associated to the dynamic glass transition. Both of the two processes are proportional to the monometric friction coefficients [1] and hence have the same temperature dependence as seen on the inset of Fig 1. A counterbalance between finite-size effects and surface effects are expected to influence molecular dynamics of these processes when the polymer melt is confined in cylindrical nanopores especially when the pore diameter is less than the radius of gyration of the polymer. From previous studies it is noted that the confinement effects is strongly dependent on the topology and dimensionality of the confining matrices [2,3,4]. In the current study [5], 2-D confinement of cis-1,4 polyisoprene in unidirectional nanoporous silica matrices will be compared with 1-D confinement in spin cast thin films where silica nanostructures are used as spacers leaving one interface free. Nanoporous silica matrices are obtained after oxidation of porous silicon prepared by anodization of highly p- doped (100) oriented silicon substrates in HF electrolyte solution. This process leads to highly anisotropic pores running perpendicular to the surface of the wafer (Fig. 2a). Self-diffusion coefficients of cis 1,4 polyisoprene in bulk state and when confined in the nanoporous host systems will also be probed using both dielectric spectroscopy and pulse field gradient NMR spectroscopy.

References:

Collaborators: J. Kärger, R. Valiullium (U Leipzig)

Funding: Financial support from DFG (Germany) and NOW (The Netherlands) within IRTG “Diffusion in Porous Materials” is highly appreciated.

2.16 The effective hydrodynamic radius of single DNA-grafted colloids as measured by fast Brownian motion analysis

O. Ueberschär, C. Wagner, T. Stangner, C. Gutsche and F. Kremer

Optical tweezers accomplished with fast position detection enable one to carry out Brownian motion analysis of single DNA-grafted colloids (grafting density: ~1000 molecules per particle, molecular weight: 4000 bp) in media of varying NaCl concentration. By that the effective hydrodynamic radius of the colloid under study is determined and found to be strongly dependent on the conformation of the grafted DNA chains. Our results compare well both with recent measurements of the pair interaction potential between DNA-grafted colloids (Kegler et al. [2]) and with microfluidic studies (Gutsche et al. [3]). The observed scaling of the brush height with the ion concentration is in full accord with the pertinent theoretical predictions by Pincus, Birshtein and Borisov.

Fig. 1: (a) The centre of the colloid as determined by our two-dimensional intensity profile fit is subject to Brownian motion, which becomes apparent from the depicted trajectory. (b) Schematic of a streptavidin-coated microsphere to which DNA molecules are grafted. (c) The increase of the hydrodynamic radius with respect to different NaCl concentrations as measured for a single DNA-grafted colloid in the salted regime (to logarithmic scale). The linear fit of $\Delta R$ vs. the NaCl concentration $c$ yields a power law scaling $\Delta R \propto c^\gamma$ with an exponent of $\gamma = 0.35 \pm 0.04$. The molecular weight of the DNA molecules is 4000 base pairs. The reversibility of the salt-induced conformational change of the DNA brush as reflected in $\Delta R$ has successfully been verified.

References:

Funding: Financial support by the BuildMoNa Graduate School is gratefully acknowledged.
2.16 Interaction forces between a single pair of charged colloids as measured by Optical Tweezers

C. Gutsche, T. Stangner, M. M. Elmahdy, and F. Kremer

Optical Tweezers are an excellent tool to investigate the interaction force between a single pair of spherical charged colloids (diameters: polystyrene 2.24 ± 0.02 µm; silica 4.85 ± 0.05 µm) [1,2,4]. The concentration dependence was recorded under different conditions e.g. varying salt concentration and valency (see Fig. 1 (a-f)). The data are well described by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [2,3]. A comparison of the fitted Z and R among different colloidal pairs of PS with monovalent counterions reveals that the radii are virtually the same whereas the obtained charges range from Z = 200 000 to 450 000. For a given pair of colloids, at an increasing counterion valence, the fitted radius R remains essentially constant whereas the fitted charge Z decreases [2,4]. For reasons of comparison, data for silica colloids (diameter 4.85 ± 0.05 µm) are plotted in Fig. 1 (d-f) and show a similar valence dependence. We attribute the latter effect to the neglect of the small-ion correlations in the DLVO theory, which gain importance at increasing counterion valence. The neglect of those leads to an underestimate of screening of the colloids while the functional force–separation dependence is essentially preserved.

2.5 Rotational and translational diffusion in hyperbranched polyglycerols

T. Schubert, J. R. Sangoro, C. Iacob and F. Kremer

Dendritic polyglycerols are under intense investigation due to the wide range of applications envisaged in biomedical sciences and especially drug delivery. In the current study, rotational and translational diffusion in a series of hyperbranched polyglycerols (HPGs) are investigated by a combination of broadband dielectric spectroscopy (BDS), pulsed field gradient nuclear magnetic resonance (PFG NMR), rheology, frequency-dependent (ACC) as well as differential scanning calorimetry (DSC). The dielectric spectra are dominated by conductivity contribution at higher temperatures (and lower frequencies) whereas two closely adjacent secondary dipolar relaxation processes are observed at lower temperatures for all the samples investigated. Analysis of the real part of the complex dielectric function based on the Kramers-Kronig relations enables the separation of the latter. The slower dipolar relaxation is attributed to rotational diffusion – an assignment supported by rheological and calorimetric results. The Stokes-Einstein relation linking rotational and translational diffusion is shown to hold for the (low molecular weight) polymers investigated.

References:

Collaborators: R. Buchner (University of Regensburg), V. Strehmel (Niederrhein University of Applied Sciences), J. Kärger (University of Leipzig), R. Vallinlin (University of Leipzig)

Funding: DFG under the priority program SPP 1191 on “Ionic Liquids”

Fig. 1: (a-c) Force F vs. separation D for one single pair of Polystyrene (PS) colloids (diameter = 2.24 ± 0.02 µm) in aqueous solution of varying salt and salt concentrations from experiments (symbols) and the DLVO theory with fitted values of the parameters Z and R (curves). (a) NaCl at 0.3 mM (black squares), 0.55 mM (red circles), 1 mM (green triangles), 2 mM (blue nabs), 4 mM (cyan diamonds), 10 mM (magenta left triangles), and 30 mM (orange right triangles). To ensure full reproducibility of the exchange of the medium and to exclude hysteresis effects due to possible adsorption effects on the colloids the sample cell was flushed again with 0.3 mM NaCl (gold diamonds). (b) CaCl2, at 0.15 mM (black open squares), 0.3 mM (red open circles), 0.5 mM (green open triangles), 1 mM (blue open nabs), 1.5 mM (cyan open diamonds), 3 mM (magenta open left triangles), 0.15 mM (orange open right triangles), and finally 0.3 mM NaCl (gold open diamonds). (c) LaCl3 at 3 µM (black red filled square), 10 µM (black green filled square), 30 µM (black blue filled triangle), 100 µM (black cyan filled nabs), 3 µM (black magenta filled diamonds), and 0.3 mM NaCl solution (black gold filled diamonds). Some indicative error crosses given. (d-f) Force F vs. separation D for a single pair of blank polystyrene (PS) colloids (diameter ~ 2.24 ± 0.02 µm) in aqueous solution of varying salt and salt concentrations from experiments (symbols) and the DLVO theory with fitted values of the parameters Z and R (curves). (d) Concentration dependence of KCl: 0.04 mM (black squares), 0.06 mM (green up-triangles), 0.1 mM (blue down-triangles), 0.2 mM (cyan diamonds), 0.3 mM (magenta left-triangles), 0.4 mM (yellow right-triangles), 1 mM (dark yellow diamonds), 4 mM (navy blue stars). To ensure the full reproducibility of the medium exchange, the cell was flushed again with 0.04 mM (open red squares). (e) Concentration dependence of CaCl2: 0.01 mM (dark cyan circles and open grey circles for reproducibility), 0.02 mM (orange up-triangles), 0.04 mM (black squares), 0.06 mM (green up-triangles), 0.1 mM (blue up-triangles), 0.4 mM (yellow right-triangles), 0.6 mM (violet crossed open squares) and 1 mM (dark yellow diamonds). (f) Concentration dependence of LaCl3: 1 µM (pink half open up squares and light magenta half open down squares for reproducibility), 5 µM (grey open stars), 0.01 mM (dark cyan circles), 0.06 mM (green up-triangles) and 0.1 mM (blue down-triangles).

Fig. 1: (a) Thermal activation plot of the structural α-relaxation rates (squares) of polyglycerols with indicated molecular weights in aqueous solution of varying salt and salt concentrations from experiments (symbols) and the DLVO theory with fitted values of the parameters Z and R (curves). (a) NaCl at 0.15 mM (black open squares), 0.3 mM (red open circles), 0.5 mM (green open triangles), 1 mM (blue open nabs), 1.5 mM (cyan open diamonds), 3 mM (magenta open left triangles), 0.15 mM (orange open right triangles), and finally 0.3 mM NaCl (gold open diamonds). (c) LaCl3 at 3 µM (black red filled square), 10 µM (black green filled square), 30 µM (black blue filled triangle), 100 µM (black cyan filled nabs), 3 µM (black magenta filled diamonds), and 0.3 mM NaCl solution (black gold filled diamonds). Some indicative error crosses given.
2.6 Dielectric properties of ionic liquids: the effect of temperature and pressure
J. R. Sangoro and F. Kremer

Broadband dielectric spectroscopy is employed to investigate the influence of temperature and pressure on charge transport in ionic liquids (ILs). The dielectric spectra are dominated – on the low-frequency side – by electrode polarization effects while, for higher frequencies, charge transport in a disordered matrix is the underlying physical mechanism. Identical Vogel-Fulcher-Tammann-type dependence of the main quantities characterizing charge transport with respect to temperature and pressure is obtained (Fig. 1a). While the absolute values of dc conductivity and the characteristic charge transport rate vary over more than 10 decades with temperature, pressure and upon systematic structural variation of the ILs, a coinciding plot of the transport parameters is obtained (Fig. 1b). This is discussed within the framework of the concept of glassy dynamics assisted charge transport traced back to Einstein, Einstein-Smoluchowski, and Maxwell relations [1,2].

References:

Collaborators: M. Paluch and M. Mierzwa (University of Silesia, Poland)

Funding: DFG under the priority program SPP 1191 on “Ionic Liquids”

2.15. Forces of interaction between grafted, blank and grafted-blank colloids by using optical tweezers
T. Stangner, M.M. Elmahdy, C. Gutsche and F. Kremer

The forces of interaction between blank SiO₂ colloids (diameter: ~ 4.85 ± 0.05 µm), poly (acrylic-acid) (PAA) grafted colloids and the asymmetric blank-grafted colloids are measured with high precision (± 50 fN) by means of Optical Tweezers. Parameters to be varied beside the surface modification are the concentration and the valency of the added salt. The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [1] is used for the characterization of the blank colloids. Good agreement was found (Fig. 1a). Therefore electrostatic contributions dominate the interaction [1,2]. The interaction between PAA-grafted colloids is characterized by a model published by Jusufi et al. including entropic parts to the overall interaction force (Fig. 1b). The asymmetric case, blank vs. grafted, was fitted by using the Alexander-De Gennes-Model (AdG model), which only take into account the ateric force and non-charged colloids (Fig. 1c). Using the model-independent interaction length at a force of F=2 pN, the experimental results suggest that the interaction between the asymmetric case can be described as a superposition of half the interaction length of the blank and half of the interaction length of the grafted colloids (Fig. 1d).

References:

2.14 Forces within single pairs of charged colloids in aqueous solutions of ionic liquids as studied by optical tweezers

M. M. Elmahdy, C. Gutsche and F. Kremer

Forces of interaction within single pairs of negatively charged microsized colloids in aqueous solutions of water miscible room temperature ionic liquids (RTILs) have been measured at varying concentrations and pH by using optical tweezers (OT) [1]. Three different water miscible RTILs (1-Butyl-3-methylimidazolium tetrafluoroborate [BMIM-BF₄], 1-Butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM-TfO] and 1-Butyl-3-methylimidazolium chloride [BMIM-Cl]) having the same organic cation [BMIM]⁺ and different inorganic anions ([BF₄]⁻, [TfO]⁻ and Cl⁻) are used and compared with the high temperature molten salt (KCl). The experimental data are well described by a size-corrected screened Coulomb interaction approach which originates from the linearized Poisson-Boltzmann (PB) equation [2].

The effective surface charge density \( \sigma \) derived from the fitted force-separation data is found to be concentration and pH dependent.

Fig 1: Forces vs. separation \( D \) as measured for a single pair of blank PS colloids in aqueous solution of two different types of salts (BMIM-Cl and KCl). Symbols represent the experimental data while the solid lines represent the fits with the size-corrected screened Coulomb interaction approach. (a) BMIM-Cl at fixed pH 5.8 and different concentrations: \( 2.2 \times 10^{-5} \) M (black full circles), \( 5 \times 10^{-5} \) M (red open up-triangles), \( 1 \times 10^{-4} \) M (blue open down-triangles), \( 5 \times 10^{-4} \) M (cyan open diamond), \( 1 \times 10^{-3} \) M (orange open hexagon), and the reproducibility at \( 2.2 \times 10^{-5} \) M (black open circles). (b) KCl at fixed pH 5.8 and different concentrations: \( 1.2 \times 10^{-5} \) M (black full squares), \( 5 \times 10^{-5} \) M (red open up-triangles), \( 1 \times 10^{-4} \) M (blue open down-triangles), \( 5 \times 10^{-4} \) M (cyan open diamond), \( 1 \times 10^{-3} \) M (orange open hexagon), and the reproducibility check at \( 1.2 \times 10^{-5} \) M (black open squares). (c) BMIM-Cl at fixed concentration of \( 1 \times 10^{-4} \) M and different pH values of 2.1 (olive full pentagon), 2.6 (orange open hexagon), 3.1 (navy full diamond), 3.7 (magenta open down-triangles), 4.2 (blue full up-triangles), 4.8 (red open circles), 5.8 (black full squares) and the reproducibility at pH 2.1 (black open squares). Inset of (c): interaction length at force of 2 pN \( (\lambda_{F=2 \text{pN}}) \) versus pH at fixed BMIM-Cl concentration of \( 1 \times 10^{-4} \) M (black full circles). The pH-dependence of the effective surface charge density \( \sigma \) obtained from the fitting of the force separation curves.

References:

Funding: DFG priority program SPP 1191 on Ionic Liquids.

2.7 Diffusion in ionic liquids: the interplay between molecular structure and dynamics

J. R. Sangoro, C. Iacob and F. Kremer

Diffusion in a series of bis(trifluorosulfonyl)imide-based ionic liquids is investigated by a combination of Broadband Dielectric Spectroscopy (BDS) and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR). It is demonstrated that the mean jump lengths increase with the molecular volumes determined from quantum-chemical calculations. This provides a direct means – via Einstein-Smoluchowski relation – to determine the diffusion coefficient by BDS over more than 8 decades unambiguously and in quantitative agreement with PFG NMR measurements (see Fig. 1). Unprecedented possibilities in the study of charge transport and dynamic glass transition in ionic liquids are thus opened [1].

Fig 1: (a) Diffusion coefficients determined from broadband dielectric spectra by employing the Einstein-Smoluchowski equation (using \( \omega_c \) as the characteristic hopping rate) and independently measured by PFG NMR (open symbols). The lines denote fits by the Vogel-Fulcher-Tammann equation. Inset: One of the possible conformations of the [OMIM] cation. (b) The apparent activation energy, \( \Delta G \), of diffusivity in a series of bis(trifluoromethyl-sulfonyl)imide-based ionic liquids at different temperatures (determined from the VFT fits presented in Figure 2). \( \Delta G \) increases with the mean ion jump lengths (indicated in brackets). Inset: The mean jump lengths (from a combination of broadband dielectric spectroscopy and PFG NMR measurements) as a function of the molecular volume (from quantum chemical calculations) of the ionic liquids investigated.

References:

Collaborators: R. Buchner (University of Regensburg), V. Strehmel (Niederrhein University of University of Applied Sciences), J. Kärger (University of Leipzig), R. Valliulin (University of Leipzig)

Funding: DFG under the priority program SPP 1191 on "Ionic Liquids"
2.8 Charge transport and dipolar relaxations in metal-based ionic liquids

J. R. Sangoro, C. Iacob, W. K. Kipnusu, T. Schubert, and F. Kremer

Charge transport and dipolar relaxations in novel alkali metal-based carboxylate ionic liquids are investigated in a wide frequency and temperature range by means of Broadband Dielectric Spectroscopy (BDS) [1,2]. The dielectric spectra are described at lower temperatures in terms of dipolar relaxations whereas hopping conduction in a random spatially varying energy landscape is quantitatively shown to dominate the spectra at higher temperatures (see Fig. 1 (a)). Based on detailed analysis of the dielectric relaxation strength in its temperature dependence, the slower secondary relaxation process is attributed to molecular fluctuation of ion-pairs (sodium and carboxylate ions) while the localized motion of the carboxylate anion gives rise to the faster process observed (see Fig. 1 (b)). Experimental evidence for the existence of long-lived ion pairs in an ionic liquid is thus provided [2].

Fig. 1: (a) Imaginary part of the complex dielectric function versus frequency at different temperatures illustrating the secondary relaxation processes in the sodium 2,5,8,11-tetraoxatridecan-13-oate ([Na][TOTO]) ionic liquid. Inset: Arrhenius-type temperature dependence of the secondary relaxation rates (1/\(\tau\)) of [Na][TOTO] at lower temperatures (114 K to 225 K). The activation energies are indicated. (b) The temperature dependence of the dielectric relaxation strength corresponding to charge transport \(\Delta\varepsilon\) as well as the two secondary dipolar relaxations \(\Delta\varepsilon_{\beta1}\) and \(\Delta\varepsilon_{\beta2}\).

References:

Collaborators: R. Buchner (University of Regensburg), P. Papadopolous (MPIP Mainz)

Funding: DFG under the priority program SPP 1191 on “Ionic Liquids”

2.13 Receptor/ligand-interaction as studied on a single molecule level

C. Wagner, D. Singer, R. Hoffmann and F. Kremer

Optical tweezers-assisted dynamic force spectroscopy is employed to investigate specific receptor/ligand-bonds on a single contact level. The specific binding of two monoclonal antibodies, HPT-110 and HPT-104, to synthetic tau-peptides with different phosphorylation pattern is analyzed. The specificity of HPT-110 to the tau-peptide containing a phosphorylation at Ser235 and of HPT-104 to the tau-peptide containing a phosphorylation at Thr231 is confirmed (Fig. 1 a). Additionally, our approach allows for a detailed characterization of the unspecific interactions that are observed between HPT-104 and the peptide phosphorylated only at Ser235 and between HPT-110 and the peptide phosphorylated only at Thr231. By analyzing the measured rupture-force distributions it is possible to separate unspecific from specific interactions. Thereby for the latter characteristic parameters like the lifetime of the bond without force \(\tau_0\), the characteristic length \(x_\tau\) and the free energy of activation \(\Delta G\) are determined (Fig. 1 b). The results are in accordance with conventional ELISA tests but offer a much more refined insight.

Fig. 1: a) The median relative binding frequency of each of the mAbs HPT-104 and HPT-110 to double-phosphorylated peptides and to peptides mono-phosphorylated at Thr231 and Ser235 is shown. The median frequency of both, HPT-104 and HPT-110 to the double-phosphorylated peptide is \(>0.8\). The binding frequency of HPT-104 to the peptide only phosphorylated at Thr231 is similar, whereas its binding frequency to the peptide phosphorylated at Ser235 is \(<0.25\) significantly lower. For the mAb HPT-110 the result is vice versa: its binding frequency to the peptide mono-phosphorylated at Ser235 is significantly higher than to the peptide mono-phosphorylated at Thr231. The last column indicates the level of the “background”, which consists of interactions that are not caused by an interaction between receptor and ligand molecules. This “background” is with a binding frequency of \(<2\%\) found to be negligible. b) The lifetime \(\tau\) of the interaction between HPT-110 and the double-phosphorylated peptide is shown in dependence on the force for 6 different loading rates as indicated by the different symbols. The data is fitted globally to a well-known theoretical model. Inset: Histogram of the measured rupture forces at a loading rate of 77 pN. The red line indicates the theoretical distribution of rupture forces according to the theoretical model after inserting the parameters obtained by fitting \(\tau(F)\).

References:

Funding: Buildmona, Europäischer Sozialfonds (ESF)
2.12 Hierarchies in the structural organization of spider silk – A quantitative combined model
R. Ene, P. Papadopoulos, F. Kremer

Polarized IR-spectroscopic and mechanical measurements are combined to analyse the conformational changes in hydrogenated and partially deuterated major ampullate spider silk of Nephila edulis Fig. 1a) [1]. Special attention is given to supercontraction and to the case where the latter is hindered by mechanical constraints. Crystal stress can be measured from the frequency shift of main-chain vibrations. The results show that in both states of silk a serial arrangement between the crystalline and amorphous phase dominates the nanostructure. The determination of the molecular order parameters of the different moieties proves that the amide hydrogen exchange is a selective process, taking place at the surface of β-sheet nanocrystals, implying that these regions are accessible by water [2]. The mechanical properties are changing dramatically when the fiber is wet (“supercontraction”) due to the fact that the pre-stress of the chains interconnecting the nanocrystals is irreversibly released. In course of this a novel network of H-bonds is formed, a process which can be suppressed if supercontraction is hindered. A three-component combined model of crystals in serial arrangement with amorphous chains and a fraction of chains bypassing them can describe all states of spider silk, assuming hydrogen bonding of worm-like chains at low pre-strain Fig. 1b) [3].

Fig.1 (a) IR absorption spectrum of major ampullate silk from Nephila edulis in native state (black curve) and supercontracted state (H2O-blue curve and D2O-red curve). The spectral region highlighted in the rectangle contains the ND bands resulted from the exchange of hydrogen with deuterium. (b) Accessibility of silk proteins to water. The exchange of amide hydrogens takes place primarily at highly ordered moieties, including amorphous chains with high pre-strain and possibly parts of the alanine nanocrystal surface (marked with blue).

References:

Funding: Graduate School BuildMoNa

2.9 Charge transport in confined ionic liquids
C. Iacob, J. R. Sangoro and F. Kremer

Charge transport in tetrafluoroborate (BF4-) and bis(trifluoromethylsulfonylimide (NTf2) based ionic liquids (ILs) in nanoporous silica membranes (average diameters: 7.5, 9.5 and 10.4 nm) – prepared by electrochemical etching of (100) p-type silicon - is investigated in a wide frequency and temperature range by a combination of Broadband Dielectric Spectroscopy (BDS) and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) [1,2]. By applying the Einstein-Smoluchowski relation to the dielectric spectra, diffusion coefficient is obtained in quantitative agreement with independent PFG NMR measurements (Fig. 1A) (our PFG-NMR data are in agreement with the results reported by Bogno et al.) We experimentally show for the first time that the ionic mobility of the studied ILs at lower temperatures is enhanced by more than two decades under nanoconfinement geometry in comparison with the bulk value. The results are interpreted in terms of changes in the ion packing under condition of geometrical confinement.

Fig 1: (A) Diffusion coefficients determined by applying the Einstein-Smoluchowski equation to the dielectric spectra of BMIM BF4 (in bulk and nanopores denoted by filled symbols) and measured by PFG NMR (represented by half filled symbols). The star symbols represent the experimental diffusion coefficients using DOSY NMR from Bogno et al., which are in a good agreement with our PFG NMR and BDS measurements [3]. Inset: (a) enlargement of the spectra at lower temperatures and (b) effective number density of charge carriers of BMIM BF4 in silica membranes with different pore sizes as a function of inverse temperature. (B) Diffusion coefficients of BF4- based ionic liquids in 7.5nm silica nanopores versus bulk diffusion coefficients. Arbitrary dotted line represents 1:1 ratio between diffusion coefficients in pores and in bulk. Insets: Molecular weight for the BF4- and NTf2- based ionic liquids as a function of the ratio of the glass transition temperatures in pores, and bulk respectively. The structure of BF4-based ionic liquids is indicated.

References:

Collaborators: J. Kärger, R. Vallulinn, S. Naumov (U Leipzig), M. Alexe (MPI, Halle), D. Hirsch (IOM, Leipzig)

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.

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.
2.10 Liquid crystals in confining geometry
M. Jasiurkowska, C. Iacob, P. Papadopoulos, F. Kremer, M. Massalska-Arodź

The molecular dynamics of 4-heptan-4'-isothiocyanatobiphenyl (abbreviated as 7BT) in confinement of cylindrical nanopores is studied by means of Broadband Dielectric Spectroscopy (BDS). In bulk, the investigated compound shows only one liquid crystalline phase [1,2], the highly ordered smectic E (SmE) phase, characterised by the orthorhombic arrangement of molecules within the layers. The confinement leads to modification of the dynamics of the molecular motion. The relaxation process around short axis ($\delta$-relaxation) is faster in the pore than in the bulk and its temperature dependence is described by Arrhenius formula. The value of activation energy of the $\delta$-relaxation is slightly higher for sample into pores then this obtained for a bulk of the SmE phase. The second process attributed to a librational motion of the molecules appears in the relaxation rates two decades faster then $\delta$-relaxation. With decreasing temperature both processes merge and their sum follows the temperature curve of the II process. The crystallization temperature is significantly reduced in comparison to the value for bulk and it dependence on pores size.

![Graph](image1.png)

Fig. 1: a) Dielectric loss $\varepsilon''$ for 7BT measured at 3.21 kHz as a function of temperature on cooling and subsequent heating of the bulk sample and in pores of 7.5 nm and 9.5 nm. b) The activation plot, relaxation process I corresponds to $\delta$-relaxation, process II is assigned to the librational motion of the molecules close to walls.

References

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

2.11 Infrared transition moment orientational analysis (IR-TMOA)
W. Kossack, P. Papadopoulos, F. Kremer

A novel spectroscopic approach has been developed, that reveals a complete characterization of the quadratic averaged orientation of the different infrared transition dipole moments in any IR-translucent material. Using a rotary measurement setup, the electric field in the sample can be varied in all three dimensions (see inset). Since, the absorption coefficient is explicitly dependent on the relative orientation of the transition dipoles and the electric polarization (see Figure), one is enabled to quantify the fraction of ordered molecular moieties and their orientation [1]. Based on this technique thin, substrate supported, polymer films are studied in order to investigate their interaction with solid-state interfaces according to their specificity and range for different combinations of polymers and substrates, addressing the recent question of confinement and its extension.

![Graph](image2.png)

Fig. 1: Polarization (with respect to the y axis) and inclination (tilt) dependence of baseline corrected CH$_2$ stretching vibrations of polystyrene (~40 nm) on BaF$_2$. For comparison the bands for different electrical polarizations are put neat to each other: The x axis shows wavenumbers from 2833 to 2981 cm$^{-1}$ for each polarization (between each two upright lines). The small peaks correspond to symm. CH$_2$ stretching (2850 cm$^{-1}$), the big peaks to asymm. CH$_2$ stretching (2920 cm$^{-1}$). The black and blue lines show the spectra for 0° and 60° inclination, where the latter is shifted by 0.3x10$^{-2}$ units upwards. The red lines are the corresponding fits. As expected absorption shows no polarization dependence for normal incidence, where the 60° incidence spectra vary symmetrically around 90° polarization direction. The inset shows the measurement geometry.

References:

Funding: Leipzig School of Natural Sciences, “Building with Molecules and Nano-Objects” (BuildMoNa)